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Determination of carboxylic SWCNTs in river water by microextraction in ionic liquid and determination by Raman spectroscopy

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ABSTRACT

The paper proposes a simple approach for the preconcentration of carboxylated single-walled carbon nanotubes and their determination in river water samples. The method is based on a microliquid–liquid extraction into an ionic liquid (bmim PF_6) in the presence of a cationic surfactant (CTAC). 10 μL of the ionic liquid phase are microfiltrated by using a home-made filtration device having a small diameter. The membrane was of cellulose with a pore size of 5 μm. Finally, the carbon nanotubes retained in the membrane are directly analyzed by Raman spectroscopy, which allows their direct characterization and quantification. The limit of detection was 0.050 mg L^{-1}. The precision, for a 1.4 mg L^{-1} concentration of carbon nanotubes, is 3.2%.

1. Introduction

The increasing use of nanoparticles in industrial applications will inevitably lead to the release of such materials into the environment. However, very little is known on emissions of engineered nanomaterials to the environment due to a lack of quantitative techniques for monitoring nanomaterials emissions and determining its concentrations in the environment. Exposure might occur during the production, use and disposal of CNTs and CNT-containing products. CNTs may be released into the aquatic environment from point sources, such as factories, landfills and wastewater effluents or from nonpoint sources, such as stormwater runoff, attrition from composites and from wet deposition from the atmosphere [1]. It has been described the fact that a considerable part of the CNT, utilized in mass consumer products such as batteries and textiles, can be dispersed in the technosphere or the environment, e.g. by wear and tear from products as well as recycling processes which could cause occupational exposure [2]. It can be assumed that environmental and human exposure to CNT is likely to occur. Moreover, Gottschalk et al. calculated predicted environmental concentrations based on a probabilistic material flow analysis from a life-cycle perspective of engineered nanomaterials containing products. A concentration of carbon nanotubes in STP effluent in the ng L^{-1} range in Europe has been predicted [3,4].

The properties of nanomaterials raise concerns about adverse effects on biological systems, which, at the cellular level, include structural arrangements that resemble nanomaterials and nanostructures in terms of their function [5]. This is the subject of considerable debate regarding the open questions on toxicology and environmental impact [6,7].

Effectively monitoring nanoparticles in environmental samples entails meeting several requirements. One is using analytical methods capable of detecting environmentally relevant concentrations, which fall in the nanogram per litre range, and another is avoiding the potential interference of natural nanoparticles frequently present in environmental samples [8]. Separating nanoparticles is one of the most critical steps in their analytical processing. Available methods for this purpose are still unrefined.

For carbon nanotubes (CNTs), their extremely low solubility in water, variable sizes of the particles, small diameters and the complexity of aggregates formed make characterizations of these nanomaterials extremely difficult in aqueous exposure experiments [9]. CNTs are usually functionalized to prevent them from sticking together and make them water soluble. Functionalization (e.g. carboxylation) is also a common practice in industry in the case of CNT-polymer matrices in order to achieve better dispersion, alignment and strong interfacial interactions [10]. Oxidized CNT is an important and widely used derivative of CNTs both for dispersing CNTs in aqueous systems and further functionalizing

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CNTs via carboxyl group reactions [11]. It is assumed that the better de-bundled and individually suspended the CNTs are, the longer they remain in the water column [12]. Thus, oxidized CNT may be one of the most possible forms of CNT pollutant in aqueous environment [13] and hence the importance of determining them. In the case of CNTs (both single and multi-walled), Nowack and Bucheli [14] reported that no method existed for their quantification in natural media. However, a recent approach to the extraction of carboxylic carbon nanotubes from surface water uses a filter modified with multiwalled carbon nanotubes as a preconcentrator and determines them by capillary electrophoresis. It has the limitation that does not provide information about the carbon nanotubes and also standards are needed [15].

On the other hand, ionic liquids (ILs) have attached more and more attention over the last few years. Wei et al. [16] demonstrated the possibility to extract nanomaterials (nanoparticles and nanowires of Au, Cu and CuO) from aqueous phases to the $[C_4MIM][PF_6]$ ionic liquid. CdTe nanocrystals have been also extracted in $[C_4MIM][Tf_2N]$ [17]. Recently, a method for the preconcentration of gold nanoparticles from river water samples and liver tissue in ionic liquid has been also developed [18]. It has been described the dispersion of carbon nanotubes (SWNTs) in ionic liquid through weak van der Waals interaction. The ionic liquid can effectively shield the strong π–π stacking interaction among SWNTs and disperse them [19]. The aim of this work is to use the affinity of carbon nanotubes to ionic liquids from an analytical point of view, to extract this nanomaterial from water samples and their subsequent quantification by Raman spectroscopy. As far as we are concerned this is the first time ionic liquid are used for microextraction of carbon nanotubes.

2. Experimental

2.1. Materials and reagents

SWNTs were obtained from Shenzhen Nanotech Port Co. Ltd (NTP) (China), with a purity over 90%, an outer diameter of < 2 nm, a length of 5–15 μm and a special surface area of 500–700 m^2/g. H_2SO_4 and HNO_3 were purchased from Panreac (Barcelona, Spain). 1-butyl-3methyl-imidazolium hexafluorophosphate ($BMIM\ PF_6$) (MERCK) was selected as the ionic liquid (IL) to extract the carboxylated single-walled carbon nanotubes from the samples. Hexadecyltrimethylamonium chloride (CTAC) and hexadecyltrimethylamonium bromide (CTAB) were obtained from Fluka. Cellulose membranes of 5.0 μm pore sizes were purchased from Millipore. Chemicals were used as received with safety precautions taken as according to their respective MSDS.

2.2. Equipments

Raman measurements were performed with a portable Raman spectrometer system provided by B&W TEK Inc., known as innoRam with a wavelength of 785 nm and a maximum laser output power at system's excitation port of 348 mW and 285 mW in the probe. For measurements the laser power at the probe was 28.5 mW in order to avoid sample damage. UV/Vis measurements were performed using a halogen lamp as excitation and the monocromator and photonic detector of a PTI QuantaMasterTM Spectrofluorometer (Photon Technology International) system as a detector with FeliX32 software.

2.3. Functionalization of single-walled carbon nanotubes

Carboxylated carbon nanotubes (c-SWNTs) were prepared by adding into a glass flask 100 mg of single-walled carbon nanotubes to 20 mL of H_2SO_4/HNO_3 mixture (3:1). The mixture was refluxed for 1 h. Afterwards, diluted fractions of the mixture were centrifuged at 10000 rpm for 10 min and washed with water until the supernatant phase ceased to have acidic pH. Finally, carboxylated derivates were dried at 60 °C in a heater. After the acid treatment, the SWNTs were negatively charged by covalently attached carboxylic (–COOH) groups on the sidewalls and the open ends which make them highly soluble in water. The method of carboxylation is based on the described by Xue and Cui [20]with some modifications.

2.4. c-SWNTs preconcentration procedure

2 mL of river water sample containing 3.12 mM of CTAC (from a 0.1 M stock solution) at a $pH = 1.4$, adjusted with HCl 1 M, were treated with 0.1 g of ionic liquid ($BMIM\ PF_6$). The system was manually shaken for 30 s. Then the system is allowed to stand in order to achieve ionic liquid from water phase separation. The river water samples were fortified with certain volume of a stock solution of carboxylated single-walled carbon nanotubes, the solution was homogenized and mixed for 2 h. The pH of the solution is acid due to the carboxylic groups in carbon nanotubes and it was adjusted to 1.4 for the extraction. For Raman measurements 10 μL of the extract were filtered through a Millipore cellulose membrane with a pore size of 5 μm, where the nanotubes are retained homogeneously. Carbon nanotubes are retained in the membrane owing to their length and flexibility by physic impediment, since there is a network of pores in the membrane and not straight holes. The viscosity of ionic liquid phase in this case helps to their retention. A home-made designed microfiltration device with sandwich configuration (Fig. 1) was

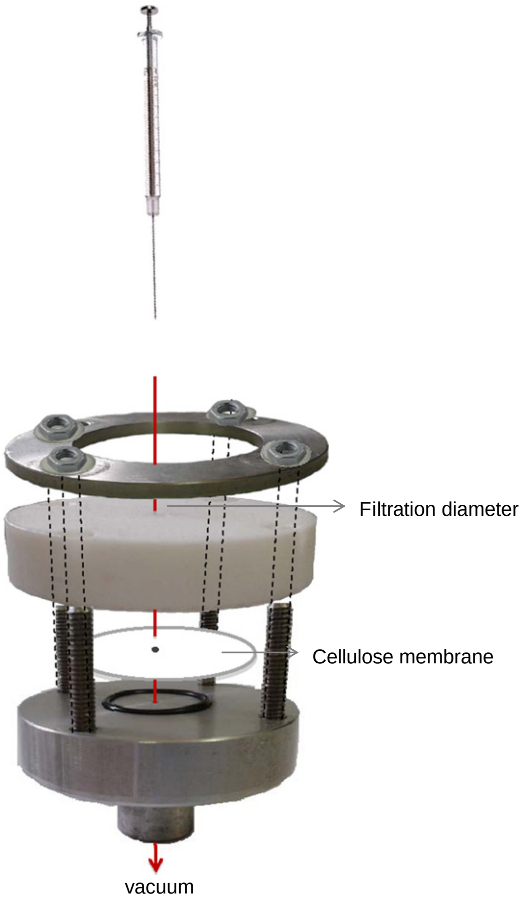

Fig. 1. Scheme of the microfiltration device.

employed. The diameter of filtration is 1.3 mm. Both, the volume of ionic liquid phase and the diameter of filtration were optimized in order to have an appropriate signal in Raman spectroscopy. For samples with very low concentration (<0.8 mg L^{-1}), a modified procedure is proposed. Maintaining the proportion of ionic liquid to water, the volumes can be increased. Finally, instead of 10 μL, a major volume is filtrated on the cellulose membrane.

Raman measurements were performed with a laser of 785 nm with a power of 28.5 mW. A 1-sec CCD exposure was used, with averaging the Raman signal over 10 signal acquisitions. Raman measurements were acquired from five randomly selected locations within each membrane and repeated over three samples, giving a total of 15 Raman measurements for each nanotube concentration. For these measurements a 20 × objective was employed, resulting in an area of measurement in each spot of 109 μm of diameter. It should be remarked the homogeneity of carbon nanotubes in the membrane since spectra measured at different points of the sample provide a similar signal.

3. Results and discussion

3.1. Selection of the ionic liquid

The interaction of imidazolium-based ionic liquid with single-walled carbon nanotubes through weak van der Waals interaction has been described [19]. The ionic liquids can effectively shield the strong π–π stacking interaction among SWNTs. The objective of this work was to take advantage of this affinity in order to develop an extraction procedure which allows preconcentration of the analyte (carboxylated carbon nanotubes), so the main requirement that ionic liquid must fulfill is a low solubility in water although both water-soluble and insoluble ionic liquids containing1-butyl-3-methyl imidazolium cation has been proved to interact with carbon nanotubes. Ionic liquids' solubility is dependent on its anion, presenting a low solubility in water those composed by hexafluorophospate (PF_6^-), so they are suitable for the purpose of our work. For this reason, the selected ionic liquid was 1-butyl-3-methylimidazolium hexafluorophosphate (BMIM PF_6). Additionally, it has been demonstrated the suitability of 1-hexyl-3-methylimidazolium hexafluorophosphate (HMIM PF_6) to perform the extraction procedure.

3.2. Effect of the amount of cationic surfactant

The negatively charged nanotubes are covered by cationic surfactant molecules forming ionic pairs. Thus, the effect of the amount of a cationic surfactant, CTAB and CTAC, on the extraction procedure was studied. Similar results were obtained for both surfactants in terms of carbon nanotube extractions; however CTAC was selected because it produces lower modifications in the viscosity of the ionic liquid. The influence was studied in a range 0.4–35 mM of CTAC. The signal of carbon nanotubes extracted on ionic liquid increased when increasing the amount of CTAC up to 3.12 mM, being observed a better dispersion of the nanotubes within the ionic liquid. From these results, the optimum amount of CTAC was selected to be 3.12 mM.

3.3. Effect of the pH

We have observed that when carboxylated single-walled carbon nanotubes are put in contact with ionic liquid, the extraction is not quantitative and carbon nanotubes are not homogeneously distributed in the ionic liquid phase. As the carboxylated carbon nanotubes are negatively charged it may influence the low efficiency of the extraction. Thus, pH is thought to be a variable that may condition the performance of the extraction. By decreasing the pH the negative charge of the nanotubes may be neutralized and the protonated carboxylate specie extracted in the ionic liquid phase. We studied the influence of the pH in the range 0.72–3.32 (3.32 is the pH of the initial solution), adjusting the pH with a solution of HCl 1 M. The best results were obtained for a pH of 1.37, at which most of the carboxylic groups will be protonated. We discarded the adjustment of the pH as the only step to improve the extraction by neutralizing the charges due to the fact that although the extraction was quantitative, the ionic liquid phase with the carbon nanotubes within it showed to be more homogeneous when CTAC was present.

Consequently, we also studied the influence of the pH in the extraction with CTAC present in the media at the optimized concentration. The study was conducted in a range 1.10–3.46, finding that in this case the pH plays a less significant role in the efficiency of the extraction. Nevertheless, prior extraction with ionic liquid the pH was adjusted to 1.4. Probably CTAC molecules surrounding the carbon nanotubes are not enough to neutralize the negative charges due to steric impediment, thus a decrease of pH benefits the extraction.

3.4. Selection of the nature of the membrane

The microfiltration of the extracted nanotubes in the ionic liquid was assayed with membranes of different nature: cellulose, PTFE and PVDF, with a diameter of pore of 5.0 μm. Carbon nanotubes are retained in the membrane owing to their length and flexibility by physic impediment. Moreover, the viscosity of the ionic liquid creates a lattice of carbon nanotubes that remains retained on the membrane after vacuum filtration. Excess of ionic liquid is removed by filtration and the one that remains adsorbed on carbon nanotubes surface is used to normalize spectra of carbon nanotubes.

PVDF and cellullose membranes showed less operational problems maintaining their integrity after the filtration procedure, while the PTFE ones tended to wrinkle. A cellulose membrane was finally selected because it was easier to handle and the nanotubes were homogeneously distributed. This membrane do not interfere in Raman measurements and it is not damaged during the laser irradiation.

3.5. Raman spectra of carbon nanotubes in ionic liquid retained in the membrane

The most significant Raman spectral features for single-walled carbon nanotubes are the radial breathing mode (RBM, 100–300 cm^{-1}), the disorder peak (D peak, ∼1350 cm^{-1}), the tangential mode (G band, 1400–1700 cm^{-1}), and the second-order overtone of the D peak (G', 2500–2800 cm^{-1}) [21]. The RBM band is originated from the out-of-plane tangential acoustic modes of monolayer graphene sheet and all carbon atoms vibrate in phase along the radial direction [22]. It is the characteristic mode for SWNTs, although can sometimes be observed in MWNTs with a small diameter inner tube (less than 2 nm) when good resonance condition is established [23]. The G-band, in the case of SWNTs, comprises several tangential modes due to stretching vibrations in SWNT sidewall C–C bonds. Two double resonance features commonly found in the Raman spectra of CNTs bundles are the D-band feature, stemming from the disorder-induced mode in graphite with the same name [24], and its second harmonic, the G' band. In nanotubes, both the D-band and the G'-band are sensitive to the CNT diameter and chirality, since these features depend sensitively on how the 2D electronic and phonon structure is folded into a 1D structure. In the case of carboxylated

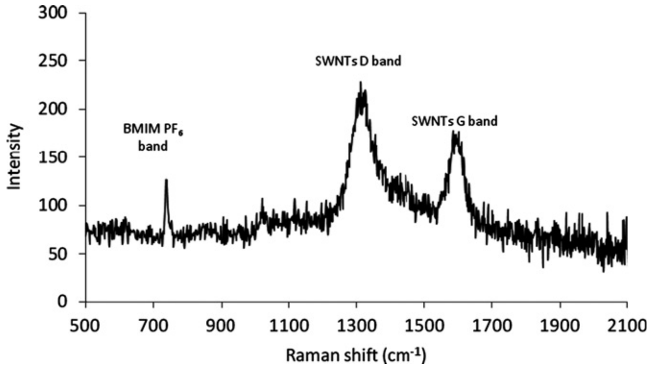

Fig. 2. Raman spectrum of carboxylated single-walled carbon nanotubes preconcentrated in ionic liquid and microfiltrated on a cellulose membrane. The peak at 739 cm^{-1} corresponds to the ionic liquid (BMIM PF$_6$). The bands at 1313 and 1595 cm^{-1} correspond to the D and G band of carbon nanotubes, respectively.

carbon nanotubes a difference in the spectrum with respect to pristine carbon nanotubes is a distintive D-band to G-band intensity ratio [25].

In the spectra obtained with this procedure the most predominant bands are D and G, while the RBM was barely distinguishable (see Fig. 2). The intensity of the D band has been used in order to quantify the samples. Ionic liquid bands also appear in the spectrum, such as a characteristic one at 739 cm^{-1} produced by the symmetric stretching of PF_6^- anion, which was used as internal reference to normalize the spectra. It must be pointed out that there is no effect of the surfactant on the Raman spectrum of carbon nanotube after the filtration step.

The instrumental variables for measurement were optimized. We studied the influence of laser power in the spectra. The optimum laser power was found to be 28.5 mW with a laser wavelength of 785 nm. This power was selected due to the fact that it proved to be enough to record a good spectrum resulting higher laser powers into sample damage.

Furthermore, spectra were performed with an acquisition time ranging from 0.5 to 20 s and a number of acquisitions ranging from 1 to 10. The minimum time of acquisition necessary to visualize the spectrum has been proved to be 1 s, but it is necessary to accumulate more than one spectrum in order to achieve a good signal-to-noise ratio. A compromise between the duration of the acquisition and the quality of the spectrum has to be reached being 10 acquisitions enough to record an acceptable spectrum. Thus, the better conditions in terms of shape of the spectrum and duration of the acquisition were 1 s accumulating a sum of 10 spectra.

3.6. *Analytical features of the proposed method*

The analytical performance of the proposed method was studied in order to evaluate its usefulness for quantitative analyses. Calibration graphs of the analytical signal versus concentration for standard solutions were registered. The intensity of the D band of carbon nanotubes in the Raman spectra divided by the intensity of the ionic liquid band at 739 cm^{-1} was adopted as analytical signal.

The calibration curve was determined for concentrations ranging from 0.6 to 4 mg L^{-1}. Each concentration level was analyzed in triplicates (measuring each sample at five randomly selected location in the membrane), and the response was linear in the range of concentrations tested ($R^2=0.9856$). The precision of the measurements was evaluated at a concentration of 1.4 mg L^{-1} obtaining a relative standard deviations ($n=5$) of 3.2%. The detection and quantification limits were calculated as three and 10 times the signal of Sa between the scope and were 0.169 and 0.565 mg L^{-1}, respectively. In the case of the modified procedure for large volume (samples with a concentration <0.8 mg L^{-1}), the limit of detection was 0.050 mg L^{-1}. The interval of linearity was from 0.07 to 0.8 mg L^{-1}, which was the measured interval. In this case the RSD for a concentration of 0.8 mg L^{-1} was 12.6%, higher than with the normal procedure, but with this modified protocol we can determinate carbon nanotubes at lower concentrations. The analytical features of the method developed are summarized in Table 1.

3.7. *Application to the determination of water-soluble carboxylated carbon nanotubes in river water samples.*

In order to check the analytical usefulness of the proposed method, samples of water from Guadalquivir river were fortified and analyzed following the recommended procedure. Before fortification the samples were analyzed and no carbon nanotubes were found in them since the analytical signal was equal to zero.

To demonstrate the accuracy of the proposed method, a recovery test of the analysis of spiked samples was also carried out. For the recovery study, four fortification levels were assayed being the recoveries values shown in Table 2. The obtained results displayed good agreement obtaining acceptable recoveries between 70.1% and 101.7% depending on the concentration level. Each sample was analyzed in triplicate in order to evaluate the precision of the method. The coefficients of variation ranged from 8.98% to 3.63%.

Interferences of other components of the matrix have not shown effect on the performance of the extraction procedure. Selectivity is achieved in the first place by the use of ionic liquid for the extraction acting as a sieve for other components present in water samples.

Table 1
Analytical features of the method.

Calibration equation	S=(0.54 ± 0.03) [c-SWNTs]+(0.39 ± 0.01)
R^2	0.9856
Lineal range	0.4–4 mg L^{-1}
LOD[a]	0.169 mg L^{-1}
LOD[b] (Large volume procedure)	0.050 mg L^{-1}
RSD[c] (%)	3.2%
RSD[d] (%) (Large volume procedure)	12.6%

[c-SWNTs]: Concentration of c-SWNTs in the aqueous media in mg L^{-1}.

[a] Limit of detection, determined as $(3S_a)/b$, for $y=bx+a$.

[b] Limit of detection, determined as $(3S_a)/b$, for $y=bx+a$.

[c] Relative standard deviation, determined from five measurements of 1.4 mg L^{-1} c-SWNTs.

[d] Relative standard deviation, determined from five measurements of 0.8 mg L^{-1} c-SWNTs.

Table 2
Recovery study of spiked river samples.

Sample	Added concentration (mg L^{-1})	Found concentration[a] (mg L^{-1})	Recovery (%)	RSD (%)
1	0.94	0.68 ± 0.08	70.1–81.2	8.98
2	1.41	1.11 ± 0.07	73.8–84.6	4.98
3	1.88	1.83 ± 0.08	92.8–101.7	3.63
4	2.35	2.2 ± 0.1	93.9–100.3	4.04

[a] Average of three independent spiked samples ± CI ($p<0.05$).

4. Conclusions

It has been demonstrated that ionic liquid with a cationic surfactant are a good combination for the extraction of carboxylated single-walled carbon nanotubes from river water samples. Thanks to the high affinity of imidazolium group for the carbon nanotube, it is possible to preconcentrate the nanotubes in a low volume of ionic liquid. Regards detection, carbon nanotubes present a characteristic Raman spectrum which has been used as analytical signal. It should be remarked that the use of a cationic surfactant is crucial for avoiding the carbon nanotube aggregation within the ionic liquid phase and then for obtaining a homogeneous dispersion of carbon nanotubes on the membrane, which allow for quantitative and reproducible Raman measurements of the extracted nanomaterials.

The limit of detection achieved with the proposed methodology is $50\,\mu g\,L^{-1}$ is higher than the estimated concentrations reported until date. However this work can be considered as a first approximation to the quantification of this nanomaterial in water matrices. It could be applied as the screening method to control the release of this nanomaterial in the source points of contamination, such as factories, landfills and wastewater effluents, where concentrations of carbon nanotubes will be considerably higher.

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