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ORIGINAL PAPER

Electrokinetic removal of creosote from treated timber waste: a comprehensive gas chromatographic view

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Abstract The applicability of electro-remediation to remove creosote contaminants from treated wood wastes and to assess the behaviour of its components when submitted to an electric field was studied on woodchips from treated railway sleepers of *Pinus pinaster* Ait. 15 days experiments were performed using a laboratory cell, with constant current density set at 0.2 mA cm^{-2} and an open electrolyte flow rate of 0.5 mL min^{-1}. The anolyte and catholyte solutions were collected and extracted by solid phase extraction. The resulting extracts were analysed by one dimensional gas chromatography hyphenated with mass spectrometry (1D-GC/MS) and comprehensive two-dimensional gas chromatography with time-of-flight mass spectrometry (GC × GC/TOFMS). The chemical groups of creosote components were identified and its behaviour on process described. Polycyclic aromatic hydrocarbons, phenols and the majority of the S- and O- heterocycles were found to move in the electrokinetic cell towards the anode compartment, due to electroosmosis, whereas the majority of the positively charged N-heterocycles (aza-heterocycles) moved towards the cathode compartment, due to electromigration.

Keywords Creosote · Timber waste · Electrokinetic remediation · PAHs · Phenols · Heterocycles

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1 Introduction

Creosote, a distillation product of coal tar is one of the most widely used wood preservatives in the world. According to the United States Environmental Protection Agency (USEPA) [1], its major preservative application, around 70%, is on the treatment of wooden railway sleepers. Other common preservative applications are on electricity and telecommunication wooden poles and in timber used for bridges, garden fences and household construction [2, 3]. Due to its intensive worldwide use an increase in the amount of waste of wood treated with creosote is expected over the next decades. This raises a growing concern about the environmental issue of treated wood waste management. In France, for instances, the potential volume of this waste is estimated in 1 million m^3 per year (after replacement of impregnated timber), due to the production of approximately 2–3 million m^3 of railway wood sleepers, during the period 1993–1995 [4].

Creosote is a variable and complex mixture composed of various compounds, where around 300 have been identified, among the 10000 chemicals that are estimated to be in the mixture [2, 5]. Although the composition of the organic compounds in creosote varies considerably, depending upon the actual production technique, Mueller et al. [6] and Broholm et al. [7] stated that polycyclic aromatic hydrocarbons (PAHs) constitute the main constituents with 70–85% of total

weight, followed by the phenolic compounds around 10%, monoaromatic hydrocarbons (BTEXs) less than 3%, and the polycyclic compounds containing N, O or S in the ring structure (N,S,O-heterocycle compounds) between 3 and 15%.

The majority of the identified chemicals have been classified as toxic, carcinogenic and mutagenic, and therefore related to harmful health effects. In the last decades PAHs, the main chemical components of creosote, have been one of the major concerns of environmental agencies and research groups [8–14]. This focus resulted on creosote classification in several countries, such as Canada, United States of America, Australia and in the European Union (EU), as a hazardous substance and as potential human carcinogen (group 2A) by the International Agency for Research on Cancer (IARC), USEPA, Agency for Toxic Substances and Disease Registry (ATSDR) or National Occupational Health & Safety Commission (NOHSC) [15–18].

The analytical characterization of creosote and the analysis of its extracts have been considered a challenging task. The standard analytical methods, such as one-dimensional gas chromatography (1D-GC), often coupled to a mass spectrometer (GC/MS) as a specific detection method, used in the past decades, for its characterization and analysis, usually did not achieve satisfactory results (especially for the bulk of the minor components) and at best had provided broad, though valid, data for its gross chemical composition, constituting the majority of the published studies reports for target or main components [19–21] indicating that a considerable amount of information is unexploited.

This analytical handicap is due both to the larger number of creosote components, present in a wider range of concentrations and to the similarity of the physical–chemical properties of high percentage of its components. As consequence creosote components are hard to separate and to be analyzed even by gas chromatography, due to the large amount of coelutions promoted, resulting in difficult or ambiguous compound identification [22] if additional sample fractionation methodologies prior the final analysis are not used used.

A new GC technology, called comprehensive two-dimensional gas chromatography (GC × GC), in tandem with mass spectrometry or with common detectors, has recently been shown to be an excellent tool for the analysis of complex samples such as edible oils, environmental and petrochemical samples [5, 23–27]. The technique uses two GC columns, coupled in series by a modulator interface, which submit the whole sample compounds to two different (orthogonal) separation mechanisms resulting in high increase of analyte separation and sensitivity than does conventional GC in a single analysis. The basic principles of comprehensive two-dimensional GC have been reviewed in detail by Adahchour et al. [28] and Ong and Marriot [29].

Concerning the environmental issue of treated wood waste management and from a long-term perspective, the disposal of preservative treated wood into landfills is considered to be the least preferred method. This solution is becoming increasingly expensive, the approved landfill sites are becoming scarcer and it will even be forbidden in some countries [30]. Some spent, creosote treated wood have been combusted with energy recovery; however, recent regulations regarding ash disposal present further limitations [31]. Biodegradation seems to be another option, since it is the primary route through which creosote is removed from other contaminated environments [6, 32], but it requires answers related to emissions from contaminated leachate and runoff, and the development of extraction processes to lower preservative concentrations, so that degradation by composting microorganisms will not be inhibited [31]. Earlier recycling of creosote impregnated products for subsequent uses in garden fences and burning wood for domestic use has also lead to situations which increase human exposure [33, 34]. As a result of the restrictions on use, concerns about toxicity and harmful health effects, creosote preserved wood waste treatment/disposal represents a challenge. Additionally alternative options for remediation, particularly the ones that may promote recycling/re-use of wastes are becoming more attractive to study in opposition to the disposal options.

The electrokinetic process is a remediation technique for removal of contaminants that has been applied to polluted soils [35–41], impregnated wood waste [42], fly ash from straw combustion [43] or municipal solid waste incinerators fly ash [44]. The method uses a low-level direct current as the "cleaning agent", to remove matrix contaminants. The applied electric field leads to electrolysis of water at the electrodes, generating an acidic medium at the anode, which promotes an acidic front that advances across the cell towards the cathode and a basic medium at the cathode, which promotes a alkaline front towards the anode. The removal of contaminants, on the process, mainly relies on electromigration, the movement of charged species, electroosmosis, the mass flux of pore fluid (water) due to dipolar interactions between water molecules and contaminated matrix surfaces which is responsible for the removal of uncharged compounds, and electrophoresis, the movement of charged particles. The pollutants are then transported towards one of the electrode compartments where they will become concentrated. The general principle of the electrokinetic process is presented elsewhere and several authors have critically reviewed its state of knowledge [32, 41, 45–48].

The main application of electrokinetics to the remediation of organic compounds has been focused so far on contaminated soils. Examples of the use of electrokinetic (EK) for organic pollutants remediation can be found on the removal of pesticide/herbicides [49, 50], chlorinated

solvents [51, 52], petroleum hydrocarbons [53, 54], phenol [55] and PAHs [56–58]. EK of organics is often applied using surfactants or cyclodextrins to improve hydrophobic compounds removal [56, 59], coupled with biodegradation [52, 57, 60, 61] (e.g. EK supply of nutrients or moving the organic pollutants towards degradative microorganisms) or to perform electrochemical oxidative reactions (e.g. Fenton's reaction or two-stage process EK remediation and liquid electrochemical oxidation) [51, 54, 56]. The present study reports results from the application of the electrodialytic process to a Portuguese creosote treated railway wood sleeper, without the use of facilitating agents. The main goal is to assess whether the method can be applied to remove creosote components from the treated timber waste. The emphasis was put on the movement of creosote components in the EK system as described by chromatographic data. The set up of a remediation strategy requires the previous characterization of the polluted matrices in terms of its chemical composition and its success improves with the level of this characterization. This work is supposed to be the first study to assess the behaviour of components from a complex matrix when submitted to electro-remediation using GC × GC/MS and illustrates the potential of the method in the elucidation of the behavior of organic contaminants present in complex matrices when submitted to the EK remediation.The process is described, for the conditions used, and the main chemical groups are identified/confirmed by comprehensive gas chromatography in tandem with time of flight mass spectrometry (GC × GC/ToF-MS).

No individual quantitative analysis was performed.

2 Materials and methods

2.1 Creosote treated timber waste

The laboratory experiment was carried out using wood chips prepared from a Portuguese creosote treated *Pinus pinaster* Ait. railway sleeper. The sleeper was collected after 20 years of use at Pampilhosa Railway Station, Portugal and was treated at the wood preservation unit from the Portuguese Railways located at Entroncamento. The original creosote formulation and classification were unknown, as was the wood impregnation treatment process.

2.2 Procedures and equipments

2.2.1 Electrokinetic laboratory cell

The experiments were run in a laboratory electrokinetic cell, developed at the Technical University of Denmark [62] and is described in detail elsewhere [39, 47].

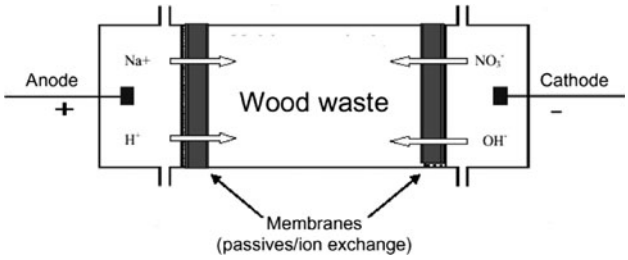

Fig. 1 Schematic representation of electrokinetic laboratory cell (adapted from Ribeiro [39])

The cell consists of three compartments—two electrode compartments and a central one (L = 3 cm, internal diameter = 8 cm), in which the waste wood samples were placed (Fig. 1). The electrode compartments and the wood chips/sawdust were separated, in 3 experiments, by passive membranes (cellulose filter paper supplied from Bio & Berntsen, Denmark) and ion exchange membranes [cation-exchange membrane (CAT): IC1-61CZL386; anion-exchange membrane (AN): IA1-204SXZL386, both supplied from Ionics Inc., USA], in two experiments. Both electrode compartments contained 1 L of 10^{-2} M $NaNO_3$ as an electrolyte solution, and were set with a open electrolyte circulation system at a constant flow rates of 0.5 mL min^{-1}, maintained by a multichannel peristaltic pump (Watson Marlow 503 U/R, USA). The pH value of the catholyte solution was adjusted to about 2.8–3 by periodical addition of concentrated HNO_3, thus neutralizing the hydroxyl ions as they were generated at the cathode. During the experiment a current density of 0.2 mA cm^{-2} was kept constant and the duration of treatment was 15 days. The electrodes were platinised titanium bars with a diameter of 3 mm and length of 5 cm (Bergsøe Anti Corrosion A/S, Denmark). A power supply (Hewlett-Packard E3612A, USA) was used to adjust the desired initial direct current (DC), which was monitored by a Fluke 37 multimeter.

The following experimental conditions were used: 30 g of wood chips were sampled. Before be placed in the cell central compartment, the wood was saturated with 100 mL of distilled water.

2.2.2 Chemicals and materials

All solvents used were chromatographic or gradient grade and were purchased from Merck (Darmstadt, Germany). The solid phase extraction ENVI-18 disks (octadecyl bonded silica) were purchased from Supelco (Bellefont, USA). A Polynuclear Aromatic Hydrocarbon mix solution (acenaphthene, acenaphthylene, anthracene, benz[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[ghi]-perylene, benzo[a]pyrene, chrysene, dibenz[a,h]anthracene,

fluoranthene, fluorene, indeno[1,2,3-cd]pyrene, 1-methylnaphthalene, 2-methylnaphthalene, naphthalene, phenanthrene and pyrene) attained from terpene standards (Sigma-Aldrich, Steinheim, Germany) and a mixture of C_8 to C_{27} hydrocarbons (AccuStandard, New Haven, CT, USA) were used to assist the identification task. Benzo[a]pyrene standard was purchased from Supelco (Bellefonte, PA, USA).

2.2.3 Creosote determination and analysis

The amount of creosote present in the railway sleepers, before and after electro-remediation, was determined following the European Standard Method prEN 12490 [63]. Wood chips samples (± 10 g) were placed inside a Soxhlet apparatus with a Dean-Stark water trap and extracted for 4 h with 200 mL of toluene. The creosote content of the wood chips was evaluated, by gravimetric measurements, as the average of the values obtained for three replicates.

For creosote qualitative analysis 1.0 mL of the soxhlet final extract was collected and 1.0 μL analyzed by gas chromatography hyphenated with mass spectrometry (1D GC/MS).

2.2.4 Benzo[a]pyrene determination

Determination of the benzo[a]pyrene content of creosote was determined, by High Performance Liquid Chromatography (HPLC) following the European Standard Method EN 1014-3 [64], using a Agilent LC 1100 series equipped with a quaternary pump and a 3D Fluorescence detector. The column used was a Nucleosil 100-5 C18 PAH (150 × 4.6 mm i.d., 5 μm). The injection volume was 20 μL, and the eluent (acetonitrile and water) was pumped at a rate of 0.5 mL min^{-1} at gradient mode. The gradient started with 70:30% acetonitrile/water, going to 100% acetonitrile in 10 min were it remained for 20 min. The fluorescence detector was set at $\lambda_{exc} = 380$ nm and $\lambda_{em} = 405$ nm.

2.2.5 Electrolytes extraction and analysis

During the experiment, the electrolyte solutions (catholyte and anolyte) were collected every 24 h (first 7 days) or 48 h and extracted by solid phase extraction (SPE) using ENVI-18 Disks. The resulting extracts were concentrated to 1.0 mL under a gentle stream of nitrogen. 1.0 μL of the final extract were analysed by one dimensional gas chromatography and comprehensive two-dimensional gas chromatography with time-of-flight mass spectrometry detector (GC × GC/ToF-MS) on a LECO Pegasus 4D system.

2.2.6 1D GC/MS

The creosote and electrolyte extracts were qualitatively analysed using a Trace GC chromatograph (ThermoUnicam) coupled to a Trace MS mass spectrometer (ThermoUnicam, Walthman, MA, USA), operating in electron ionization mode (EI: 70 eV). The compound separations were performed on a DB-5 (5% phenyl polysilphenylene-siloxane) capillary column (J&W Scientific, Folson, USA) with 30 m × 0.25 mm i.d. and 0.25 μm film thickness (d_f). The injector was set at 270 °C, the ion source at 250 °C and interface at 295 °C. Helium was used as carrier gas at a flow rate of 1.0 mL min^{-1} set at constant flow. The oven was programmed from 80 °C (2 min), then to 125 °C at 10 °C/min and to 295 °C at 8 °C/min, where it was kept for 20 min.

2.2.7 GC × GC/ToF-MS

Two systems with different modulators were used to perform the qualitative analysis of the samples.

Both systems comprised an Agilent 6890 N (both from Agilent Technologies: system 1 from Palo Alto, CA, USA and system 2 from Burwood, Australia) gas chromatograph and a Pegasus time-of-flight mass spectrometer (system 1 a Pegasus III and system 2 a Pegasus II both from LECO, St. Joseph, MI, USA). The collected data from the total ion chromatograms (TIC) were processed, in both systems, using the automated data processing software ChromaTOF™ (LECO, St. Joseph, MI, USA).

System 1: Dual-stage jet modulator The ToF-MS was operated at a storage rate of 200 Hz, using a mass range of m/z 35–450 and a multi-channel plate voltage of 1700 V; the MS was operated in electron ionization mode (Ion Source Energy: 70 eV, EI). The MS interface was set at 300 °C and the MS source 220 °C. The Modulator temperature offset was −50 °C and the modulation cycle was 3 s (with 1.05 s hot pulse).

The column set used, to separate the analytes, comprised an Equity-5 ms primary column (50 m × 0.25 mm i.d., 1.0 μm d_f), directly-coupled to a Supelcowax second column (polyethyleneglycol phase), (2.5 m × 0.1 mm i.d., 0.1 μm d_f).

The system was equipped with 2 ovens which temperature programs are given in Table 1.

The injector temperature was 250 °C and the injection was performed in Split mode (1/5). The carrier gas was Helium at 1.0 mL min^{-1}, set at constant flow.

System 2: Longitudinally modulated cryogenic system (LMCS) The ToF-MS was operated at a storage rate of 100 Hz, using a mass range of m/z 45–600 and a multi-channel plate voltage of 1700 V; the MS was operated in electron ionization mode (70 eV). This system was retrofitted with a LMCS operating with a modulation period of 6 s at −20 °C. One microliter sample volume was injected at 300 °C in pulse splitless mode (purge time 1 min, purge flow 50 mL min^{-1}, total flow of 51 mL min^{-1} and pulse pressure of 50 psi for 1 min). After 2 min the split ratio

Table 1 Oven temperature programs used in GC × GC/ToF-MS system 1

Primary oven	Secondary oven
Initial temperature: 40 °C	Initial temperature: 45 °C
Isotermic #1: 1.0 min.	Isotermic #1: 1.0 min.
Rate #1: 10.0 °C min^{-1}	Rate #1: 10.0 °C min^{-1}
Final temperature: 300 °C	Final temperature: 300 °C
Isotermic #2: 11 min	Isotermic #2: 11 min

was set to 1:20. The column sets used comprised a BPX5 primary column (30 m × 0.25 mm i.d., 0.25 μm d_f, SGE International, Ringwood, Australia, with a BPX50 (50% phenyl polysilphenylene-siloxane) column as the second dimension (1.0 m × 0.15 mm i.d., 0.15 μm d_f; SGE International). The oven temperature program began at 60 °C (held for 0.2 min) and was then raised to 170 °C at 20 °C min^{-1} (held for 5 min at 170 °C), then to 290 °C at 2 °C min^{-1} and held for 20 min at 290 °C. The carrier gas was helium at a constant flow rate of 1.0 mL min^{-1}. The interface column was a 0.50 m length of deactivated silica column with 0.1 mm inner diameter (0.17 m inside the transfer line and 0.33 m inside the oven), from SGE International. The oven temperature program was the same, apart from an initial temperature of 60 °C (held for 0.2 min). The transfer line was set at 350 °C and the source at 200 °C.

3 Results and discussion

3.1 Creosote characterization

The creosote content of the wood samples were determined gravimetrically, after soxhlet extraction with toluene, according the European standard EN 12490 and was estimated to be 70.0 ± 10.0 g of creosote per kg of wood.

Benzo(a)pyrene (B[a]P), one of the most toxic and investigated PAHs, was monitored as a marker for creosote toxicity. Its concentration, determinate by HPLC according the European standard EN 1014-3 was estimated to be 87 mg of B[a]P *per* kg of creosote, an amount higher than the limit stated (50 mg kg^{-1}) on the directive 2001/90/EC of the European Council [34].

The overall composition of the creosote impregnated in the wood samples was studied by gas chromatography and mass spectrometry. Figure 2 presents the total ion chromatogram (TIC) of the extract from the creosote treated sample with the identification of the main compounds after 1D GC/MS. The main compounds present in the creosote formulation used to preserve the wood samples used in the electro-remediation experiments are presented in Table 2.

The major components of the creosote formulation are phenanthrene, fluorene and fluoranthene, 3 and 2 ring PAHs. In the ten major components 8 are PAHs together with 2 heterocycle compounds, dibenzofuran (O-heterocycle) and benzothiophene (S-heterocycle).

3.2 Anolyte and catholyte solutions

The anolyte and catholyte solutions from creosote treated wood (railway sleepers) submitted to the remediation by the electrodialytic process were extracted by solid phase extraction (SPE) and analyzed by one dimensional and comprehensive gas chromatography/mass spectrometry (1D GC/MS and GC × GC/ToF-MS).

Figure 3 present the TIC (normalized to the highest component) of the anolyte and the catholyte solutions, respectively, collected after 3 days of running the electro-remediation process. The main peaks and chemical classes are indicated or identified on Table 3. It can be observed

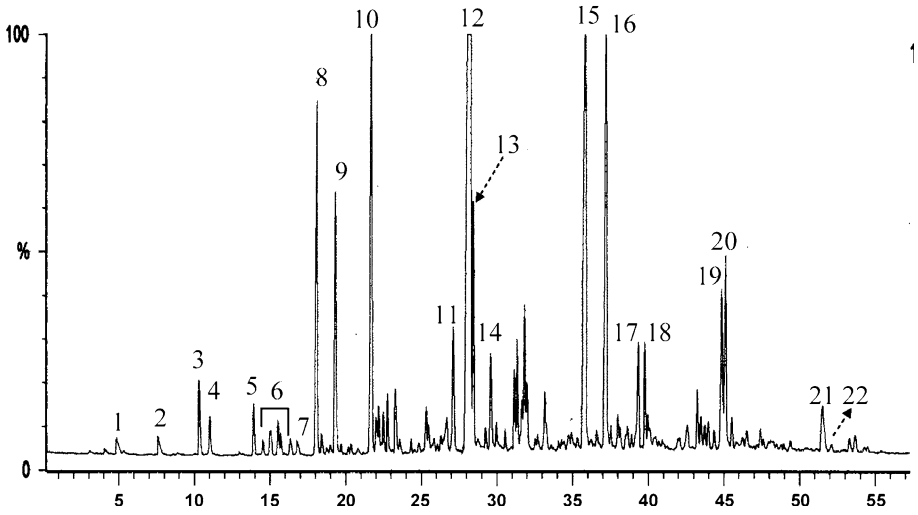

Fig. 2 Reconstructed one dimensional TIC from the toluene extracts of the preserved wood samples used in the EK remediation experiments. Peaks are numbered according to Table 2. For analytical conditions see text

Table 2 Main compounds identified the toluene extracts of the preserved wood sample used in the electrokinetic remediation experiments after 1D-GC/MS

Peak number	Compound
1	Naphthalene
2	Quinoline/isoquinoline
3	C_1-naphthalene
4	C_1-naphthalene
5	1,1-Biphenyl
6	C_2-naphthalenes
7	Acenaphthylene
8	Acenaphthene
9	Dibenzofuran
10	Fluorene
11	Dibenzothiophene
12	Phenanthrene
13	Anthracene
14	Carbazole
15	Fluoranthene
16	Pyrene
17 and 18	Benzofluorenes
19	Benzo[a]antracene
20	Chrysene
21	Benzofluoranthenes
22	Benzo[a]pyrene

that the composition of the individual electrolyte solutions is very different from the creosote formulation: the main compounds of creosote formulation are present in small quantities (see figure and table) and some of its minor components are the major compound classes found in the electrolyte extracts, such as phenols and heterocycles compounds. It can also be observed that the majority of the compounds are removed to the anolyte and thus the composition of both compartments is different. The anolyte is mainly constituted by azaarenes whereas phenols and PAHs are removed to towards the cathode. The major compounds found in the catholyte are the C2-phenols (dimethyl an ethyl) followed by the methyl phenols. Diethylhxylphathalate (DEHPH) is an ubiquous artifact from the system originated by the plastic materials used.

In spite of the apparent visual simplicity of the chromatograms presented in Fig. 3, they are intrinsically complex due to the large amount and variety of compounds present which are intended to be separated in order to allow a better compound detection, identification and thus monitorization. The evolution in the analytical techniques, especially in the last two decades, from multidimensional GC (MD-GC) and comprehensive two-dimensional GC (GC × GC) provided more 'chromatographic space' in order to obtain a suitable (or even increased) separation of all, or a selection of compounds present in the sample, since for a single GC column it is known its physical and statistical limitations provided by the maximum number of theoretical

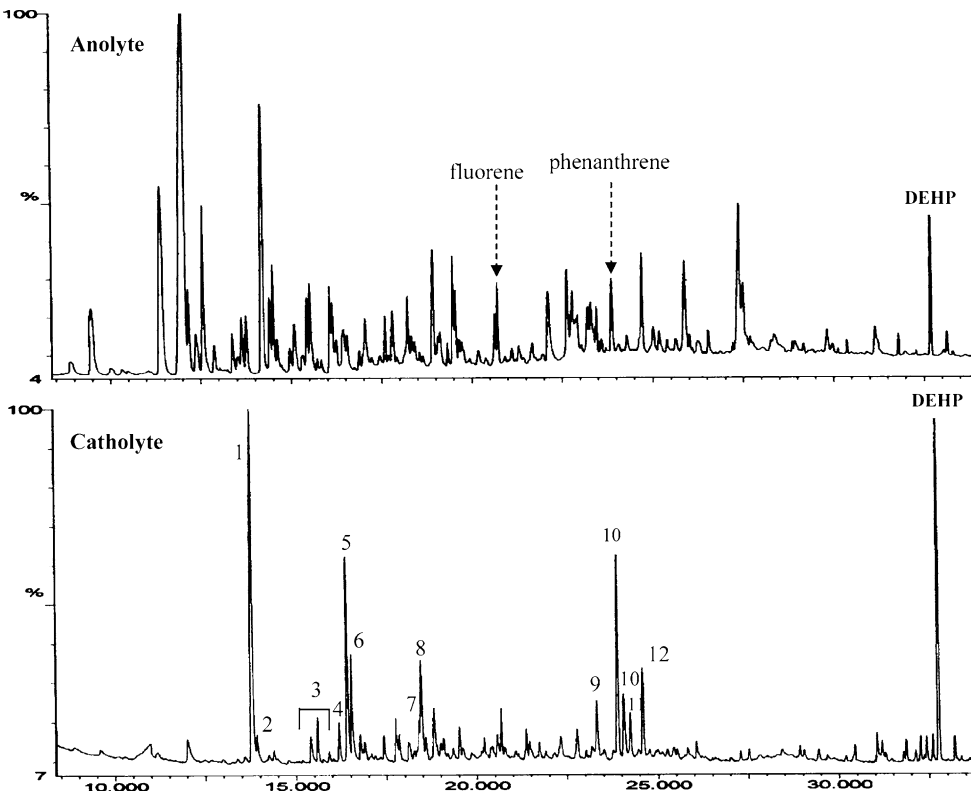

Fig. 3 Reconstructed one dimensional TICs from the catholyte and anolyte extracts obtained in the electrokinetic remediation experiments. Peaks are numbered according to Table 2. For analytical conditions see text (DEHPH—diethylhxylphathalate)

Table 3 Main compounds and chemical classes identified in the electrolyte extracts obtained in the electrokinetic remediation experiments after 1D-GC/MS

Anolyte	Catholyte	
Compound classes	Peak number	Compound
C1-phenols	1	Quinoline/isoquinoline
C2-phenols	2	C_1-nitrophenol
C3-phenols	3	C_1-quinolines/C_1-isoquinolines
C4-phenols	4	C_2-nitrophenol
C5-phenols	5 and 6	C_1-quinolines/C_1-isoquinolines
C3-benzenes	7	C_2-quinoline/C_2-isoquinoline
PAHs	8	Phenylpyridine
Hydroxy PAHs	9	Dibenzothiophene
Fatty acids	10	Benzoquinolines
Terpenes	11	Acridine
Phthalates	12	Phenantridine
O-heterocycles		
S-heterocycles		

plates and peak capacity [65–67]. Considering that the compounds in the samples are presented in high amounts and over a wide concentration range and thus co-elutions are inevitable. This can be illustrated in Fig. 4, where a section of a 1D and 2D separations are compared. When 1D separation is performed, 4 compounds coelute in a single, almost symmetrical peak, whereas all the compounds are well separated when the sample is submitted to GC × GC.

This resolution power obtained by the 2D system, allow consequently that the eluted compounds are obtained as pure components, which significantly increases the likelihood that pure mass spectra can be obtained and thus compared with mass spectral libraries in a more reliable way. This is significant and offers a considerable advantage over 1D GC systems.

Using the European standard methods EN 1014-3 and EN 1014-4 the benz[a]pyrene and phenolic compounds quantitative determination in creosote and creosote impregnated wood samples has limited effect when one intend to study, in detail, a remediation process of a complex formulation (more then 200 analytes), and to identify their components. Those goals can only be achieved using a high resolution technique, in order to separate all the components in the sample, together with mass spectrometric detection and consequently be able to promote the individual peak identification.

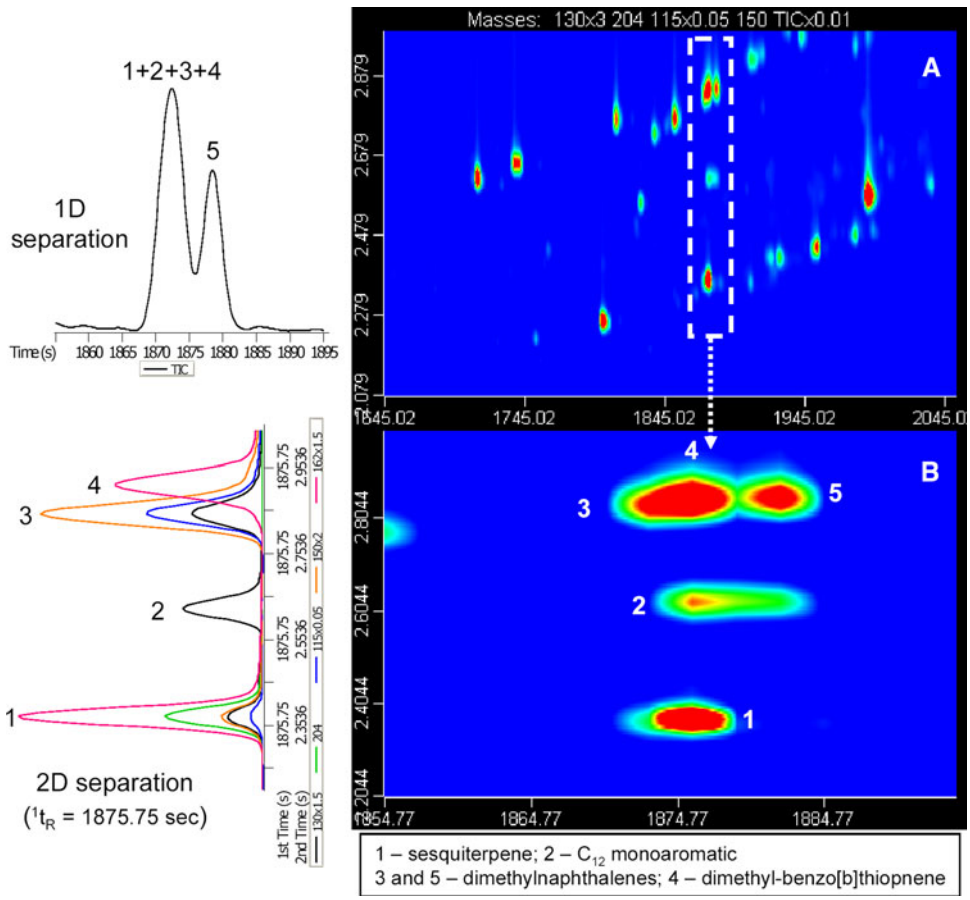

Fig. 4 Comparison of 1D and GC × GC separations obtained from a creosote preserved wood sample extract. Expanded view (B) of the GC × GC/ToF-MS contour plot (A) with its TICs for the first and second dimension separations. For presentation of the second dimension ^1t_R was locked at 1875.75 seconds. The peak identifications are presented. Analytical conditions in text system 1

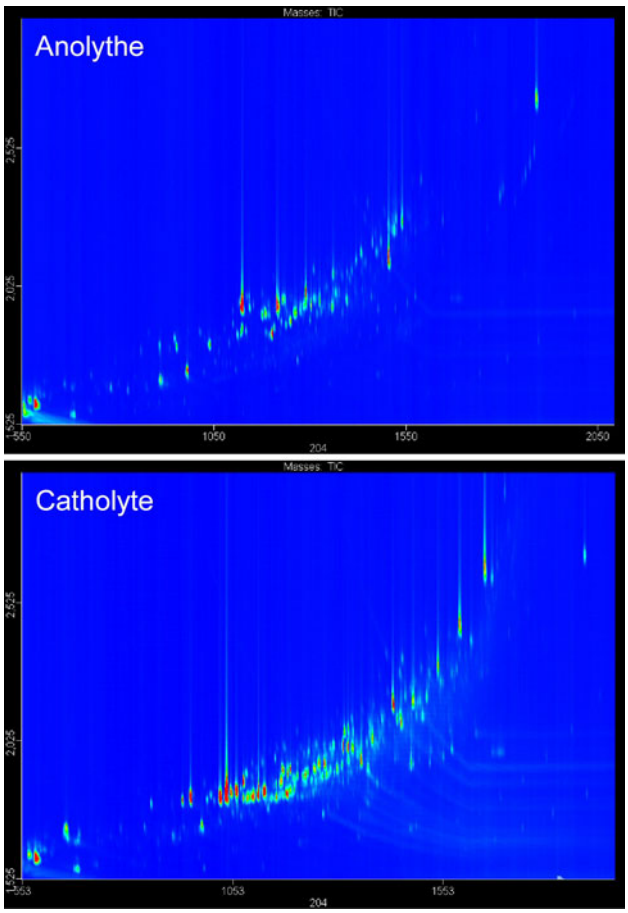

Fig. 5 GC × GC/ToF-MS contour plots obtained for the analysis of the anolyte and catholyte extracts showing the analytes separation in the two-dimensional space. Experimental conditions in text system 1

Qualitative analysis of the electrolyte extracts was achieved with good peak resolution and "true" mass spectra which allows a "better" compound detection and identification was achieved. Figure 5 presents the contour plots (normalized to the highest components) obtained for the anolyte and catholyte solutions and illustrates the chromatographic resolution obtained.

On the figure, due to the broader amplitude of concentrations of the different compounds present in the anolyte solution when compared to the catholyte one, more peaks are observable in the catholyte than in the anolyte contour plots. This is the result of the scale effect due to the contour plot normalization to the highest peaks. However the qualitative analysis obtained with the automated data processing software ChromaTOF at S/N > 50, resulted in the detection of about 300 analytes in the catholyte solution and 500 analytes in the anolyte solution. 76 of the detected analytes were found to be common to both electrolyte solutions (see Figs. 5 and 6).

To exemplify the powerfulness of the technique, in the monitorization of the EK remediation process, when ion extraction is applied to the contour plots obtained after the GC × GC/ToF-MS experiment, one can easily group family compounds, as it is shown in Fig. 6. Some compound classes are presented and the respective TIC for both catholyte and anolyte solutions are shown. Phenol and their derivatives are obtained when the diagnostic m/z fragments are chosen: 94, 108, 122 and 136, for phenol, C1, C2 and C3 phenol derivatives respectively. The presence of quinolines and isoquinolines and their methyl derivatives (C_1-quinoline/C_1-isoquinolines families) are detected and identified by the characteristic m/z fragments 129 and 143, and some PAHs through m/z fragments 128, 142, 154, 166 and 178.

3.3 Electro-remediation process

During the EK process the PAHs are found in the anolyte solution in lower concentrations (Fig. 3), in opposition to higher amounts present in the extract of the treated wood (Fig. 2). The phenolic compounds moved in the cell mainly towards the anode compartment. They are found in higher amounts in the anolyte solution (Fig. 3) than in the extract of the treated wood (Fig. 2). The S, O and acid N heterocycles are mainly found in the anolyte solution (Fig. 3). However, the positively charged N-heterocycles (azaarenes) move towards the cathode compartment, and are found in the catholyte solution (Fig. 3).

The efficiency of the EK process, as a remediation process for creosote preserved wood, is according to the data, as expected, directly related with the solubility of the different compounds present in the matrix. As the development of the acid front was expected to occur, a significant effect on the magnitude of the process, as well as on the solubility, ionic state and charge, and level of adsorption of the contaminants must also be considered (e.g. lower pH will increase azaarenes solubility but also will decrease phenols solubility).

The preliminary results shown that phenols and the more soluble heterocycle compounds are efficiently removed by the process. By opposition the removal of PAHs, especially those with more that 4 rings (the more toxic), under the used experimental conditions were not efficient. The highest removal of BaP estimated after HPLC analysis of the wood sample at the end of the experiments was 6%. The overall removals of creosote, from the wood, estimated according to EN 12490, were between 60 and 64% for the experiments with the passive membranes and less that 30% for the experiments with the ion exchange membranes. The lower removal rate achieved with the ion exchange membranes is due to the fact creosote tend to accumulate in the central compartment in contact with those membranes which may constitute a physical barrier to the creosote and its components movement towards the electrolytes. The removal rates achieved for the passive membranes is a very

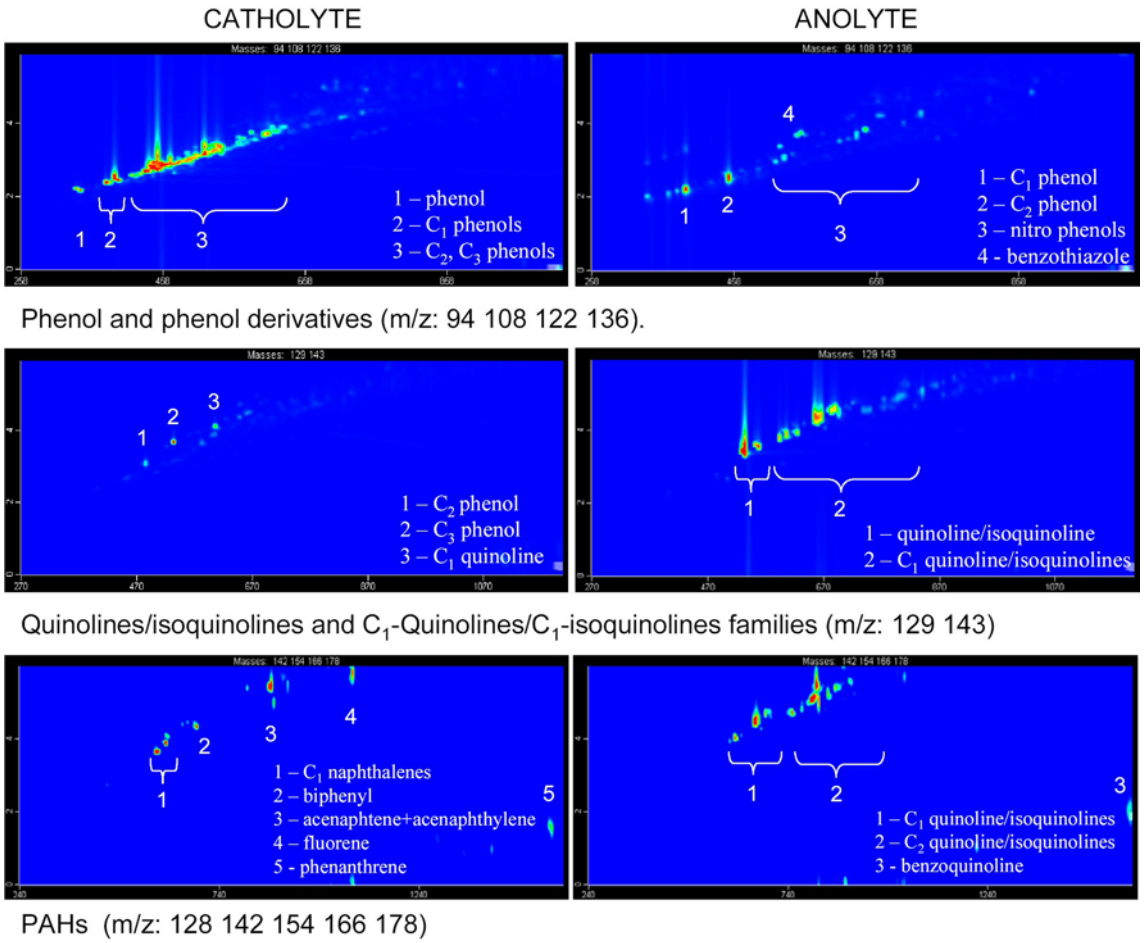

Fig. 6 Structured GC × GC/ToF-MS extracted ion chromatograms for the anolyte and catholyte solutions for some group family compounds. Analytical conditions in text system 2

interesting result for the condition used as it allows future optimization using co-solvents or surfactants. Additionally the removal of toxic compounds such as the azaarenes and phenols decrease the toxicity of the matrix and may allow a complementary and more efficient biodegradation step.

4 Conclusions

Under the action of the electric field, applied to remediate creosote preserved wood wastes (railway sleepers), polycyclic aromatic hydrocarbons, phenols and the majority of the S- and O- heterocycles were found to move in the EK cell towards the anode compartment, due to electroosmosis, whereas the majority of the positively charged N-heterocycles (aza-heterocycles) moved towards the cathode compartment, due to electromigration. The efficiency of electrodialytic and EK removal of creosote from treated wood seems to be related to the water solubility of the different creosote components. The phenols and the more soluble heterocycles are efficiently removed. In contrast, the PAHs removal, at the experimental conditions used, was not very effective. The experimental conditions used in this study were the least favourable for a process depending on the organic solubilities (PAHs; electrolyte solutions with a pH < 3). However, this technique could be improved with the use of chemical agents (such as surfactants) that could increase the solubility of creosote components and be used as a "pre-treatment" before biodegradation.

GC × GC by using a bidimensional separation space presented an enhanced analyte separation capability when compared with one dimensional techniques. This capability made possible the identification, detection and monitorization of the creosote constituents and thus contributed to a detailed knowledge and better understanding of the EK remediation of creosote preserved wood wastes.

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