



ORIGINAL ARTICLE

Synthesis and assessment of a novel ionic material for removing polycyclic aromatic hydrocarbons with ultrasound



María A. Schiel, Claudia E. Domini*, Alicia B. Chopa¹, Gustavo F. Silbestri^{*,2}

Instituto de Química del Sur (INQUISUR), Departamento de Química, Universidad Nacional del Sur, Av. Alem 1253, B8000CPB Bahía Blanca, Argentina

Received 23 March 2016; accepted 8 November 2016
Available online 16 November 2016

KEYWORDS

PAHs;
Ultrasound;
Buthylthiophenium salt

Abstract A novel ionic material from thiophene and bromobutane was synthesized using ultrasound assistance as an alternative energy source. The optimal sonochemical reaction was carried out at 185 W, 20% duty cycle, 60 min in an ice bath. Its extractive capacities with chrysene model system in hexane were studied. The polycyclic aromatic hydrocarbons (PAHs) extraction process, also assisted by ultrasound, was achieved just in 20 min, at 0 °C (ice bath), at 10 s “on” – 20 s “off” cycle and 90 W, and a ratio of thiophenium salt solution to sediments of 4:0.2 (ml/g).

The buthylthiophenium salt was tested for PAHs extraction in sediment samples from the Bahía Blanca Estuary (BBE). Recoveries of 65% or higher were assessed by molecular fluorescence spectrometry.

© 2016 Production and hosting by Elsevier B.V. on behalf of King Saud University. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

1. Introduction

Several research groups have devoted to the study of new adsorbent materials for environmental remediation treatments (Zhang et al., 2016). Jiao et al. (2015) developed nanohybrids composed of graphene

oxide (GO) and Fe₃O₄ nanoparticles for highly efficient removal of dyes such as methylene blue and Rhodamine B. The authors stated that this is a highly efficient adsorbent material for removing organic contaminants, expanding the field of applications related to the environment. Wang et al. (2015a,b) reported the preparation of new composite adsorbent by hierarchical core-shell manganese oxide nanocomposites (Fe₃O₄@MnO₂ and Fe₂O₃@MnO₂), via a facile hydrothermal procedure. The obtained nanocomposites were employed to adsorb the same dyes used in a previous work from wastewater systems. With a similar purpose, hydrogels such as GO/polyethylenimine (PEI) resulted in efficient adsorbents (Guo et al., 2015). Zhang et al. (2013) demonstrated that efficient nanocomposites adsorbents were novel hybrid nanomaterial formed by ZrO₂ into spherical polystyrene beads (MPS) covalently bound with charged sulfonate groups. In addition, the adsorbent material presented good Pb (II) sorption. Moreover, new applications were developed in the biomedical field (Xing et al., 2016a–c).

* Corresponding authors.

E-mail addresses: cdomini@criba.edu.ar (C.E. Domini), gsilbestri@uns.edu.ar (G.F. Silbestri).

¹ Member of CIC.

² Member of CONICET.

Peer review under responsibility of King Saud University.



Production and hosting by Elsevier

Research related to analyte separation by liquid–liquid extractions or solid–liquid extractions (Zhang and Lee, 2012; Tan et al., 2012; Vidal et al., 2007; Martinis et al., 2008) in diverse analytical applications of ionic liquids (ILs), and the synthesis and use of ionic compounds as solvents (Martins, 2008) significantly increased in recent decades.

ILs, also called “designed solvent”, are constituted by salts with melting points below 100 °C and their decomposition temperature is usually between 300 and 400 °C. They have attracted interest owing to their chemical and physical properties; for example: wide range of temperatures in which they remain liquid, negligible vapor pressure, variable viscosity and density, not flammable characteristics, and also low volatility at atmospheric pressure. The most common ILs are pyridinium and imidazolium derivatives. Also, phosphonium and tetraalkylammonium compounds can be used for the same purpose (Mantz and Trulove, 2008; Ruiz-Aceituno et al., 2013).

The first precedent about the synthesis of *S*-alkylthiophenium salts has been reported by Brumlick et al. (1964) by reaction of thiophene with trimethyloxonium tetrafluoroborate or methyl iodide and silver perchlorate. Ten years later, Acheson and Harrison (1970) obtained these salts by treatment of the corresponding thiophenes with alkyl halides in the presence of AgBF₄. Unfortunately, low yields of a series of 1-ethyl- and 1-methyl-thiophenium salts were obtained. It is important to mention that the *S*-alkyl salts were strong alkylating agents. Following the chronological order, Heldeweg and Hogeveen (1974) modified the method proposed by the former authors and, after two hours of filtration, extraction and anion exchange process, the salt was obtained in 60% yield. It was not until 1997 that Lee et al. (1997) took up research about the synthesis of such salts and synthesized thiophene manganese derivatives by nucleophilic attack of Grignard reagents to sulfur atom, yielding *S*-*R*-thiophene manganese carbonyl (R = Me, Et, Ph). The treatment of this compound with NOBF₄ and subsequent photolysis gave rise to *S*-*R*-thiophenium in high yields. In general, the synthesis of ILs involves two steps: (i) the cation formation and (ii) the ionic exchange reaction to generate the desired product. It is important to mention that both reactions take from 24 h to 2 or 3 days using an external conventional heat source (Fraga-Dubreuil et al., 2002).

In order to decrease the time, both in the synthesis of ionic materials and in the treatment of samples, ultrasound (US) energy was incorporated (Lévêque et al., 2002; Cravotto et al., 2008; Lévêque et al., 2006). Effects of high power US have been studied since 1927 in organic synthesis (Cravotto and Cintas, 2006; Barge et al., 2011; Cintas et al., 2011), while US has been applied for analytical purposes since 1996 (Domini et al., 2006, 2009; Bendicho et al., 2012). We can mention that Huddleston and Rogers (1998) were the first researchers to use an IL as an extracting phase replacing the conventional organic solvents in a liquid–liquid extraction.

The US effects observed in irradiated organic reactions are due to cavitation, a physical process to create, expand and implode gaseous cavities in a liquid. Cavitation induces very high local temperatures (5000 K) and pressure (2000 atm) inside the bubbles (cavities) (Cravotto and Cintas, 2006; Cintas et al., 2011; Sadjadi et al., 2010; Cravotto et al., 2008; Pereira et al., 2007). By virtue of the effects mentioned above, the US irradiation constitutes a convenient way to accelerate and improve a great number of organic and organometallic reactions (Domini et al., 2012; Luong et al., 2013; Mason and Lorimer, 2002; Mason and Peters, 2002; Luche, 1998).

Finally, we want to remark that polycyclic aromatic hydrocarbons (PAHs), organic compounds that consist of fused aromatic rings, can act as pollutants entering the coastal or marine environment from natural or anthropogenic sources such as crude oil, incomplete fuel combustion processes or industrial discharges. Due to their high affinity for solid particles (Wang et al., 2015a,b) and their low solubility in water, the accumulation in fine-grained sediments poses a risk to health and aquatic ecosystems. For such reason, PAHs have been identified as toxic, mutagenic and/or carcinogenic substances (Tobiszewski and Namieśnik, 2012).

The extraction of PAHs by commercial ILs has been documented in the literature. To our knowledge, one of the two most representative investigations is the work of Markiewicz et al. (2013), who studied the dissolution of organic matter and PAHs from soil using 1-methyl-3-octyl imidazolium chloride ([OMIM]⁺ [Cl][−]), and the research of Feng et al. (2012) who developed a novel ionic liquid, 1-vinyl-3-octylimidazolium 2-naphthalene-sulfonate, from a commercial one (1-vinyl-3-octylimidazolium bromide, [VOIm]⁺ [Br][−]) to be used as absorbent material for solid phase microextraction.

This work explores environmental friendly conditions to generate ionic salts, from thiophene and bromobutane, using ultrasonic energy to prompt the *S*-alkylation reaction (Scheme 1). Moreover, the screening results show a promising ability to extract PAHs from natural sediments.

2. Materials and methods

2.1. General methods

Reagents were obtained from commercial sources and used as received (thiophene and chrysene, Sigma Aldrich; bromobutane, Merck). Organic solvents were distilled prior to use. Deionized water (type II quality) was obtained with a Millipore Elix 10 UV Water Purification System. Thin layer chromatography was performed with commercial silica-gel plates 60 F254 (Fluka), visualized under UV light and revealed with 5% phosphomolybdic acid on ethanol. ¹H NMR spectra were recorded on a Bruker ARX 300 (300.1 MHz for ¹H, 75.5 MHz for ¹³C) using D₂O as solvent. Organic phases were analyzed by gas–liquid chromatography (GLC) in an instrument equipped with a flame-ionization detector and a HP5 capillary column (30 m × 0.25 mm × 0.25 μm). Program: 36 °C for 2 min increasing 2 °C/min up to 280 °C. Ultrasound assisted reactions were carried out using a Cole Parmer 4710 series ultrasonic homogenizer operating at 20 kHz (375 W). Ultrasound assisted extractions were carried out using a Sonics Vibra cell, VCX130 with a nominal power of 130 W and a frequency of 20 kHz. In both cases the titanium probe tip (9.5 mm diameter) was immersed in the mixture. The fluorescence spectrometer used for the measurement of PAHs signal was a JASCO SP6500 with 266 nm of excitation wave length. A quartz 700 μL cell was chosen for the spectra measurement.

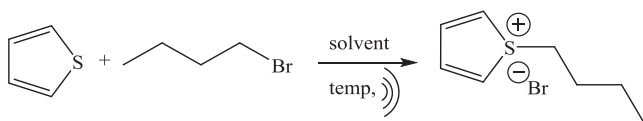
2.2. General procedure for the synthesis of buthylthiophenium salt

To a solution of 1.0 mmol of thiophene in 4.0 mL of water, 1.5 mmol of bromobutane was added and the reaction mixture was exposed to ultrasonic irradiation at 0 °C (ice bath) for 60 min (monitoring by ¹H NMR) and then washed with pentane or dichloromethane (1 × 4.0 mL) to finally store at −18 °C. Organic phase containing unreacted thiophene, was analyzed by GLC to determine, indirectly, the reaction yield.

2.3. General procedure for PAHs' extraction

2.3.1. Analytical performance

A series of solutions containing chrysene (25–100 μg L^{−1}) in thiophenium salt solution were prepared for the calibration curve. The correlation coefficient was 0.993.



Scheme 1 Synthesis of buthylthiophenium salt.

2.3.2. Model system

2.0 mL of a standard solution of chrysene in hexane (1.2×10^{-3} g/L) was extracted (ultrasonically, 90 W and cycles of 10 s on and 20 s off), during 20 min, with 2.0 mL of the thiophenium salt solution.

2.3.3. Real system

PAHs containing sediment from the Bahía Blanca Estuary (0.200 g), previously evaluated by a conventional method (Arias et al., 2010), and thiophenium salt solution (4 mL) were sonicated with a titanium probe at a nominal output power of 90 W and cycles of 10 s on and 20 s off in an ice/water bath for 30 min. To determine the optimum extraction time, fluorescence spectra were taken every 5 min.

3. Results and discussion

The research for new synthetic approaches for ionic materials and, particularly, the development of green methodologies is a field of enormous and growing interest. On this basis we have focused on the study of this new ionic material. First of all we carried out the synthesis and characterization of the thiophenium salt. The analytical study involved the optimization of the extraction capacity by the thiophenium salt. Finally the application in sediment samples was performed.

3.1. Synthesis and characterization

Our initial exploration started with the cation formation reaction between thiophene and bromobutane using conventional heat source. First, a solvent free system with both reagents (1:1.1) was refluxed under a nitrogen current for 24 h; under these conditions the reagents were completely evaporated, even when extra solvent (CH_2Cl_2) was added, and the no desired product was observed. Afterward, the same reaction was carried out at room temperature in a closed vessel. In this case, no changes in appearance were perceived even after a week, so one equivalent of potassium hexafluorophosphate (KPF_6) was added to achieve the anion metathesis producing the precipitation of KBr . NMR spectra and thin layer chromatography (TLC) did not show positive results.

After considerable experimentation, we decided to work directly under ultrasound energy conditions. Initially, a series of parameters have been assessed to find the optimal conditions, such as power, external temperature, reaction time and internal atmosphere (air or inert gas).

The first reaction was also carried out at room temperature, solvent free, nitrogen atmosphere and with the same reagent ratio (1:1.1), but at high power output (80%) and duty cycles (80%). Under these conditions the reagents evaporated so fast that it was impossible to keep the reaction going on for more than 2 min. Moreover, the addition of a few milliliters of solvent (hexane or toluene) did not improve the situation. In

order to avoid the evaporation of the reagents we decreased duty cycles to 20%. Nevertheless, after 30 min the reagents were completely evaporated and no product was formed. With the main goal, we decreased reaction temperature immersing the vessel in an ice/water bath (duty cycles 20%). Under these conditions, reagents did not evaporate but, after 80 min under sonication, even traces of the desired product were not detected. In order to shift the equilibrium by precipitation of the thiophenium salt, a Lewis acid (ZnCl_2) was used to form the ZnCl_2Br^- anion, and KPF_6 to produce the anion metathesis of Br^- by PF_6^- . However only starting materials were recovered, in both cases.

Considering that the salt was formed but it was unstable under the different conditions mentioned above, we thought that stabilization by solvation, in aqueous medium, may be possible. So, we carried out an experiment using the same reagents ratio (1:1.1), in water (3 mL) during 120 min under mild conditions (222 W and 60% duty cycle). A thick emulsion was formed (Supplementary electronic material, Fig. A1). TLC analysis suggested that the desired compound might have been formed: after developing in hexane:ether (30:70) under UV light, a dark spot remained in the seed point, indicating that an ionic or highly polar compound was present in the system.

However, all the attempts to isolate the compound up to this point were fruitless. We tried to precipitate the salt by changing the anion (by metathesis or using a Lewis acid) or by lowering the polarity of the medium by addition of less polar solvents, once the reaction finished. All of these attempts gave negative results. Solvent removal was also investigated. The aqueous system was subjected to evaporation by different techniques (lyophilization, speed-vac, vacuum) but in all cases no residue was recovered. Then, we supposed that the ionic compound was not stable in isolated form, so, we decided to carry out the reaction in deuterated water in order to verify the generation of the salt by ^1H NMR (Fig. 1).

In the aromatic zone the hydrogens on carbons 2 and 5 move from 6.76 ppm to 7.19 ppm and the hydrogens on carbons 3 and 4 move from 6.64 ppm to 7.00 ppm from thiophene to thiophenium salt, respectively. On the other hand, the alkylic tail appears to be on higher fields than in bromobutane: thus, methylene 1 moves from 3.44 ppm (bromobutane) to 3.24 ppm (6, thiophenium salt); the other shifts are more subtle; from 1.88 (2) to 1.70 (7), 1.53 (3) to 1.35 (8) and 0.99 (4) to 0.84 (9).

Taking into account that the reaction product could not be isolated, an indirect approach was employed for its quantification. Once the reaction finished, the mixture was extracted with CH_2Cl_2 and injected in the gas chromatograph in order to quantify the unreacted thiophene. A series of experiments summarized in Table 1 were carried out in water.

Even though the signals (^1H NMR) corresponding to the thiophenium salt were clearly discernible, the intensities of those belonging to the initial reagents were higher, indicating that the reaction yield was low (entries 1–3). These experiences suggested that water has a limited capacity to dissolve and stabilize the thiophenium salt, thus making it impossible for the reaction to keep evolving. By lowering the amount of reagents in the reaction mixture it was possible to enhance the relation of areas in favor of the product (entry 4).

Two additional experiments were performed: experiments 5 and 6 showed that an increase in sonication time did not affect

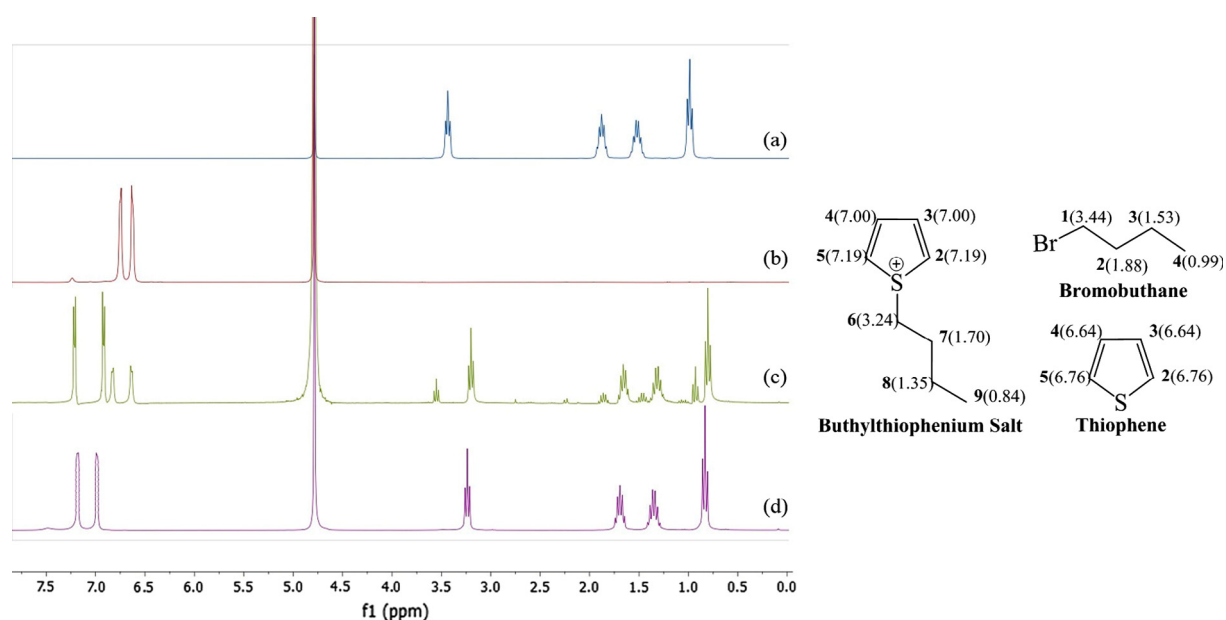


Figure 1 ^1H NMR spectrum sequence: (a) bromobutane; (b) thiophene; (c) reaction progress (30 min); (d) buthylthiophenium salt (60 min).

Table 1 Synthesis of thiophenium salt. Optimization in water medium.

Entry	Power (W)	Cycles (%)	Time (min)	Water (mL)	Thiophene (mmol)	Bromobutane (mmol)	Reagents ratio	Yield (%)
1	222	60	120	3	12.5	13.8	1:1.1	32
2	187	20	90	4	3	4.5	1:1.5	37
3	187	20	60	4	3	4.5	1:1.5	56
4	187	20	60	4	1	1.5	1:1.5	90
5	187	20	90	4	1	1.5	1:1.5	92
6	187	20	60	4	1	1.2	1:1.2	79

the yield (92%) while a decrease in the molar ratio of reactants produced a decrement in the reaction yield (79%).

In order to confirm that the signals belonged to the thiophenium salt and not to degradation by-products of the reagents, both starting materials were subjected to the same procedure described above. In the case of bromobutane no degradation by-products were identified. On the other hand, thiophene degradation showed a shift to lower fields along the reaction progress: from 6.76 and 6.64 ppm (thiophene) to 7.53 and 7.24 ppm. These signals appeared after 15 min of sonication and increased until 60 min (Fig. 2) (NOTE, Wu and Ondruschka, 2006a). At this point it is appropriate to cite that hydroxyl radicals and hydrogen peroxide can be formed by decomposition of water under ultrasound conditions (Maklno et al., 1983). Moreover, it is well documented that these decomposition products may oxidize thiophene and its derivatives to the corresponding thiophene sulfone (Wu and Ondruschka, 2006b, 2010). The absence of sulfone signals during the synthesis of the buthylthiophenium salt indicates that the oxidation reaction is not competitive, probably due to the characteristics of the equipment employed (20 kHz). Furthermore, Ondruschka has determined that usually the sono-degradation of organic compounds in aqueous solutions is much more efficient at high frequencies (200–850 kHz) than at low frequencies (20–80 kHz) (Wu et al., 2006).

Based on the identification (NMR) and quantification (GC) we conclude that the optimal condition for the synthesis of the thiophenium salt was 187 W of power, 20% duty cycle and 60 min employing a reagents ratio 1:1.5 in 4 mL of water (entry 5).

3.2. Analytical application

Recent studies on the application of 1-hexadecyl-3-methylimidazolium bromide (HDMIm-Br) to the extraction and/or preconcentration of PAHs from sediments, have been reported (Pino et al., 2008; Delgado et al., 2012). Here, we proposed an extraction method to assess PAHs screening in an easy and simple way, using the buthylthiophenium salt as extracting agent and the assistance of US. This technique was chosen for monitoring taking into account that PAHs fluoresce. The fluorescence spectra of chrysene in thiophenium salt solution ($\lambda_{\text{exc}}250/\lambda_{\text{em}}378$ nm) were consistent with the literature reports (Sharma et al., 2007). The emission maxima of chrysene dissolved in the salt solution exhibit a bathochromic shift with respect to the emission maxima obtained in hexane. A similar trend was observed for a solution of PAHs in ionic liquid (BMIM PF₆) compared with that obtained in acetonitrile (Fletcher et al., 2002).

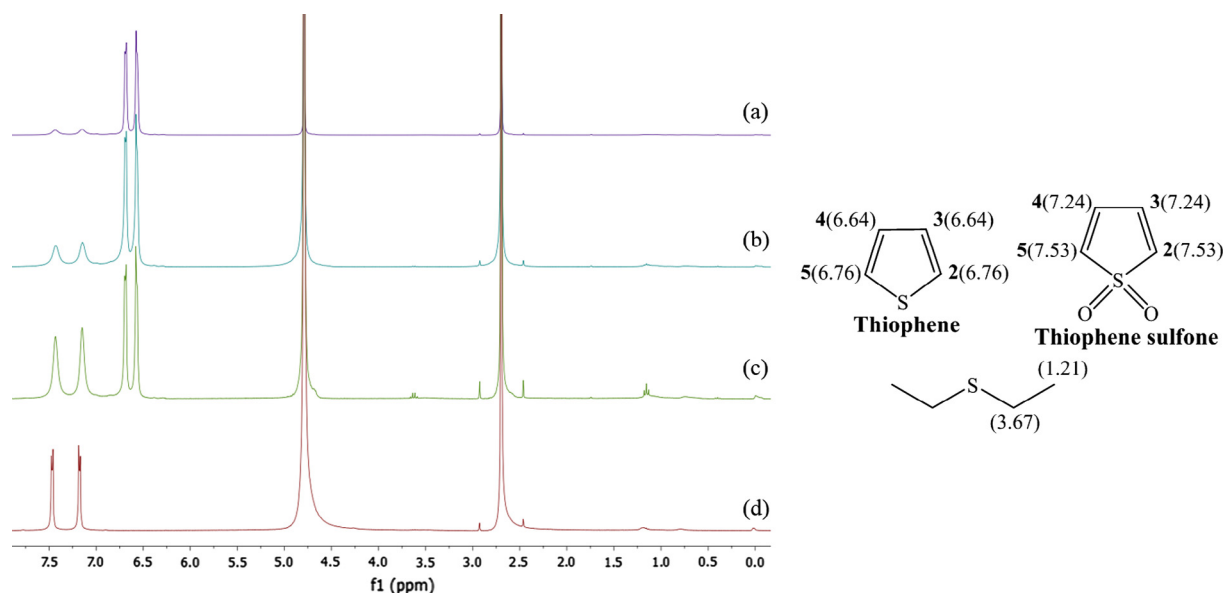


Figure 2 Thiophene degradation (187 W and 20% duty cycle): (a) 15 min; (b) 30 min; (c) 45 min; (d) 60 min. DMSO was used as internal standard.

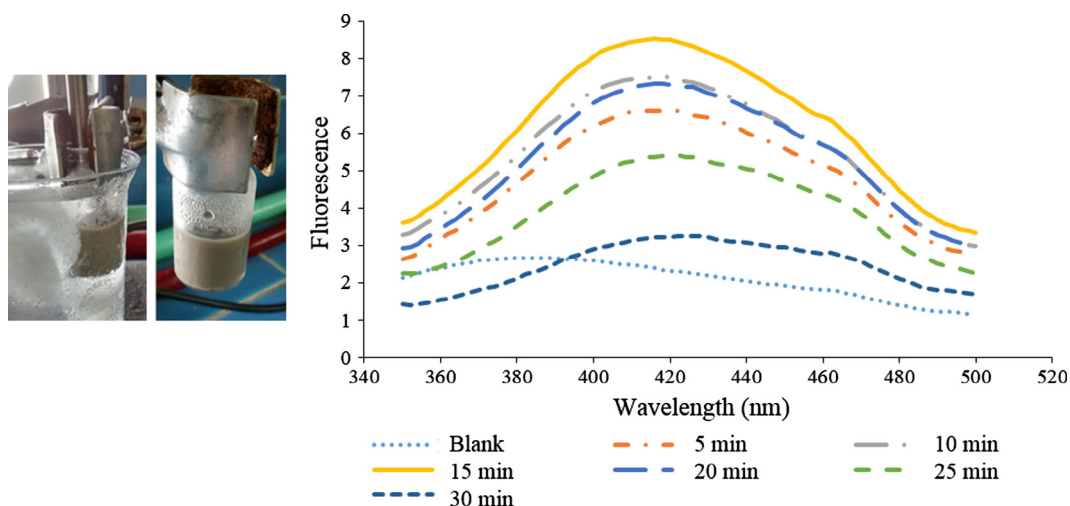


Figure 3 Fluorescence spectrum of real system's extraction.

3.2.1. Optimization of thiophenium salt extraction capacity

To evaluate the capacity of the thiophenium salt solution to extract one selected PAHs (chrysene in hexane) we carried out a simple test using US energy, which is described in Section 2.3 of Materials and method. It is necessary to optimize several operational variables which can influence the process of ultrasound extraction such as cycle of ultrasound exposure, sonication time and power output. The sonication time was studied in the range of 5–30 min. Nevertheless, 20 min was sufficient to achieve high recoveries for the PAHs tested. Ultrasonic horn was operated in pulsed mode (10 s on followed by 20 s off) at 90 W power, obtaining recoveries around 90%. We supposed that the increase in power generates cavitation bubbles collapse, transmitting more energy to the solution and promoting the degradation. This is in accordance with the work of Psillakis et al. (2004), who proved that an

increasing applied power and ultrasound frequency is a viable tool for the effective degradation of PAHs.

A decrease in the chrysene signal in the organic phase and an increase in the fluorescence signal in the aqueous phase were observed along sonication time (Supplementary electronic material, Fig. A2). It is important to mention that once the salt was synthesized it was necessary to wash it with CH_2Cl_2 , since traces of unreactive thiophene quench the PAHs' fluorescence. The extraction efficiency was accomplished working at 0 °C (ice bath) during 20 min at 10 s “on” and 20 s “off” cycle and 90 W, ratio of thiophenium salt solution to sediments of 4:0.2 (ml/g).

Previous literature shows that liquid–liquid extraction improves by increasing the salt concentration (salting out). In our case, the results demonstrated that even at 10% NaCl, the extraction efficiency does not improve.

3.2.2. Application in sediment samples

PAHs have very low water solubility due to hydrophobicity. As a consequence, their concentrations in water are very low causing rapid adsorption in sediments (El Nemr and Abd-Allah, 2003). The applicability of the extracting agent (thiophenium salt) in sediment samples with different PAHs level concentration (up to 20,000 ppb) was evaluated. Fig. 3 clearly shows that the fluorescence signal increased up to 15 min of sonication indicating that the extraction was taking place. After that maximum, the fluorescence intensity started to fall until it flattened at 30 min. Both PAHs and thiophenium salt were degraded, this being confirmed by a ^1H NMR spectrum in deuterated water. As a consequence, it was impossible to reuse the salt in a further extraction. The recovery values fall between 65% and 90% for low and high PAHs level, respectively.

4. Conclusions

It was possible to obtain a new ionic compound in the context of a sustainable chemistry using US energy (187 W, 20% duty cycles, 60 min) in an ice bath for cooling. The buthylthiophenium salt formed is stable in aqueous solution (for more than 30 days), especially if it is cooled, and proved to be an excellent extractant for PAHs in sediment samples. However, so far, the ionic compound could not be recovered after the extraction procedure. Further work is under development in our laboratories focused on the problems encountered.

Author contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Acknowledgments

This work was partially supported by CONICET, CIC, ANPCYT, and the Universidad Nacional del Sur, Bahía Blanca, Argentina. CONICET is thanked for a research fellowship to M.A.S.. The authors acknowledge to the Empresa Neuquina de Servicios de Ingeniería S.E., Argentine, for the provision of D_2O .

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.arabj.2016.11.002>.

References

- Acheson, R.M., Harrison, D.R., 1970. The synthesis, spectra, and reactions of some S-alkylthiophenium salts. *J. Chem. Soc. (C)*, 1764–1784.
- Arias, A.H., Vazquez-Botello, A., Tombesi, N., Ponce-Vélez, G., Freije, H., Marcovecchio, J., 2010. Presence, distribution, and origins of polycyclic aromatic hydrocarbons (PAHs) in sediments from Bahía Blanca estuary, Argentina. *Environ. Monit. Assess.* 160, 301–314.
- Barge, A., Tagliapietra, S., Binello, A., Cravotto, G., 2011. Click chemistry under microwave or ultrasound irradiation. *Curr. Org. Chem.* 15, 189–203.

- Bendicho, C., De La Calle, I., Pena, F., Costas, M., Cabaleiro, N., Lavilla, I., 2012. Ultrasound-assisted pretreatment of solid samples in the context of green analytical chemistry. *TrAC-Trend. Anal. Chem.* 31, 50–60.
- Brumlick, G.C., Kosak, A.I., Pitcher, R., 1964. The synthesis of the S-methylthiophenium ion. *J. Am. Chem. Soc.* 86, 5360–5361.
- Cintas, P., Palmisano, G., Cravotto, G., 2011. Power ultrasound in metal-assisted synthesis: from classical Barbier-like reactions to click chemistry. *Ultrason. Sonochem.* 18, 836–841.
- Cravotto, G., Calcio Gaudino, E., Boffa, L., Lévêque, J.-M., Estager, J., Bonrath, W., 2008. Preparation of second generation ionic liquids by efficient solvent-free alkylation of N-heterocycles with chloroalkanes. *Molecules* 13, 149–156.
- Cravotto, G., Cintas, P., 2006. Power ultrasound in organic synthesis: moving cavitation chemistry from academia to innovative and large-scale applications. *Chem. Soc. Rev.* 35, 180–196.
- Delgado, B., Pino, V., Anderson, J.L., Ayala, J.H., Afonso, A.M., González, V., 2012. An in-situ extraction-preconcentration method using ionic liquid-based surfactants for the determination of organic contaminants contained in marine sediments. *Talanta* 99, 972–983.
- Domini, C.E., Hidalgo, M., Marken, F., Canals, A., 2006. Comparison of three optimized digestion methods for rapid determination of chemical oxygen demand: closed microwaves, open microwaves and ultrasound irradiation. *Anal. Chim. Acta* 561, 210–217.
- Domini, C.E., Silbestri, G.F., Fernández Band, B., Chopa, A.B., 2012. Ultrasound-assisted synthesis of unsymmetrical biaryls by Stille cross-coupling reactions. *Ultrason. Sonochem.* 19, 410–414.
- Domini, C.E., Vidal, L., Cravotto, G., Canals, A., 2009. A simultaneous, direct microwave/ultrasound-assisted digestion procedure for the determination of total Kjeldahl nitrogen. *Ultrason. Sonochem.* 16, 564–569.
- El Nemr, A., Abd-Allah, A.M.A., 2003. Contamination of polycyclic aromatic hydrocarbons (PAHs) in microlayer and subsurface waters along Alexandria coast, Egypt. *Chemosphere* 52, 1711–1716.
- Feng, J., Sun, M., Li, J., Liu, X., Jiang, S., 2012. A novel aromatically functional polymeric ionic liquid as sorbent material for solid-phase microextraction. *J. Chromatogr. A* 1227, 54–59.
- Fletcher, K.A., Pandey, S., Storey, I.K., Hendricks, A.E., Pandey, S., 2002. Selective fluorescence quenching of polycyclic aromatic hydrocarbons by nitromethane within room temperature ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate. *Anal. Chim. Acta* 453, 89–96.
- Fraga-Dubreuil, J., Famelart, M.H., Bazureau, J.P., 2002. Ecofriendly fast synthesis of hydrophilic poly (ethyleneglycol)-ionic liquid matrices for liquid-phase organic synthesis. *Org. Process Res. Dev.* 6, 374–378.
- Guo, H., Jiao, T., Zhang, Q., Guo, W., Peng, Q., Yan, X., 2015. Preparation of graphene oxide-based hydrogels as efficient dye adsorbents for wastewater treatment. *Nanoscale Res. Lett.* 10, 1–10.
- Heldeweg, R.F., Hogeveen, H., 1974. Synthesis and some properties of s-alkylthiophenium ions. *Tet. Lett.* 11, 75–78.
- Huddleston, J.G., Rogers, R.D., 1998. Room temperature ionic liquids as novel media for 'clean' liquid-liquid extraction. *Chem. Commun.*, 1765–1766.
- Jiao, T., Liu, Y., Wu, Y., Zhang, Q., Yan, X., Gao, F., Bauer, A.J.P., Liu, J., Zeng, T., Li, B., 2015. Facile and scalable preparation of graphene oxide-based magnetic hybrids for fast and highly efficient removal of organic dyes. *Sci. Rep.* 5, 12451–12461.
- Lee, S.S., Lee, T.-Y., Choi, D.S., Lee, J.S., Chung, Y.K., 1997. Manganese thiophene tricarbonyl complexes: nucleophilic addition to sulfur and synthesis of thiophenium salts. *Organometallics* 16, 1749–1756.
- Lévêque, J.-M., Desset, S., Suptil, J., Fachinger, C., Draye, M., Bonrath, W., Cravotto, G., 2006. A general ultrasound-assisted

- access to room temperature ionic liquids. *Ultrason. Sonochem.* 13, 189–193.
- Lévêque, J.-M., Luche, J.-L., Pétrier, C., Rouxa, R., Bonrath, W., 2002. An improved preparation of ionic liquids by ultrasound. *Green Chem.* 4, 357–360.
- Luche, J.L., 1998. *Synthetic Organic Sonochemistry*. Plenum Press, New York.
- Luong, M., Domini, C.E., Silbestri, G.F., Chopra, A.B., 2013. Ultrasound-assisted synthesis of benzophenones by Stille cross-coupling reactions. Optimization via experimental design. *J. Organometal. Chem.* 723, 43–48.
- Makino, K., Mossoba, M.M., Rlesr, P., 1983. Chemical effects of ultrasound on aqueous solutions. Formation of hydroxyl radicals and hydrogen atoms. *J. Phys. Chem.* 87, 1377–1385.
- Mantz, R.A., Trulove, P.C., 2008. Viscosity and density of ionic liquids, In: Wasserscheid, P., Welton, T. (Eds.), *Ionic Liquids in Synthesis*, pp. 77–88.
- Markiewicz, M., Jungnickel, C., Arp, H.P.H., 2013. Ionic liquid assisted dissolution of dissolved organic matter and PAHs from soil below the critical micelle concentration. *Environ. Sci. Technol.* 47, 6951–6958.
- Martinis, E.M., Olsina, R.A., Altamirano, J.C., Wuilloud, R.G., 2008. Sensitive determination of cadmium in water samples by room temperature ionic liquid-based preconcentration and electrothermal atomic absorption spectrometry. *Anal. Chim. Acta* 628, 41–48.
- Martins, M.A., 2008. Ionic liquids in heterocyclic synthesis. *Chem. Rev.* 108, 2015–2050.
- Mason, T.J., Lorimer, J.P. (Eds.), 2002. *Applied Sonochemistry. The uses of power ultrasound in chemistry and processing*. Wiley-VCH, New York.
- Mason, T.J., Peters, D. (Eds.), 2002. *Practical Sonochemistry*. second ed. Ellis Horwood, London.
- NOTE: Additionally, two other signals (triplet in 1.21 and quartet in 3.67) were observed at 45 min (Fig. 3c). Ondruschka reported the thermal decomposition of volatile diethyl sulfide during its aquasonolysis (Wu, Z., Ondruschka, B., 2006a. Aquasonolysis of thioethers, *Ultrason. Sonochem.* 13, 371–378).
- Pereira, C.M.P., Stefani, H.A., Guzen, K.P., Orfão, A.T.G., 2007. Improved synthesis of benzotriazoles and 1-acylbenzotriazoles by ultrasound irradiation. *Lett. Org. Chem.* 4, 43–46.
- Pino, V., Anderson, J.L., Ayala, J.H., González, V., Afonso, A.M., 2008. The ionic liquid 1-hexadecyl-3-methylimidazolium bromide as novel extracting system for polycyclic aromatic hydrocarbons contained in sediments using focused microwave-assisted extraction. *J. Chromatogr. A* 1182, 145–152.
- Psillakis, E., Goula, G., Kalogerakis, N., Mantzavinos, D., 2004. Degradation of polycyclic aromatic hydrocarbons in aqueous solutions by ultrasonic irradiation. *J. Hazard. Mater.* B108, 95–102.
- Ruiz-Aceituno, L., Sanz, M.L., Ramos, L., 2013. Use of ionic liquids in analytical sample preparation of organic compounds from food and environmental samples. *TrAC Trend. Anal. Chem.* 43, 121–145.
- Sadjadi, S., Sadjadi, S., Hekmatshoar, R., 2010. Ultrasound-promoted greener synthesis of benzoheterocycle derivatives catalyzed by nanocrystalline copper(II) oxide. *Ultrason. Sonochem.* 17, 764–767.
- Sharma, H., Jain, V.K., Khan, Z.H., 2007. Identification of polycyclic aromatic hydrocarbons (PAHs) in suspended particulate matter by synchronous fluorescence spectroscopic technique. *Spectrochim. Acta A: Mol. Biomol. Spectrosc.* 68, 43–49.
- Tan, Z., Liu, J., Pang, L., 2012. Advances in analytical chemistry using the unique properties of ionic liquids. *TrAC Trend. Anal. Chem.* 39, 218–227.
- Tobiszewski, M., Namieśnik, J., 2012. PAH diagnostic ratios for the identification of pollution emission sources. *Environ. Pollut.* 162, 110–119.
- Vidal, L., Psillakis, E., Domini, C.E., Grané, N., Marken, F., Canals, A., 2007. An ionic liquid as a solvent for headspace single drop microextraction of chlorobenzenes from water samples. *Anal. Chim. Acta* 584, 189–195.
- Wang, C., Wu, S., Zhou, S., Wang, H., Li, B., Chen, H., Yu, Y., Shi, Y., 2015a. Polycyclic aromatic hydrocarbons in soils from urban to rural areas in Nanjing: concentration, source, spatial distribution, and potential human health risk. *Sci. Total Environ.* 527–528, 375–383.
- Wang, W., Jiao, T., Zhang, Q., Luo, X., Hu, J., Chen, Y., Peng, Q., Yan, X., Li, B., 2015b. Hydrothermal synthesis of hierarchical core-shell manganese oxide nanocomposites as efficient dye adsorbents for wastewater treatment. *RSC Adv.* 5, 56279–56285.
- Wu, Z., Ondruschka, B., 2006b. Aquasonolysis of thiophene and its derivatives. *Ultrason. Sonochem.* 13, 86–91.
- Wu, Z., Ondruschka, B., 2010. Ultrasound-assisted oxidative desulfurization of liquid fuels and its industrial application. *Ultrason. Sonochem.* 17, 1027–1032.
- Wu, Z.-L., Lifka, J., Ondruschka, B., 2006. Comparison of energy efficiency of various ultrasonic devices in aquasonochemical reactions. *Chem. Eng. Technol.* 29, 610–615.
- Xing, R., Jiao, T., Liu, Y., Ma, K., Zou, Q., Ma, G., Yan, X., 2016a. Co-assembly of graphene oxide and albumin/photosensitizer nanohybrids towards enhanced photodynamic therapy. *Polymers* 8, 181–192.
- Xing, R., Liu, K., Jiao, T., Zhang, N., Ma, K., Zhang, R., Zou, Q., Ma, G., Yan, X., 2016b. An injectable self-assembling collagen-gold hybrid hydrogel for combinatorial antitumor photothermal/photodynamic therapy. *Adv. Mater.* 28, 3669–3676.
- Xing, R., Jiao, T., Ma, K., Ma, G., Möhwald, H., Yan, X., 2016c. Regulating cell apoptosis on layer-by-layer assembled multilayers of photosensitizer-coupled polypeptides and gold nanoparticles. *Sci. Rep.* 6, 26506–26516.
- Zhang, Y., Lee, H.K., 2012. Ionic liquid-based ultrasound-assisted dispersive liquid-liquid microextraction followed high-performance liquid chromatography for the determination of ultraviolet filters in environmental water samples. *Anal. Chim. Acta* 750, 120–126.
- Zhang, Q., Du, Q., Hua, M., Jiao, T., Gao, F., Pan, B., 2013. Sorption enhancement of lead ions from water by surface charged polystyrene-supported nano-zirconium oxide composites. *Environ. Sci. Technol.* 47, 6536–6544.
- Zhang, Q., Teng, J., Zou, G., Peng, Q., Du, Q., Jiao, T., Xiang, J., 2016. Efficient phosphate sequestration for water purification by unique sandwich-like MXene/magnetic iron oxide nanocomposites. *Nanoscale* 8, 7085–7093.