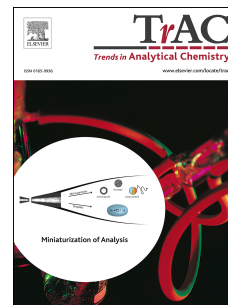


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Synergistic analytical preconcentration with ionic liquid-nanomaterial hybrids

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Abstract

Nanomaterials and ionic liquids (ILs) have very attractive properties for improved analytical preconcentration methods. Thus, ILs have been used as excellent tools to functionalize nanomaterials, giving them specific chemical properties for higher selectivity, extraction efficiency and extended re-utilization in preconcentration. Moreover, incorporation of IL-nanomaterial hybrids in miniaturized solid phase and liquid phase microextraction procedures is being increasingly exploited to obtain high analytical recoveries while developing environmentally friendly analytical methods. In this review, the design and application of innovative and efficient analytical methods for sensitive and selective determination of inorganic and organic analytes is described. The synthesis of some IL-nanomaterial hybrids is presented along with a revision of the most important synergistic physicochemical properties useful for the extraction of analytes. Finally, practical considerations concerning the application of IL-nanomaterial hybrids for the development of modern analytical separation and preconcentration techniques are fully discussed in this work.

Keywords: Ionic liquids; Hybrid nanomaterials; Functionalization; Sample preparation; Microextraction; Preconcentration.

Abbreviations: DI-SPME, Direct-immersion-solid-phase microextraction; DLLME, dispersive liquid-liquid microextraction; DLS, dynamic light scattering; D-M-SPE, Dispersive-magnetic-solid-phase extraction; D- μ -SPE, Dispersive-micro-solid-phase extraction; D-SPE, Dispersive-solid-phase extraction; EFS, Emission fluorescence spectroscopy; EF, Enhancement factor; ETAAS, Electrothermal atomic absorption spectrometry; FAAS, Flame atomic absorption spectroscopy; FES, Fluorescence emission spectrometry; GC-FID, Gas chromatography-flame ionization detector; GC-MS, Gas chromatography-mass spectrometry; [diBOHTMG], N,N,N,N-tetramethyl-N'N'-butanol-guanidinium chloride; HF-SLPME, Hollow fiber-solid/liquid phase microextraction; HF-SPME, Hollow fiber-solid-phase microextraction; HPLC, High performance liquid chromatography; HPLC-DAD, High performance liquid chromatography-diode array detector; HPLC-FLD, High-performance liquid chromatography-fluorescence detection; HPLC-PDA, High performance liquid chromatography-photodiode array detector; HPLC-UV-Vis, High performance liquid chromatography-ultraviolet-visible detector; HPLC-UV-VWD, High performance liquid chromatography-ultraviolet-variable wavelength detector; HS-SDME, Head space-single drop microextraction; HS-SPME, Headspace-solid-phase microextraction; ICP-OES, Inductively coupled plasma optical emission spectrometry; IR, Infrared spectroscopy; LLE, Liquid-liquid extraction; LLME, Liquid-liquid microextraction; LOD, Limit of detection; M-SPE, Magnetic-solid-phase extraction; NBs, Nitrobenzene compounds; AFDCIL, 1,2-Ethanediaminium, N,N'-bis(2-aminoethyl)-N,N,N',N'-tetramethyl chloride; PAHs, Polycyclic aromatic hydrocarbons; RS, Raman scattering; SDME, Single drop microextraction; SEM, Scanning electron microscopy; SPE, Solid-phase extraction; SPME, Solid-phase microextraction; TEM, Transmission electron microscopy; [TMG], Tetramethylguanidinium; UHPLC-MS/MS, Ultra high performance liquid chromatography-mass spectrometry/mass spectrometry; UV-vis, Ultraviolet-visible spectroscopy; XPS, X-ray photoelectron spectroscopy; XRD, X-ray diffraction spectroscopy; [cmmim]Cl, 1-Carboxymethyl-3-methylimidazolium chloride; DABCO, 1,4-Diazabicyclo[2.2.2]octane; [C₁₀C₁₀mim]Cl, 1,3-Didecyl-2-methylimidazolium chloride; [C₁₆mim]Br, 1-Hexadecyl-3-methylimidazolium bromide; [Simam]Cl, (2-Hydroxyethyl)-N,N-dimethyl-3-(triethoxy)silypropyl-ammonium chloride; [C₁₈mim]Br, 1-Octadecyl-3-methylimidazolium bromide; [C₆mim][PF₆], 1-Hexyl-3-methylimidazolium hexafluorophosphate; [C₆mim][Tf₂N], 1-Hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide; [C₇mim][PF₆], 1-Heptyl-3-

methylimidazolium hexafluorophosphate; [C₈mim][PF₆], 1-Octyl-3-methylimidazolium hexafluorophosphate; [mim][PF₆], Methylimidazolium hexafluorophosphate; [Vmim]I, 1-Vinyl-3-methylimidazolium iodide; [VC₈im]I, 1-Vinyl-3-octylimidazolium iodide.

1. Introduction

Current trends in modern analytical chemistry are focused on the development of green, simple and highly sensitive methods for the determination of trace analytes. Sample preparation methods based on extraction and preconcentration prior to analyte determination have undergone intensive research, due to increasing need for accurate and precise measurements at extremely low concentration levels of inorganic and organic analytes in complex matrices [1]. Furthermore, innovations following green chemistry concepts have been introduced for the development of modern preconcentration methods through miniaturization and the use of new extractant phases and emerging materials that might be more environmentally friendly when compared with conventional volatile organic solvents [2].

The introduction of nanotechnology in analytical chemistry and, particularly, the application of emerging materials like nanoporous materials and nanoparticles for developing novel solid phase extraction (SPE) or liquid-liquid extraction (LLE) methods, is a very attractive alternative for the separation and preconcentration of trace elements [3]. This is due to the high surface area of several nanomaterials and their chemical stability in both organic and inorganic media -which allows their effective application in samples with diverse chemical matrices- along with other favorable properties such as large adsorption capacity and fast sorption kinetics, key factors concerning their analytical applicability [3]. On the other hand, it has been demonstrated that ionic liquids (ILs) can be efficient tools to improve limits of detection, selectivity

and sensitivity when implemented in extraction and preconcentration methods [4]. There are no doubts that ILs represent valid alternatives to common volatile organic solvents that are normally used in analytical chemistry, due to the high recoveries and sensitivity enhancement factors obtained after their application [5]. Furthermore, practicality, safety and cost-effectiveness of implementing ILs in microextraction techniques, are real advantages for developing environmentally friendly analytical methods. However, limitations in the use of ILs for analytical extraction have been found, for example, due to high solubility of some ILs in water [6]. Therefore, the use of ILs supported on solid nanomaterials can be considered a valuable approach to overcome this difficulty. Another drawback of implementing ILs in extraction methods is caused by their high polarity, which might limit the extraction of certain analytes. In this case, dispersions of nanomaterials in ILs can be synergistically used to enhance the extraction efficiency of analytes [7]. Taking this into consideration, along with the potential advantages resulting from the combination of ILs and nanomaterials, the use of IL-nanomaterial hybrids is a promising approach for the development of microextraction techniques. In recent years, there has been a rapid growth in the number of analytical methods using IL-nanomaterial hybrids for SPE and LLE. The individual application of IL or nanomaterials in extraction/preconcentration methods has increased dramatically since the beginning of the 2000s decade. Moreover, since 2006, ILs and nanomaterials are being successfully combined to improve the performance of extraction/preconcentration techniques for several analytes (Fig. 1).

The aim of this review is to provide an overview of novel IL-nanomaterial hybrids that have been implemented as novel sorption materials in preconcentration techniques and their potential for inorganic and organic (ultra)trace ($< 1 \mu\text{g L}^{-1}$) analysis. A description of ILs, nanomaterials and their combinations, along with information on

existing classes and most significant properties, is provided. Also, a full evaluation of the performance of IL-nanomaterial hybrids during the development of extraction and preconcentration techniques is presented. Moreover, a discussion on the experimental strategies and possible mechanisms involved in the extraction of analytes by IL-nanomaterial hybrids is included. In fact, particular attention is given in this review to emerging solid-phase microextraction techniques using the synergistic potential of the sorbent materials. Finally, trends and future developments in this field are discussed.

2. Ionic liquids and nanomaterials: selected physicochemical properties useful for extraction and preconcentration

Hybrid materials resulting from the combination of ILs and nanomaterials are synthesized with the aim of retaining the properties of both counterparts. Some of these properties are: negligible vapor pressure, tunable composition and polar character, high chemical and thermal stability -from ILs-, and others like novel magnetic, optical, and surface properties, from nanomaterials. The main physicochemical properties of ILs, nanomaterials and their hybrids (IL-coated and IL-functionalized nanomaterials) are shown in Fig. 2. However, besides some selected properties of IL-nanomaterial hybrids, practical considerations to implement them during the development of extraction and preconcentration methods will be discussed.

2.1 Ionic liquids

Ionic liquids are semi-organic salts existing in the liquid phase at temperatures below 100°C [4]. They usually consist of bulky asymmetric organic cations and organic or inorganic anions. These modern solvents have specific physical properties, such as

non-combustibility, negligible vapor pressure, high heat resistance and high ionic conductivity. Some of these properties, such as the thermal stability and solubility in different solvents, depend mainly on the anion; while others, such as viscosity, surface tension and density, depend on the cation, the length of its alkyl chain, its structure and symmetry. Taking this into consideration, the aforementioned properties can be adjusted to a particular chemical application by changing the cation or anion's characteristics. For this reason, they have been named 'designer solvents' and are useful for important applications, such as liquid-liquid microextraction (LLME) methods [5]. Nevertheless, it should be pointed out that the intrinsic characteristics of some ILs may act as setbacks during LLME. For instance, ILs usually have a high viscosity, making the efficient mixing of aqueous and IL phases difficult [5]. Furthermore, partial solubilization of hydrophobic ILs in aqueous solutions not only results in extraction efficiency losses, but also modifies their properties due to water uptake [6]. Moreover, hydrophilic ILs have been scarcely used in LLE and they have found application only in in situ-dispersive liquid-liquid microextraction (DLLME). In this case, an hydrophilic IL has been employed as extractant phase and an anion exchange reagent, such as NaBF_6 , has been added to promote a metathesis reaction and transform the IL into a hydrophobic one [8]. Taking this into account, along with the possibility of coupling ILs with varied materials, the development of new solid phase microextraction (SPME) and liquid phase microextraction (LPME) methods based on IL-nanomaterial hybrids constitutes an interesting alternative.

Other important characteristics of ILs that have promoted their combination with nanomaterials, refer to their properties as surfactants. Thus, ILs have been used as stabilizers in the preparation of colloidal dispersions of silica, carbon nanotubes (CNTs) and metal nanoparticles (NPs) [9]. In the case of CNTs, for example, ILs can modify

their surfaces by changing their electronic structure and, accordingly, their electrical, optical and sorptive properties, among others [10]. Therefore, the interaction with ILs can generate surface changes on nanomaterials, which can be synergistically exploited to obtain hybrids for different uses, such as preconcentration and extraction [11].

2.2 Nanomaterials

The use of nanomaterials for various chemical applications has increased in recent years due to their unique properties, such as large specific surface area and multiple active sites for adsorbing analytes. CNTs (specific surface area: 50-1315 m²/g [12]) are the strongest of all known nanomaterials and have remarkable physical properties, such as excellent thermal conductivity and electrical properties, and outstanding field emission characteristics [13]. In fact, the highly hydrophobic surface of CNTs facilitates the strong adsorption of certain compounds by non-covalent forces, such as π - π stacking, electrostatic forces, Van der Waals forces and hydrophobic interactions. Therefore, CNTs are one of the most important sorption materials being intensively applied for analyte preconcentration [13]. Another important and more recent carbon-based nanomaterial is graphene. It is a crystalline, bidimensional carbon allotrope, with interesting physicochemical properties for extraction and preconcentration, including large surface area (2630 m²/g), high dispersibility and hydrophobicity [14]. Also, many applications have involved graphene oxide (GO), which maintains most of the properties of graphene, but shows a more hydrophilic character [15]. Moreover, both graphene and GO present advantages when compared with CNTs, mainly due to their higher surface area (890-2630 m² g⁻¹ [16, 17]), a consequence of both faces of these materials being exposed, thus increasing the availability for interactions [15].

Nanometer-sized inorganic oxides, namely nano-SiO₂, Al₂O₃, TiO₂, B₂O₃, Nb₂O₅, among others, have been widely used in SPE and its variants for preconcentration and/or separation. Among these, metal oxide NPs like Mn₃O₄ and ZrO₂, are a class of nanosized materials with notable increased surface area (108-170 m²/g [18]), high sorption capacity and strong acid sites. These characteristics make them good sorbents for removing metal ions from different samples [19].

Many benefits derive from the use of these nano-sized oxides, as their properties depend on various factors that can be controlled during their preparation. Nano-Al₂O₃ presents a variety of possible shapes, such as rod, fibrous, flake and spherical. These, along with its porous structure and size, are closely related to its physicochemical properties and, hence, to its possible applications in analytical procedures, allowing great flexibility in order to meet diverse needs [20]. Likewise, nano-TiO₂ can be obtained by simple synthesis, are stable and represent a non-toxic alternative, that has been widely used in analytical applications as support for chemical functionalization [21, 22].

However, the poor specificity of these nanomaterials towards analytes makes them unsuitable for the analysis of samples with complex matrices. Therefore, physical or chemical modification can be very attractive to overcome this drawback. Another problem concerning the use of metal oxide NPs for the development of dispersive microextraction techniques stems from the possibility of flocculation or gel formation in water based systems, turning the further separation of the analyte-enriched NPs extremely difficult. To overcome these drawbacks, in some cases such as Mn₃O₄, the NPs have been coated with an inert material like silica, in order to prevent their aggregation and lead to efficient dispersion [19].

Among the different properties showed by some nanomaterials, magnetism has been rapidly exploited in analytical chemistry, especially for the development of extraction and preconcentration methods, due to the possibility of easily collecting the magnetic NPs after the retention of analytes with the application of an external magnetic field. Their applications and magnetic properties depend highly on size distribution, morphology, structure and the surface functional groups present in the prepared nanomaterial [23]. Fe_3O_4 NPs have been widely used as magnetic nanosorbents and have found combination with ILs, as well as others nanomaterials such as graphene and CNTs, for the development of magnetic-solid-phase extraction (M-SPE) techniques [14].

2.3. Ionic liquid-coated nanomaterials

Non-covalent coating methods offer a simple manner to modify the surface of diverse nanomaterials without altering their chemical structure. In this case, the coating of nanomaterials is obtained based on physisorption phenomena. Moreover, electrostatic and Van der Waals forces are the most common interactions occurring on the surface of NPs with charged functional groups. Thus, positively or negatively charged ion clusters, instead of separate ions, surround the surface of NPs, generating an electrical double layer [24]. Hydrogen bonding is also responsible for the interaction between NPs and hydroxyl- and/or oxy- moieties on their surface (such as silica or metal oxides) and ILs with hydrogen donor or acceptor groups. In these cases, there exists a competition between NP-IL and IL-IL hydrogen bonds, which is highly dependent on environmental factors such as temperature and pressure [25].

The process to obtain IL-coated nanomaterials is usually based upon the impregnation of the nanomaterial with a specific IL. This impregnation is performed by direct contact, either by slow dropwise addition or by dispersion of the nanomaterial in

the IL phase during a defined period of time. Other reagents, such as ethanol, could be used as solvents or dispersers of the IL. Afterwards, the nanomaterial is washed, filtered and dried (Fig. 3). Then, the IL-nanomaterial hybrid can be employed for the development of preconcentration methods [14]. Although the process for preparation of IL-coated nanomaterials is simple, limited stability of the sorbent caused by the leaching of the IL from the nanomaterial has been observed [26, 27].

For the characterization of the obtained IL-nanomaterial hybrids different techniques have been employed as scanning electron microscopy (SEM), transmission electron microscopy (TEM), infrared spectroscopy (IR), Raman scattering (RS), X-ray photoelectron spectroscopy (XPS), elemental analysis, X-ray diffraction (XRD) spectroscopy (XRD), Z potential, dynamic light scattering (DLS) among others [14, 28, 29].

Several nanomaterials have been coated using the procedures mentioned in Fig. 3 and Table 1. Some examples include: single and multi-walled carbon nanotubes (SWCNTs, MWCNTs), magnetic NPs (MNPs) with core-shell structures -such as silica-coated magnetite ($\text{Fe}_3\text{O}_4@\text{SiO}_2$)-, nanocellulose, nanosilica, nanotitania, nanomagnesia and graphene. Magnetic hybrid nanomaterials show the additional advantage that the separation and collection of the sorption phase can be performed easily by an external magnetic field, thus eliminating time-consuming steps like centrifugation or filtration.

Common ILs, such as those containing the imidazolium cation, have been used in many works for coating several nanomaterials [e.g. 1-heptyl-3-methylimidazolium hexafluorophosphate ($[\text{C}_7\text{mim}][\text{PF}_6]$), 1-octadecyl-3-methylimidazolium bromide ($[\text{C}_{18}\text{mim}]\text{Br}$), 1-hexyl-3-methylimidazolium hexafluorophosphate ($[\text{C}_6\text{mim}][\text{PF}_6]$), 1-hexadecyl-3-methylimidazolium bromide ($[\text{C}_{16}\text{mim}]\text{Br}$), 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide $[\text{C}_6\text{mim}][\text{Tf}_2\text{N}]$, 1-octyl-3-methylimidazolium

hexafluorophosphate ($[\text{C}_8\text{mim}][\text{PF}_6]$) [21, 30-35]. However, less common ILs (Table 2), such as guanidinium [14], polymeric ILs (PILs) (i.e. ILs obtained by the polymerization of an IL as monomer) [13] and a thiourea-functionalized imidazolium cation with a bis(trifluoromethylsulfonyl) imide anion [36], have been used for preparing IL-nanomaterial hybrids during the development of novel preconcentration methods. In these cases, particular interactions between the ILs adsorbed on the surface of nanomaterials and the analytes could be expected. For example, when protein preconcentration was performed with guanidinium-based ILs supported on a magnetic chitosan-GO composite, the aromatic amino acids present in the proteins (i.e. tryptophan, phenylalanine and tyrosine) were responsible for the extraction, due to the hydrophobic interaction of the analytes with the long alkyl chains of the IL [14]. Also, in the extraction of phthalate esters using a fiber coated with a MWCNT-PIL hybrid, π - π , n - π and hydrophobic interactions were responsible for the extraction of the organic compounds. In this case, the improved extraction yield was attributed to an additional interaction between the protophilic esters of the phthalates and the cationic domains of the PILs [13]. In the determination of Pb, Saljooqi et al. synthesized a task-specific IL (TSIL) by attaching a thiourea group to an imidazolium cation, which was capable of selectively capturing Pb^{2+} , and immobilized it on MWCNTs [36].

Finally, a different approach has been the use of surface active ILs (SAILs), which have surfactant properties as a consequence of their amphiphilic nature. This is usually due to the presence of long alkyl chains in one or both ions of the IL structure. The ability of ILs to form organized structures such as hemimicelles and admicelles have been applied for the coating of NPs. Hemimicelles are monolayers of surfactants associated to surfaces, while admicelles are bilayer arrangements; both usually at concentrations below the Critical Micellar Concentration (CMC). This method has been

applied for the determination of flavonoids, using [C₁₆mim]Br mixed hemimicelles (a combination of hemi- and admicelles) supported on MCNTs@SiO₂, where π - π , hydrophobic and electrostatic interactions between the mixed hemimicelles and flavonoids yielded a high extraction efficiency [33]. Recently, cephalosporins in biological samples and fluoxetine in different matrices were also successfully determined with a [C₁₆mim]Br mixed hemimicelles coating on magnetic GO NPs [37] and magnetic graphene [38], respectively.

2.4. Ionic liquid-functionalized nanomaterials

In contrast with IL-coated nanomaterials, chemical functionalization with ILs involves the formation of covalent bonds between moieties within the IL structure and functional groups on the surface of the nanosorbent. This strategy offers some advantages over the non-covalent approaches based on physisorption in terms of flexibility at the time of selecting an IL and control over the functionalization degree. Nevertheless, it must be pointed out that disadvantages in terms of simplicity, time and waste generation also arise when functionalization is chosen over coating, since one or usually more chemical reactions are required [26]. Also, in certain occasions, harsh chemical treatment for functionalization results in the destabilization of the nanostructure and generation of unwanted surface alterations [39]. As for the stability of the hybrids, not much information is available from analytical works, but deeper studies have been conducted in cases where combinations of ILs and nanoparticles were used for catalysis. Although somehow obvious, different works point out the fact that chemical functionalization results in hybrids which endure a higher number of (re)uses, when compared to coated hybrids, mainly due to less leaching of the IL from the hybrid [27].

The properties of NPs depend not only on their diameter, shape and size-distribution, but also on the type of nanoparticle stabilizer and the nature of the interaction between the surface and the stabilizer [40]. Particles in the nanoscale range have an intrinsic instability, which results in the tendency to form agglomerates. For example, magnetic NPs (MNPs) are highly chemically active and are easily oxidized in air, which results in loss of magnetism and dispersibility [40]. For applications in extraction processes it is important to develop protection strategies to chemically stabilize NPs. In fact, stabilization of NPs by organic coatings allows further manipulation and solubility control, which facilitates their application in μ -SPE [41]. Among the factors involved in that stabilization, short range interactions which depend on the individual nature of the molecules, such as structural and solvophobic interactions, play an important role [42]. Structural forces arise as solvation layers around the nanomaterial are squeezed out of the closing gap when two solid surfaces approach each other, thus providing structural repulsion and preventing aggregation. Solvophobic forces, on the other hand, appear as a consequence of entropic factors related to the polar affinity between the surface of the nanomaterial and the IL, which translates into better dispersibility in systems in which the surface hydrophobicity is similar to that of the IL [43].

The use of tunable properties of ILs for surface modification of nanometer sized materials has been demonstrated to provide a new way to control the properties of the resulting ILs-nanomaterial hybrids [44-46]. Furthermore, functionalization also provides extra selectivity when nanomaterials are used as separation media.

Different nanomaterials have been chemically functionalized with ILs for diverse analytical applications. As shown in Table 3, magnetic composites such as

$\text{Fe}_3\text{O}_4@ \text{SiO}_2$ NPs and CNTs have been widely preferred to develop novel preconcentration methods. Covalent functionalization of CNTs by imidazolium-type ILs has been proposed by some authors and solubility, rheological and tribological properties of the resulting materials have been studied. [41]. These investigations have opened ways into new alternatives for the use of ILs and CNTs in analytical preconcentration. Functionalization of CNTs has been performed by two different methods [47, 48]. In one of them, CNTs were initially purified and oxidized using a strong acid to introduce carboxyl groups, which allows the grafting of amine or hydroxyl terminated ILs onto the CNT surface [48]. The carboxylic acid groups of the surface were activated using either thionyl chloride (SOCl_2) or $\text{N,N}'$ -dicyclohexylcarbodiimide (DCC) in DMF. In the other approach, the reaction between an imidazole derivative and the activated surface of the CNT through its functional group was performed. Then, the reaction with an alkyl halide gave the corresponding IL-functionalized CNTs [26, 47]. The synthetic routes are displayed in Fig. 4. The SPME technique based on IL-functionalized CNTs has been one of the most applied for preconcentration, but there have been studies on the dispersibility of IL-nanomaterial hybrids that could be exploited to expand the applications of this type of nanomaterials in extraction systems. For example, in 2006, Park et al. reported the covalent modification of MWCNTs with imidazolium salt-based ILs and studied the effect of different anions on their dispersion [41]. It was concluded that the relative dispersion and the phase-transfer of the IL-functionalized MWCNTs could be varied following an anion exchange process. New methods based on an “in situ solvent formation microextraction” technique could be further developed by taking advantage of this property.

Furthermore, ILs have been employed to functionalize the surface of MNPs (IL-MNPs) (Table 3). The coating of MNPs' surfaces with a layer of silica has been vastly applied before modification with ILs in order to prevent the oxidation of Fe_3O_4 . Furthermore, surface silanol groups offer many possibilities for covalent modification of MNPs, such as the use of ILs with an -OH functionalized cation. Generally, the functionalization procedure consisted in the dispersion of silica-coated NPs in toluene by ultrasonication during 15 min, followed by addition of the IL and stirring of this mixture at 120 °C for two days. After the reaction, the NPs were washed with a water/ethanol mixture. Finally, the particles were dried under vacuum at 70 °C for 24 h. It can be considered that IL-MNPs synergistically combine the advantages of magnetic particles and ILs, thus resulting in a sorption material with outstanding properties for SPE. The MNPs have a high surface area-to-volume ratio, which results in rapid extraction and makes the retention of target compounds with the lowest amount of sorption material feasible. Additionally, ILs have a great extraction capability towards different analytes thanks to different interactions that include electrostatic, hydrophobic and hydrogen bonding.

3. Solid-phase microextraction with IL-nanomaterial hybrids

SPE is a preconcentration technique with several advantages including: simplicity of operation, versatility, low cost of equipment, short extraction time, reduction or elimination of organic solvents and possible automation, among others. An important aspect of this technique is the material used as sorbent. In this sense, IL-nanomaterial hybrids have introduced novel dimensions into SPE due to the special properties mentioned earlier in this review [19, 35, 36, 49].

3.1. Dispersive solid-phase extraction

In addition to conventional SPE, dispersive SPE (D-SPE) is an attractive approach based on the use of a solid phase dispersed in a liquid sample or extract. A miniaturized and quite exploited variant of D-SPE technique is dispersive micro-SPE (D- μ -SPE), in which only a few micrograms of the solid phase are dispersed for analyte retention [50-53]. Strikingly good results were achieved by Serrano et al., who proposed the use of 1-butyl-3-aminopropylimidazolium chloride-functionalized GO as adsorbent for D- μ -SPE and applied it for the determination of four anabolic steroids and β -blockers in environmental water samples. Limits of detection (LODs) as low as 7 ng L⁻¹ and enhancement factors (EFs) as high as 4843 were obtained, using high performance liquid chromatography-diode array detector (HPLC-DAD) for detection [52]. Furthermore, nano-Al₂O₃ was functionalized with the hydrophobic IL Aliquat-336 was used for the preconcentration of inorganic Se species in diverse water samples. The coupling of this procedure with inductively coupled plasma optical emission spectrometry (ICP-OES) detection allowed an EF of 850 and an LOD of 4.6 ng L⁻¹, which are proof of the remarkable efficiency obtained with IL-nanomaterial hybrids.

3.2. Magnetic solid phase extraction

M-SPE is one of the most explored variants of SPE [14, 30, 33, 34, 37, 38, 44, 46, 53-83]. This is because M-SPE presents the following advantages: high extraction efficiency due to the outstanding surface area of the nanomaterials, fast separation by means of a magnetic field, possibility of modifying the surface of nanoparticles with functional groups to increase analytical selectivity, good dispersibility of the sorbent in aqueous media and the possibility of reutilizing the nanomaterial several times. ILs have

been employed along with MNPs both as classical monomeric ILs or as PILs. Generally, the MNPs are protected by a chemical layer such as -SiOH groups or -NH₂ groups, among others, to which ILs are attached. For example, Shi et al. [76] used Fe₃O₄ as magnetic nanomaterial, protected by 3-(trimethoxysilyl)propyl methacrylate. The IL employed in the functionalization was 1-vinyl-3-methylimidazolium iodide. The magnetic IL-nanomaterial hybrid was employed for the extraction of polycyclic aromatic hydrocarbons (PAHs) from tea and coffee samples. The methodology required the use of only 1 mg of nanomaterial for the microextraction process. A volume of 50 mL of sample yielded high preconcentration factors for all the evaluated analytes (between 106.3 to 123.8). Furthermore, the hybrid under study allowed 20 extraction cycles without a significant loss of the extraction efficiency and low LODs, in the range of 0.1 to 10 ng L⁻¹, were obtained. The high affinity between the analytes and the IL present on the nanomaterial was attributed to strong π - π and hydrophobic interactions between the aromatic moieties of the analytes and the IL.

Polymeric ILs have been explored as an alternative to monomeric ILs since the properties of conventional ILs such as: i) selectivity towards analytes, ii) high thermal stability and iii) viscosity, can be improved. For example, Yang et al. [81] employed Fe₃O₄ NPs protected with silanol groups that were functionalized with a PIL based on 1-vinylimidazolium as polymeric cationic backbone with bis(trifluoromethane)sulfonamide as anion. In this particular case, the nanomaterial was synthesized employing microwaves to reduce the reaction time and side reactions, while increasing yield and reproducibility. The hybrid nanomaterial was employed for the determination of sulfonylurea herbicides in soil samples, using only 60 mg of MNPs were employed. LODs were in the range of 1.62 to 2.54 μ g L⁻¹ and analytical recoveries between 81.8 and 97.6% were obtained which demonstrates the suitability of the IL-

nanomaterial hybrid for the analysis of complex samples. Relative standard deviation (RSD) values were between 3.2 and 4.5%. It has to be pointed out that these analytical figures of merit were obtained with a UV-Vis detector, which is not as sensitive as others normally used within HPLC, such as MS or DAD. It can be concluded that the remarkable efficiency of the PILs-NPs hybrids for preconcentration made the sensitive determination of the analytes feasible.

3.3. Solid phase microextraction based on coated and hollow fibers

Besides the aforementioned utilities, SPME can be considered an important technique to promote solvent-free preconcentration. Based on the use of extractant-coated fibers, SPME allows facile and effective extraction with milligram amounts of material. Different applications of this technique have been reported taking advantage of the implementation of IL-nanomaterial hybrids. Classic SPME, referred also as direct-immersion SPME (DI-SPME) involves the direct contact of the sorbent-coated fiber with the sample solution for extraction. To cite an example, fibers made of MWCNT coated with PILs have been applied for the determination of halogenated aromatic hydrocarbons [13] and PAHs [84] via DI-SPME with good results. Furthermore, headspace SPME (HS-SPME) is as an attractive choice for preconcentration of volatile analytes, since by exposing the sorbent coating to the headspace of the sample solution, contact with the sample matrix is avoided. An application of the HS-SPME technique implementing an IL-nanomaterial hybrid has been studied, involving the use of MWCNTs functionalized with a PIL (1,1'-(1,6-hexanediyl)bis(1-vinylimidazolium) bis(hexafluorophosphate) for the preconcentration of 2-naphthol in fruit samples prior to analysis by GC. Excellent repeatability (RSD = 2.56%), good recoveries and remarkable independence from matrix effects were obtained [85]. Similar results were

found in the determination of 16 volatile compounds in cheeses by HS-SPME coupled to gas chromatography-flame ionization detector (GC-FID) [86]. Most recently, the development of hollow-fiber SPME (HF-SPME) has introduced improvements related mostly to the limited lifetime due to sorbent desorption of SPME fibers by including a barrier between the extractant and the sample solution. For example, Es'hagi et al. developed a method based on HF-SPME preconcentration for the determination of benzodiazepines in hair, urine and wastewater samples. Novel TiO₂ NPs coated with 1-pentyl-3-methylimidazolium bromide were synthesized. LODs in the low ng mL⁻¹ range were achieved for several benzodiazepines, with excellent EFs between 533 and 1190 [22].

3.4. On-line extraction and preconcentration methods

Up until now, and to the knowledge of the authors of this review, there have been only three works reporting the application of IL-nanomaterial hybrids for on-line processes [49]. One of these works consisted in the preconcentration and determination of nitrophenols by capillary electrophoresis-UV-Vis (CE-UV-Vis). The sorbent material was prepared by mixing [C₆mim][PF₆] and MWCNTs in a mortar and the mixture was loaded into a fused silica channel (1 mm i.d. and 4 mm length) using a piston to compact the material inside the preconcentration unit. In the process, the sample (400-600 µL) was placed in a CE vial and the preconcentration unit was moved down into the vial, forcing the sample to flow through the sorption hybrid material by positive pressure. Once the treated sample was discarded, a methanolic KOH solution was used for elution. This design presented several advantages: the preconcentration channel could be attached directly to CE instrument, its analytical performance was good and it was a less expensive approach for preconcentration of this type of analytes.

In another work, Zou et al. determined Cd(II) and Cu(II) in environmental water by flame atomic absorption spectroscopy (FAAS) after preconcentration using a column packed with nano-TiO₂ functionalized with [C₈mim][PF₆] [35]. In this case, the IL-nanomaterial hybrid allowed faster loading of the analytes into the preconcentration column and higher retention than non-functionalized TiO₂ NPs. Likewise, better LODs, as low as 0.1 µg L⁻¹, were achieved, while excellent analytical recoveries were obtained during at least 10 preconcentration-elution cycles. Also, Abdolmohammad-Zadeh et al. prepared an Mn₃O₄@SiO₂-1-methyl-3-[(3-trimethoxysilyl)propyl]imidazolium chloride hybrid that was packed in a polypropylene cartridge and applied for the preconcentration and determination of Ag(I) in radiology films. An EF of 50.8 was achieved and no decrease in analyte recovery was observed with up to 300 adsorption-desorption cycles [19]. Therefore, the above-mentioned works show the convenience of implementing IL-nanomaterial hybrids in preconcentration techniques for efficient on line-SPE methods.

4. Conclusions and future trends

Novel sorption materials resulting from the combination of ILs and nanomaterials have fostered the development of more efficient analytical methods for trace analytes determination. The excellent properties obtained with IL-nanomaterial hybrids add further alternatives to improve preconcentration and extraction methods or to develop new ones for different analytes and in more challenging matrices. High enrichment factors have been obtained as a result of elevated sample-to-extraction phase ratios, which have been possible thanks to the remarkable surface area of these nanomaterials. Thus, the high retention capacity showed by these materials has allowed trace determination of inorganic and organic analytes. Likewise, negligible consumption

of solvents and reagents, minimal waste generation and the possibility of recycling these sorbents has contributed to develop greener extraction and preconcentration methods.

In future years, further developments and applications of IL-NP hybrid materials will be focused on the design of novel preconcentration techniques which will emerge as a consequence of the special properties of these materials (high analyte retention, dispersibility, chemical and physical stability, multiple options for functionalization, etc.). Thus, for example, MNPs functionalized with different ILs might lead to tunable retention materials designed for complex samples in addition to high retention and preconcentration. Furthermore, different procedures for synthesis, functionalization and coating of nanomaterials with ILs should be studied in order to enhance their physicochemical stability, lifecycle and selectivity. Finally, additional research on the structure-property relationships of IL-nanomaterial hybrids shall provide the possibility of preparing tunable sorption materials for specific applications and highly complex matrices. Therefore, new and automated preconcentration techniques are expected to be developed in order to fully exploit the potential of IL-nanomaterial hybrids in sample preparation.

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Fig. 1 Number of articles published in the period 2000–2016 reporting a) the use of ionic liquids (ILs) (■) and nanomaterials (■) in extraction methods; b) the use of ILs-nanomaterial hybrids in extraction methods (■). Data generated from a search performed in Scopus database (<http://www.scopus.com>) using as search filters the terms: a) “ionic liquid” and extraction; nano and extraction; b) “ionic liquid” and nano and extraction.

Fig. 2 Selected physicochemical properties for extraction and preconcentration of ILs (○), nanomaterials (●) and IL-nanomaterial hybrids (■).

Fig. 3 Schematics of a general procedure used for the preparation of IL-coated NPs.

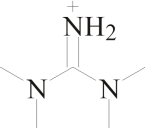
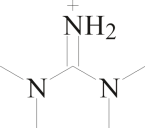
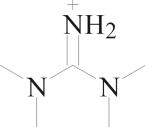
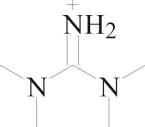
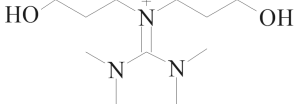
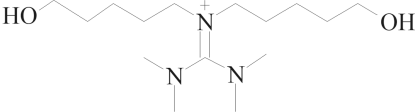
Fig. 4 Schematics of possible routes for chemical functionalization of CNTs with imidazolium-type ILs. a) via reaction with an imidazole derivative [47] and b) grafting of amine or hydroxyl terminated ILs [48].

Table 1 Comparison of the analytical performance of IL-coated nanomaterials-based methods for preconcentration

IL	Nanomaterial	IL-Nanomaterial Interaction	Extraction technique	Analyte	Detector	LOD	EF	Sample	Ref.
[C ₆ mim][NTf ₂]	S-BaFe	Physical adsorption	D-M-SPE	Acaricides	HPLC-UV-VWD	0.05-0.53 ng/mL	N.R	Fruit juice	[34]
[C ₆ mim][PF ₆]	MWNTs	Physical-coating in IL-mediated sol-gel dispersion formation	SPE	PAHs	FES	N.R	N.R	River water	[32]
[C ₇ mim][PF ₆]	Fe ₃ O ₄ @graphene	Self-aggregating IL onto the surface of the Fe ₃ O ₄ -grafted graphene	M-SPE	NBs	HPLC-PDA	1,35-4,57g/L	N.R	Environmental water	[30]
[C ₁₈ mim]Br	Fe ₃ O ₄ @IL@MO	Electrostatic and hydrophobic interactions	M-SPE	PAHs	HPLC-FES	0.1-2 ng/L	150-1000	River water	[31]
1-(3-Aminopropyl)imidazole ILs	MWCNTs	Thiourea-IL is immobilized on the solid sorbent, MWCNTs.	SPE	Pb	ETAAS	0.13 ng/mL	-	Red lipstick, pine leaves, and water	[36]
[C ₁₆ mim]Br	MWCNTs@SiO ₂	IL adsorption as hemimicelles	M-SPE	Flavonoids	HPLC-UV-Vis	0.2-0.75 ng/mL	N.R	Human urine	[33]
Cationic functionalized hexaalkylguanidinium ILs and anionic functionalized tetraalkylguanidinium ILs	MCGO	Coating-functionalization	M-SPE	Protein	UV-Vis	N.R	N.R	Aqueous protein solution	[14]
poly[VOIm]Br	MWCNTs	Physical adsorption	SPME	Hydrophilic and hydrogen-bonding-donating alcohols	GC-FID	0.005-0.05 µg/mL	N.R	Groundwater	[13]
Aliquat-336	Al ₂ O ₃	Physical adsorption	D-SPE	Inorganic Se	ICP-OES	4.6 ng/L	850	Surface water	[50]
[C ₅ mim]Br	TiO ₂	Physical adsorption	HF-SLPME	Benzodiazepines	HPLC-UV-Vis	0.08-0.5 ng/mL	533 - 1190	Hair, urine and wastewater	[22]
[C ₁₆ mim]Br	Fe ₃ O ₄ /GO	Mixed hemimicelles	M-SPE	Cephalosporines	HPLC-UV-Vis	0.6-1.9 ng/mL	N.R.	Human urine	[37]
[C ₁₆ mim]Br	Fe ₃ O ₄ /GO	Mixed hemimicelles	M-SPE	Fluoxetine	Mode-mismatched thermal lens spectroscopy	0.21 µg/L	167	Human urine, environmental water and pharmaceutical formulations	[38]
[C ₁₀ C ₁₀ mim]Cl	Fe ₃ O ₄ /GO	Mixed hemimicelles	M-SPE	Hemin	FAAS (Fe)	3 µg/L	96	Serum of breast cancer patients	[54]
1,2-dimethylimidazole	Fe ₃ O ₄ @ILs-β-CDPC	β-cyclodextrins are functionalized with ILs who acts as a coating for Fe ₃ O ₄ nanoparticles	M-SPE	Mn(II) and Mn(VII)	ICP-OES	Mn(II): 0.15 µg/L Mn(VII): 0.27 µg/L	Mn(II): 50 Mn(VI I): 25	Natural waters	[55]
AFDCIL	Fe@GO@IL	Fe nanoparticles were covered by	M-SPE	Bovine Hemoglobine	UV-Vis	11.87 µg/mL	N.R	Porcine and bovine	[56]

		GO and then, the composite was modified by the IL		protein				blood	
[1-(3-aminopropyl)-3-(4-vinylbenzyl)imidazolium] chloride	m-MWCNTs@PIL	PIL coated the magnetic MWCNTs nanomaterial	M-SPE	Cu,Zn-superoxide dismutase	UV-Vis	N.R	N.R	Blood	[57]
1-ethyl-3-methylimidazolium 1-proline (EMIMLpro)	Fe ₃ O ₄ @DIH--EMIMLpro	Physical adsorption	M-SPE	Hemoglobine	UV-Vis	N.R	N.R	Blood	[58]
[C ₁₆ mim]Br	Fe ₃ O ₄ @IL	Physical adsorption	M-SPE	Cr(III), Cr(VI)	ETAAS	0.003 µg/L Cr(VI)	112	Natural waters	[59]
Betaine based IL	Fe ₃ O ₄ @APTES@GO@IL	Physical adsorption	M-SPE	Bovine serum albumin (BSA)	UV-Vis	N.R	N.R	Bovine calf whole blood	[60]
[C ₁₆ mim]Cl	Fe ₃ O ₄ @GO@DMG@IL	Physical adsorption	M-SPE	Ni(II)	FAAS	0.16 µg/L	100	Sea water, river water, tea, cocoa powder, cigarette, spinach	[61]
[Vmim]I	Fe ₃ O ₄ @IL	Polimeric IL coating on Fe ₃ O ₄	M-SPE	Alfuzosin, Doxazosin, Terazosin and Prazosin	FES	0.027-0.035 µg/L	108.5-114.5	Pharmaceutical Formulations, plasma and urine	[62]
[C ₁₂ C ₁₂ im]Br + [C ₁₆ mim]Br	Fe ₃ O ₄ @IL	Mixed hemimicelles	M-µ-DSPE	Phenols	HPLC-DAD	1.3 µg/L	15.7-141	Water samples	[63]
Tricaprylmethyl ammonium thiosalicylate	Fe ₃ O ₄ @A336@IL	Physical adsorption	M-SPE	Cd(II)	FAAS	0.5 µg/L	50	Water and fruit samples	[64]
[C ₆ mim][NTf ₂]	Au NPs@[C ₆ mim]	Physical adsorption	µ-SPE	Pyridoxine and folic acid	HPLC-UV	3.4 – 4.8 ng/mL	130 and 98	Biological fluids	[51]
[C ₆ mim][PF ₆]	Fe ₃ O ₄ @IL	Physical adsorption	M-SPE	Pd(II)	FAAS	0.82 µg/L	150	Water samples	[65]

Table 2 Chemical structures of novel ILs used in different preconcentration methods based on IL-coated nanomaterial hybrids.

IL	CATION	ANION	Ref.
[TMG][COOH]		COOH ⁻	[14]
[TMG][CH ₂ COOH]		CH ₂ COOH ⁻	[14]
[TMG][(CH ₂) ₂ COOH]		(CH ₂) ₂ COOH ⁻	[14]
[TMG][CH ₂ CH(OH)COOH]		CH ₂ CH(OH)COOH ⁻	[14]
[diBOHTMG]Cl		Cl ⁻	[14]
[diHOHTMG]Cl		Cl ⁻	[14]

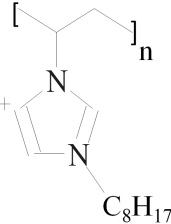
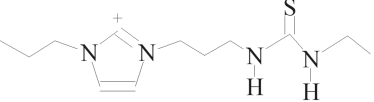
Poly-(1-vinyl-3-octylimidazolium) bromide		Br ⁻	[13]
Thiourea functionalized imidazolium cation with bis(trifluoromethylsulfonyl)imide anion		Tf ₂ N ⁻	[36]

Table 3 Comparison of the analytical performance of preconcentration methods based on chemically functionalized IL-nanomaterial hybrids

IL	Nanomaterial	Extraction technique	Analyte	Detector	LOD	EF	Sample	Ref.
[MTMSPIm]Cl	Mn ₃ O ₄ @SiO ₂	SPE	Ag	FAAS	0.2 ng/mL	50	Water and radiology films	[19]
[Simam]Cl	SiO ₂ @Fe ₃ O ₄	M-SPE	Bovine serum albumin	UV-Vis	N.R.	N.R.	Aqueous standards	[87]
[VHim]Br	Fe ₃ O ₄ @SiO ₂	M-SPE	Organophosphorous pesticides (parathion, fenthion, phoxim and temephos)	HPLC-UV-Vis	0.01 µg/L	84-161	Tea drinks	[66]
[MTOA]Cl	Fe ₃ O ₄ @Si-OH	M-SPE	Cu, Zn, Cd	ICP-OES	0.54 (Cu), 0.56 (Zn), and 0.33 µg/L (Cd)	10	Human hair and urine	[67]
[C ₈ mim]PF ₆	TiO ₂	SPE	Cd, Cu	FAAS	0.1 and 0.3 µg/L	N.R.	River, lake, pond and well water	[35]
[C ₄ mim]Br	MWCNTs Fe ₃ O ₄	D-M-SPE	Aryloxyphenoxy-propionate herbicides and their metabolites	HPLC-DAD UHPLC-MS/MS	2.8-14.3 µg/L ⁻¹ (HPLC-DAD)	N.R.	Ground and reservoir water	[44]
[mim][PF ₆]	Fe ₃ O ₄ @SiO ₂	M-SPE	PAHs	GC/MS	0.04 µg/L (fluoranthene) to 1.11 µg/L (indeno(1,2,3-cd)pyrene)	49 (naphthalene) to 158 (fluoranthene)	Tap, river, well and reservoir water	[68]
[C ₈ mim][PF ₆]	Fe ₃ O ₄ @SiO ₂	M-SPE	Linuron	UV-Vis	5.0 ng/mL	10	Water, fruits, and vegetables	[46]
poly[VOIm][PF ₆]	MWCNTs	Multiple headspace SPME	2-Naphthol	GC	0.15 ng	N.R.	Fruit samples (pomelo and orange)	[85]
[C ₆ mim][PF ₆]	MWCNT -poly(dimethylsiloxane) hybrid coating	HS-SPME	PAHs	GC	0.0005-0.004 ng/mL	N.R.	Urine	[88]
[C ₆ mim][PF ₆]	MWCNT -poly(dimethylsiloxane) hybrid coating	HS-SDME	Methyl tert-butyl ether	GC	0.007 ng/mL	N.R.	Water	[45]
PILs	MWCNT	SPME	PAHs	GC/MS	1-2.5 ng/L	N.R.	River and tap water	[84]
PILs	Fe ₃ O ₄ @SiO ₂	d-SPE	Pesticides	HPLC-UV	0.29-0.88 µg/L	N.R.	Fruit and vegetable samples	[69]
DABCO	LDHs of Zn(II) and Cr(III)	SPME	Phenolic compounds	GC-MS	0.02 - 6.3	N.R.	Environmental	[89]

				pg/mL		water		
Dimethyl octadecyl[3-(trimethoxysilyl propyl)]ammonium chloride	Fe ₃ O ₄ @SiO ₂	M-SPE	Non-steroidal anti-inflammatory drugs	HPLC-UV-Vis	0.2-0.3 mg/kg.	N.R	Human blood	[70]
[cmmim]Cl	Fe ₃ O ₄ @SiO ₂ @GO	M-SPE	Chlorophenols	HPLC-MS/MS	0.2-2.6 ng/L	N.R	Environmental water	[71]
1-Butyl-3-aminopropyl imidazolium chloride	GO	D-SPE	Steroids and β-blockers	HPLC-DAD	7-23 ng/L	4137-4843	Wastewater and natural water	[52]
1-(3-Aminopropyl)-3-butylimidazolium chloride	Fe ₃ O ₄ @MWCNT	M-SPE	Six triazole fungicides	GC-MS	0.05-0.22 ng/mL	125-1242	Canal water	[72]
Imidazolium	Fe ₃ O ₄ @SiO ₂	M-SPE	Amitriptyline and nortriptyline	UV-Vis	0.12-0.62 μg/L	N.R	Antidepressants drugs	[90]
[mim][PF ₆]	Fe ₃ O ₄ @SiO ₂	M-SPE	Endocrine disrupting chemicals	HPLC-MS/MS	0.16-1.21 μg/L	15.4-49.2	River, Sea and Swimming pool water	[73]
[C ₈ mim][PF ₆]	Fe ₃ O ₄ @SiO ₂	M-SPE	Rhodamine B	HPLC-UV	0.08 μg/L	25	Food samples	[74]
[VC ₈ mim]I, 1-Vinyl-3-octylimidazolium bromide	Fe ₃ O ₄ @SiO ₂ @G	M-SPE	Preservatives for vegetables (benzoates, azols among others)	GC-MS	0.82-6.64 μg/Kg	NR	Vegetables	[75]
[Vmim]I	Fe ₃ O ₄ @3-(Trimethoxysilyl)propyl methacrylate	M-SPE	PAHs	HPLC-FLD	1-10 ng/L	106.3-128.3	Coffee and tea	[76]
[C ₈ mim][PF ₆]	Fe ₃ O ₄ @SiO ₂	M-SPE	Bisphenol A	HPLC-UV	90 ng/L	25	Plastic tableware	[77]
N-methylimidazole	Fe ₃ O ₄ @SiO ₂	M-SPE	Paraquat	HPLC-UV	0.1 μg/L	103	Soil and water	[78]
[C ₄ mim]Br	Fe	D-SPE	Nonsteroidal anti-inflammatory drugs	HPLC-UV	1.5-5.8 μg/mL	N.R	Human Plasma	[53]
1-benzyl-3-(trimethoxysilylpropyl) imidazolium chloride	Fe ₃ O ₄ @CN	M-SPE	PAHs and chlorophenols	HPLC-DAD	0.4-0.59 0.35-0.67 μg/L	200 100	Leachate and sludge from landfill site	[79]
dimethyl octadecyl [3-(trimethoxysilyl) propyl] ammonium chloride	Fe ₃ O ₄ @SiO ₂	M-SPE	Pyrethroids residues	HPLC-UV	1.0 μg/L	119-137	Fruit and vegetable samples	[80]
1-vinylimidazole	Fe ₃ O ₄ @SiO ₂	M-SPE	Sulfonylurea herbicides	HPLC-UV	1.62-2.94 μg/L	N.R	Soil	[81]
1-vinylimidazole	Fe ₃ O ₄ @SiO ₂	M-SPE	Sulfonylurea herbicides	HPLC-UV	0.13-0.81 μg/L	N.R	Tea samples	[82]
Imidazole	Fe ₃ O ₄ @SiO ₂	M-SPE	Lossartan potassium	EFS	0.12 μg/L	N.R	Urine samples	[83]

Fig. 1

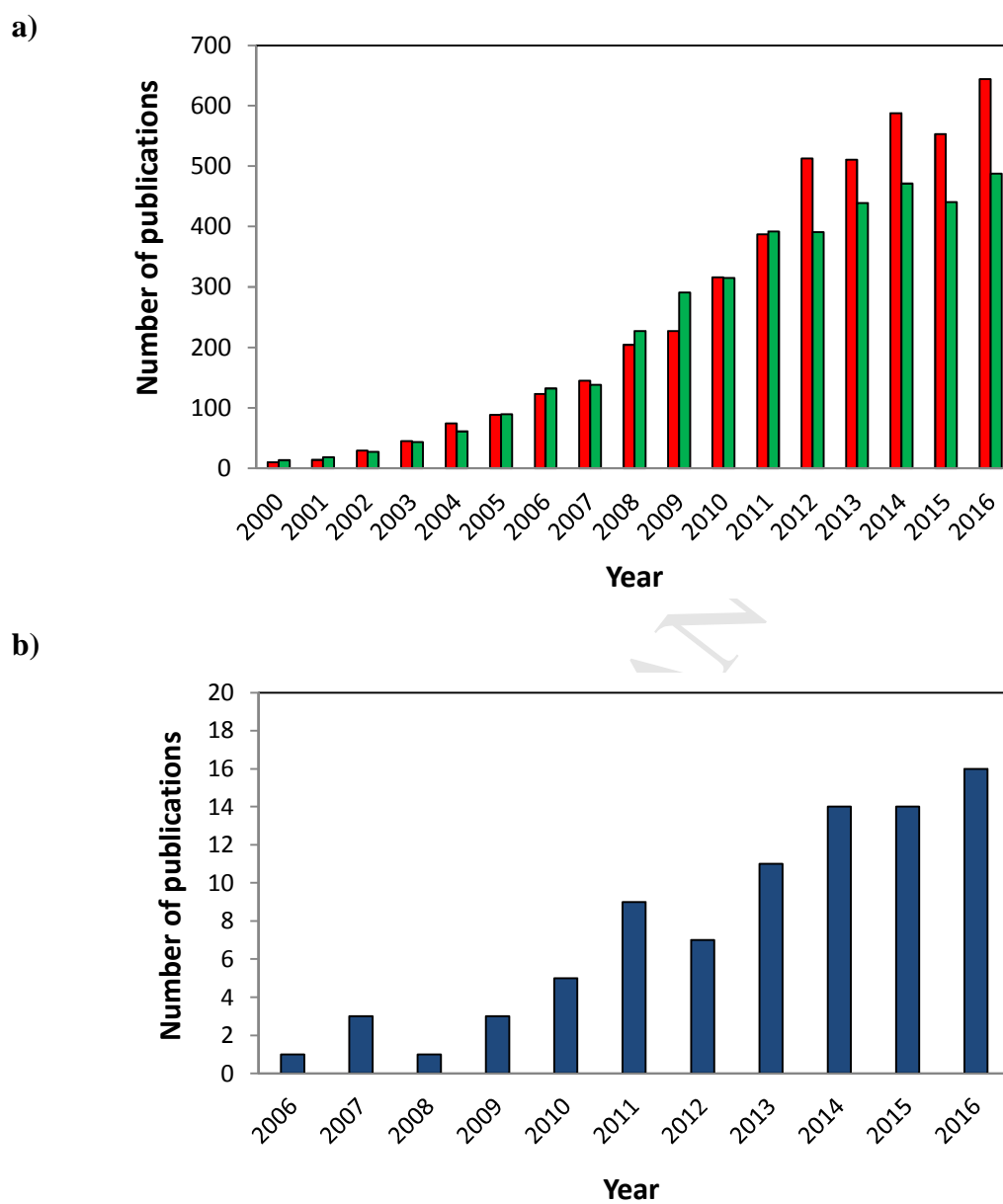
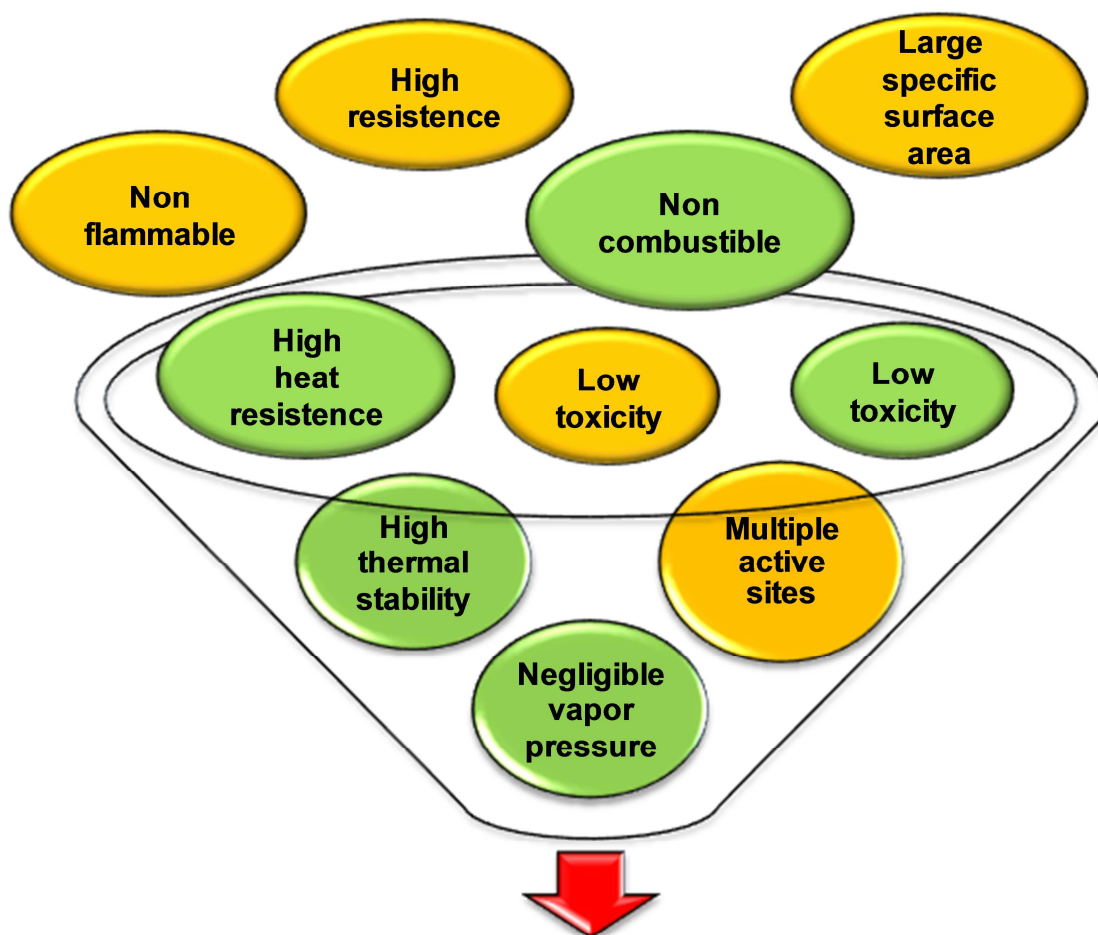


Fig. 2



IL-Nanomaterial hybrids

- Easy regeneration
- High extraction capacity
- Less solvent consumption
- High reproducibility
- High chemical stability
- Negligible vapor pressure
- Tunable composition
- Polar character
- Low toxicity
- High thermal stability
- Novel magnetic and optical properties

Fig. 3

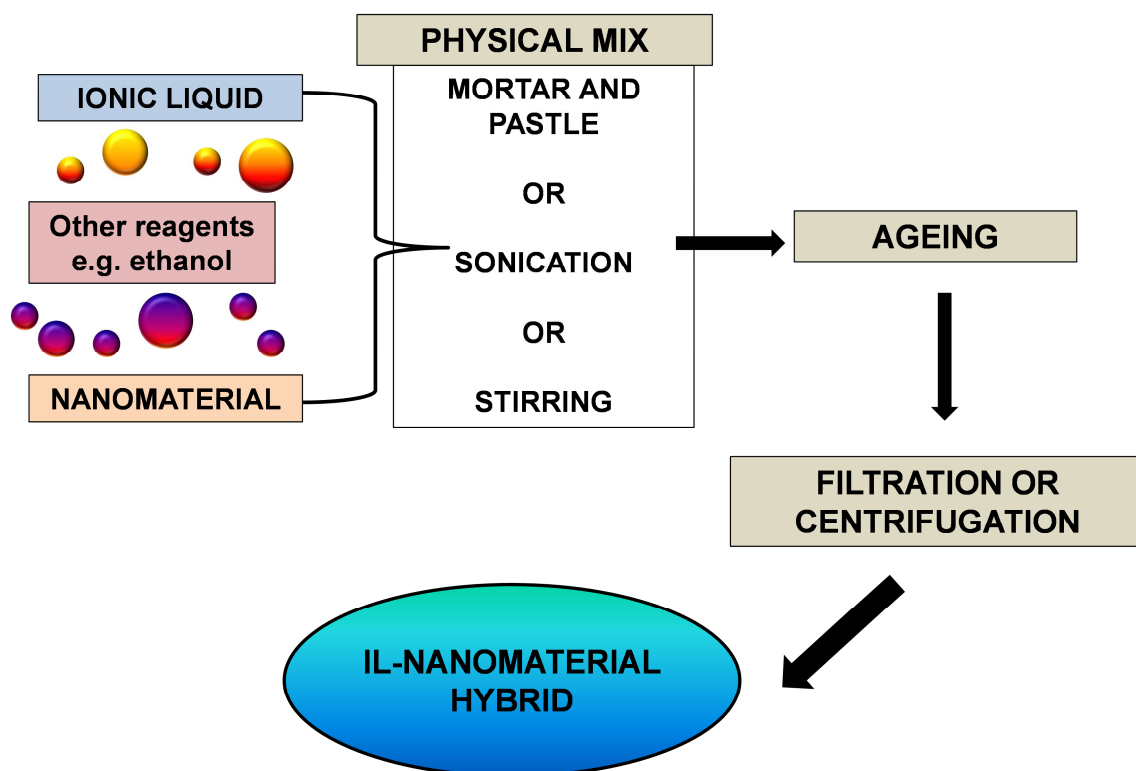
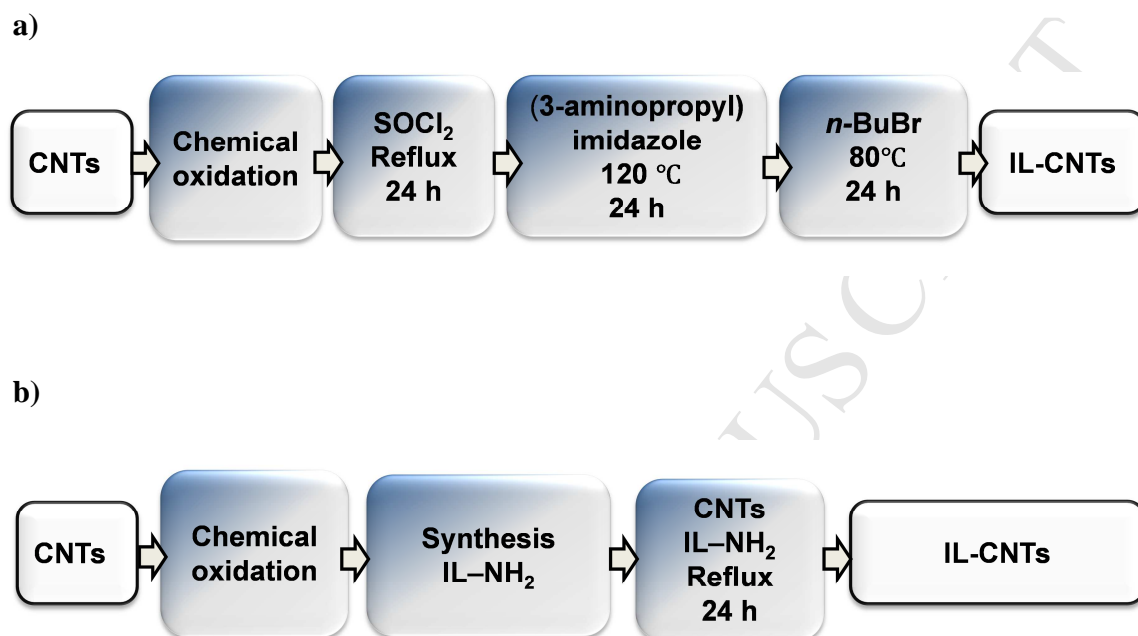


Fig. 4



Highlights

- >Interaction of ionic liquids with nanomaterials surface.
- >Latest advances on solid phase extraction with ionic liquid-nanomaterial hybrids.
- >Improved sorption performance by combining ionic liquids and nanomaterials.
- >Novel analytical developments on preconcentration are discussed.

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