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Use of Ionic Liquids in Solid-Liquid Separation Processes

Lavinia Lupa , Petru Negrea and Adriana Popa

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Abstract

This chapter reports the possible use of ionic liquids (ILs) in solid-liquid separation processes by their immobilization in suitable solid supports. This method presents some benefits such as economical one—due to the fact that a smaller quantity of ILs is used and the loss of ILs in the aqueous phase is avoided; and second the efficiency benefit—because the advantages of the ILs are combined with the properties of the solid support, and this enhances the removal process of metal ions from aqueous solutions and could be successfully used in the removal processes of metal ions from aqueous solutions containing trace amounts. The type of solid supports used for the immobilization of different ILs, and the methods used for the immobilization were discussed. Also the adsorption efficiency of these ionic liquid immobilized solid supports in the removal process of different metal ions (Cr, Hg, Pt, Au, Pd, Cs, Sr, Tl, etc.) from aqueous solutions were presented. The inorganic materials present a higher efficiency to be used as solid supports for the immobilization of the ILs. It was observed that the physical method of impregnation, especially ultrasonication, has a positive effect on the adsorption capacities of the materials obtained.

Keywords: ionic liquids, heavy metals, impregnation, encapsulation, adsorption

1. Introduction

The huge quantities of waste, discharged from various industries and from human activities, and their negative effect on human health and the environment, have led to some stringent regulations. These have driven researchers to find and develop some new efficient methods for the removal and recovery of organic and mineral contaminants from discharged wastes.

Many separation techniques have been proposed especially for the treatment of wastewaters containing heavy metals, such as precipitation [1, 2] ion-exchange [3, 4] liquid-liquid

extraction [5, 6] and membrane processes [7]. These processes may encounter some technical, economical and environmental problems, which limit their application [8]. Even if the precipitation processes results in an efficiency of 90%, the disadvantage remains that precipitation agents are needed to reach the maximum admitted value for discharge. Thus, after treatment, huge amounts of highly contaminated sludge and filter backwash liquid remain [8–10]. Ion exchange, the most extensively used method is expensive for large-scale applications [9]. Membrane processes, especially reverse osmosis, also present economic disadvantages [8, 10].

A widely applied method for the separation of metal ions from an aqueous solution is solvent extraction. Recently, this method has become more attractive because instead of using volatile organic compounds (VOCs) ionic liquids (ILs) or so-called "green extractants" were used, due to their well-known properties [11–13]. Even so, the liquid-liquid extraction method has some drawbacks such as: use of large quantities of ILs [10, 14], the possible loss of IL in the aqueous phase due to incomplete phase separations [15–19], it can only be considered efficient for the treatment of aqueous solutions with high metal concentrations [9, 18–21]. Therefore, there is an increased demand to find alternative technologies to overcome the drawbacks of the liquid-liquid extractions, which should be competitive, efficient and environmentally friendly to achieve targets for sustainable growth. An answer to this problem is the use of ionic liquid in solid-liquid separation processes. This can happen if the ILs are immobilized in a suitable solid support. In this way (i) the minimum amount of ILs is consumed, (ii) the extraction and stripping step is combined into a single step, (iii) the immobilization reduces the loss of ILs in the aqueous phase, (iv) the advantages of the ILs are combined with the properties of the solid support, and this enhances the removal process of metal ions from aqueous solutions, (v) the ILs immobilized solid support obtained can be used for the removal of metal ions from dilute and complex solutions with possible use in simple fixed bed columns for commercial applications [14, 22–25].

This chapter reports various aspects of the use of ILs in solid-liquid separation processes by their immobilization in suitable solid support such as:

1. The type of materials used as solid supports for the immobilization of various ILs.

2. The kind of methods used for the immobilization of various ILs onto suitable solid supports.

3. The use of solid support immobilized with ILs in the process of removing various metal ions from aqueous solutions using solid-liquid separation processes.

2. Materials used as solid support for ILs immobilization

The use of ILs immobilized on a suitable solid support represents a link between the solvent extraction and adsorption processes, for the separation of various pollutants from aqueous solutions. The product obtained should develop an increased selectivity, a higher degree of adsorbent-adsorbate interactions, and should have mechanical stability [26]. All these prop-

erties are influenced by the used solid support, by the type of the immobilized ILs and by the method used for the immobilization of the ILs onto the solid support.

A number of different inorganic and organic solid supports have been tested for the immobilization of ILs during the last decade. The surface properties and the specific surface area are the two most relevant criteria used for the selection of a suitable solid support [25, 26]. Some researchers consider that the macroporous organic polymers are suitable to be used as solid supports due to their high surface area and good mechanical stability, faster kinetics for the removal of contaminant even from dilute solutions, ease of regeneration and high adsorption capacity. On the other hand, other researchers consider that inorganic types of solid support present some advantages over organic supports such as higher thermal and chemical stability, well-ordered periodic pore structure and controllable pore diameter [26]. Therefore, in this section, the discussion is about the most frequently used solid supports, the ones used for immobilization of ILs, which are reported in literature, and also the considerations that have led to the researches focus on them.

Polymer-supported reagents are widely employed in the separation of metal ions. Amberlite XAD resins were a kind of commercial resin frequently used as a solid support for the immobilization of various ILs [18, 20, 24, 25] with uniform pore size distribution, high surface area and good mechanical and chemical stability. Their surface properties differ in function depending on their structure [27, 28]: XAD-2, XAD-4 are hydrophobic, XAD-7 and XAD-8 are moderate hydrophilic and have a higher polarity compared with the other two. For these reasons, the group of Guibal, Gallardo and Navarro used XAD-7 resin as a solid support for the impregnation of tetraalkyl phosphonium ionic liquid—tetradecyl (trihexyl) phosphonium chloride—Cyphos IL-101 and used the obtained materials in the removal of cadmium, zinc and bismuth, respectively [24, 27, 28]. Yang et al. impregnated the Amberlite XAD-7 resin with Cyphos IL-104 in order for it to be used for Cr(VI) removal from aqueous solutions [20]. Cr(VI) removal was also studied by Saha et al. [29] through adsorption onto Amberlite XAD-7 impregnated with Aliquat 336. Kalidhasan et al. used an ion exchange resin as a solid support because this type of resin has a high degree of metal recovery and selectivity. Their study was made with Dowex 1 x 8, a styrene-divinylbenzene polymeric resin containing quaternary ammonium functional groups with chloride (Cl$^-$) and a total exchange capacity of 1.2 mequiv/mL. They impregnated Aliquat 336 ionic liquid onto Dowex [30]. Popa and co-workers used styrene-divinylbenzene as a solid support grafted with different pendant groups (triphenyl-phosphonium, izo-propylphosphonate and aminoethylaminomethyl) [31]. Styrene-divinyl-benzene grafted with aminoethylaminomethyl groups was impregnated with three different ionic liquids: (trihexyl) tetradecyl phosphonium—Cyphos IL-101, 1-octyl-3-methyl imidazolium tetrafluoroborate—OmimBF$_4$; and 1-butyl-3-methyl imidazolium hexafluorophosphate—(BmimPF$_6$). This was done in order to determine the synergistic effect of the functional groups grafted on the polymer and the functional groups from the impregnated ionic liquid in the removal process of Tl$^+$ and Sr^{2+} ions from aqueous solutions [32].

The disadvantage of synthetic resins is the fact that at the end of their life cycle they must be degraded and their thermal degradation produces toxic gaseous compounds. For this reason, an appropriate elimination procedure should be developed. This disadvantage could be

eliminated by using some biopolymers (such as alginate, cellulose and chitosan) as a solid support as they have a thermal degradation which is much more environmentally friendly than that of synthetic resins [9, 21]. Using the biopolymers or renewable resources as a solid support for the immobilization of ILs, the process will conform with the principle of sustainable development [10]. The research group of Guibal, Vincent, Campos and other co-workers reported that the Cyphos IL-101 immobilized in biopolymer capsules of alginate and gelatin leads to the obtaining of an efficient sorbent material which was used with success in the processes of recovering of Hg, Pd, Bi, Au and Pt from acidic solutions [9, 10, 21, 33–35].

Zhang et al. [36] proposed the use of poly(vinyl alcohol) (PVA)-alginate matrix gel as a solid support for the immobilization of [A336][MTBA] IL as a new kind of solid-phase extractant for an efficient recovery of Hg(II) from aqueous solutions. PVA is a water-soluble material containing large amounts of hydroxide groups, but it cannot be degraded by microorganism, has a higher mechanical strength and larger durability in high acidic solutions than alginate gel. For this reason, they wanted to design a novel, simple, competitive and environmentally friendly solid-phase sorbent for treatment of wastewaters [36].

Kalidhasan et al. [37] studied the possible adsorption enhancement of cellulose, a natural biodegradabile polysaccharide, by its impregnation with methyl trioctyl ammonium chloride. Through appropriate modification of the cellulose by immobilization with an IL, an adsorbent with good mechanical properties is obtained.

Li et al. [38, 39] reported the adsorption performance of an ionic liquid/chitosan/graphene composite. Both materials chitosan and graphene are recognized as excellent adsorbents due to their high surface area and their active sites: amino and hydroxyl groups for chitosan and carbonyl, carboxylic and alcoholic functional groups for graphene. However, their individual use presents some drawbacks such as possible oxidation in acidic solutions, and they are difficult to recycle due to their small size. These individual problems were eliminated by Li and co-workers through the synthesis of a chitosan-graphene oxide composite (MCGO). The MCGO obtained was used as a platform for the impregnation of IL [38–40].

Other researchers focussed on the use of Fe_3O_4 magnetic nanoparticles (MNPs) as a solid support for IL immobilization because of their properties such as unique size and magnetic properties. These were also chosen due to other advantages: ease of preparation and surface modification, high adsorption capacity due to their high surface area, and their simple and convenient separation from solution using a magnetic field [41–44]. The immobilization of IL on MNPs is advantageous because it prevents the aggregation and oxidation of the nanoparticles during the solid-liquid separation processes. Mehdinia et al. [41] used the individual MNPs for the immobilization of Aliquat 336 IL; Chen et al. [42] immobilized 1-alkyl-3 vinyl imidazolium chloride onto MNPs coated with SiO_2 and Zheng et al. [43] studied the immobilization of 1-vinyl-3-hexyl imidazolium bromide on Fe_3O_4 co-precipitated with SiO_2. Cheng et al. also used a superparamagnetic mesoporous core/shell nanocomposite ($Fe_3O_4@nSiO_2@mSiO_2$) as a solid support for amino ionic liquids (Si-DHIM-NH_2). The adsorbent obtained was used for removing dye from aqueous solutions [45].

Carbon-based materials are the most widely used adsorbent materials, due to their attractive properties (large surface area, favourable chemical and thermal stability, ease of surface functionalization and modification). Thus, other researchers used these kinds of materials as solid supports for the immobilization of ionic liquids. Activated carbon obtained from palm shell was impregnated with task-specific ionic liquids (trioctyl methyl ammonium thiosalicylate (TOMATS)) by Ismaiel and his collaborators in order to remove mercury from contaminated water. The modification of palm shell-activated carbon by immobilization of the IL led to an increased efficiency in the removal of Hg(II) in comparison with the efficiency of virgin-activated carbon. This is due to the increased number of functional groups (thio groups) present on the surface of the activated carbon [46]. Tokalioglu et al. [47] reported the use of carbon nanospheres as a solid support for IL immobilization.

Nanosized metal oxides, such as Al_2O_3, SiO_2 and TiO_2, have attracted a lot of interest as adsorbents in the solid-liquid separation processes due to their high surface area; crystalline and well-ordered periodic pore structure and chemical, thermal and radiation stability. The main disadvantage of these solids is their lack of selectivity, which can lead to a decrease in adsorption capacity when, in some matrixes there are various interfering ions present with the target metal. This problem can be overcome by chemical or physical modification of the sorbent surface. Therefore, a lot of researchers studied the possible use of these metal oxides as solid supports for the immobilization of ILs [48–58]. Amjadi and Samadi [48] modified the surface of TiO_2 by coating it with 1-hexadecyl-3-methyl imidazolium bromide. Sprynskyy et al. [49] reported the adsorption performance of diatomite modified by chemical treatment with 1-ethyl-3-methyl imidazolium chloride solution in the removal of uranium ions from aqueous solutions. The metal oxide most extensively used as a solid support for IL immobilization is SiO_2. **Table 1** summarizes literature reports on the types of ILs, which have been immobilized onto silica and their applications in solid-liquid separation processes.

In addition to studying silica as a possible solid support for the immobilization of ILs, the research group of Lupa, Negrea and co-workers, tested Florisil, which is a magnesium silicate [58–60]. They impregnated onto Florisil trihexyl (tetradecyl) phosphonium chloride—Cyphos IL-101 ionic liquid and used the adsorbent obtained in the removal of Sr^{2+} [58] and Cs^+ [59] from aqueous solutions. Also they determined the adsorption performance of Florisil impregnated with various ILs: Cyphos IL-101, $OmimBF_4$ and $BmimPF_6$ in the removal process of Tl^+ ions from aqueous solutions [60]. Another study was carried out by the same group of researchers on the impregnation of Cyphos IL-101 on various organic solid supports (Dowex resin, Amberlite XAD7 and dibenzo-18-Crown-6-crown ether) and inorganic solid supports (Florisil and silica) and their use in the removal of Cd, Pb, Co, Ni, Cr, Cs, Sr, Tl and La. It was demonstrated that the type of solid support used for the immobilization of the ILs affected the adsorption properties of the resulting material [26]. In this study, the highest adsorption capacities were achieved by the inorganic solid supports. This can be explained by the fact that after the impregnation process the particles of the ILs studied were more homogenously distributed and bonded onto the surface of the inorganic solid supports compared to the organic solid supports, as can be seen from the SEM images presented [26].

No.	Type of ILs immobilized	Method of ILs immobilization	Application of the obtained ILs immobilized silica	References
1.	1-butyl-3-methyl imidazolium hexafluorophosphate [C_4MIM][PF_6]	Stirring method	Cadmium pre-concentration	[50]
2.	N-methyl imidazole	Stirring in the presence of acetonitrile and 3-chloropropyltriethoxysilane	Removal of 12 sulfonylurea herbicides	[51]
3.	Tropine-type chiral ionic liquid with proline anion	Chemical bonding method	Separation of Cu^{2+}, Fe^{3+}, Mn^{2+} and Ni^{2+} Separation of racemic amino acids	[52]
4.	Trihexyl (tetradecyl) phosphonium bis 2,4,4-trimethyl pentyl phosphopinate—Cyphos IL-104	Sol-gel method	Removal of Cr(III,VI)	[53]
5.	Trialkyl methyl ammonium bis 2,4,4-trimethyl pentyl phosphopinate—[A336][C272]	Sol-gel method	Removal of Cr(III,VI)	[53]
6.	Trihexyl (tetradecyl) phosphonium bis 2,4,4-trimethyl pentyl phosphopinate—Cyphos IL-104 mixed with imidazolium ionic liquid $C_nmim^+PF_6^-$	Sol-gel method	Extraction of Yttrium	[54]
7.	1-octyl-3-methyl imidazolium hexafluorophosphate ($C_8mim^+PF_6^-$) and trialkyl phosphine oxides (Cyanex 923)	Sol-gel method	Extraction of Yttrium	[55]
8.	N,N-EPANTf$_2$ which was impregnated onto silica gel activated through chemically bound method with 3-aminopropyltrimethoxysilane (APTMS)	Stirring method	Separation of Zr(IV)	[56]
9.	Trihexyl (tetradecyl) phosphonium chloride—Cyphos IL-101	Dry method of impregnation	Adsorption of Cs^+ from aqueous solutions	[57]
10.	Trihexyl (tetradecyl) phosphonium chloride—Cyphos IL-101	Dry method of impregnation	Adsorption of Sr^{2+} from aqueous solutions	[58]

Table 1. Type of ILs immobilized onto silica.

3. Methods used for the immobilization of ILs on solid supports

There are both chemical and physical methods used for the immobilization of ILs onto suitable solid supports. The chemical methods of immobilization include: the encapsulation of the IL into microcapsules, the chemical bonding method and the sol-gel method. The immobilization of the ILs using a physical technique may be achieved through different processes such as: wet method, dry method, impregnation in the presence of a modifying agent, the dynamic method or ultrasonication method [14, 19, 28].

The immobilization of ILs through encapsulation is, in most cases, carried out in biopolymers, this technique being intensively studied by the research group of Guibal [10, 21, 33–35]. The schematic flow process for obtaining ILs immobilized in biopolymer capsules through encapsulation is presented in **Figure 1**. In the first step, the IL is mixed with a NaOH solution,
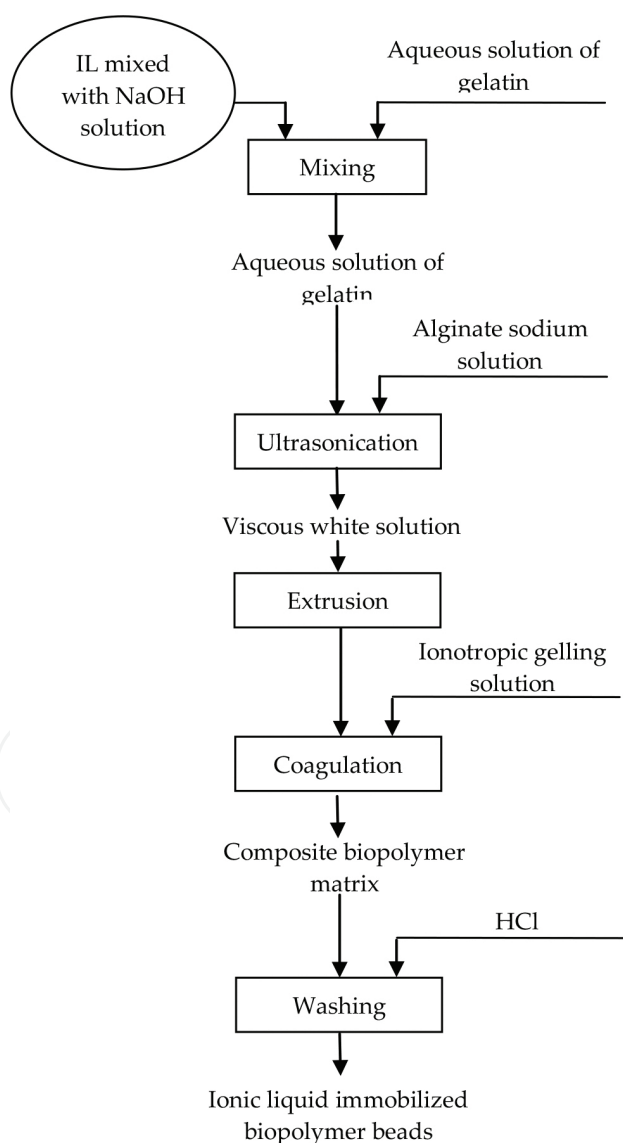
Figure 1. The process of IL immobilization in biopolymer capsules through encapsulation.

then it is mixed with an aqueous solution of gelatin. To the gelatin-ionic liquid solution is added alginate sodium solution and the suspension is ultrasonicated thus obtaining a slightly viscous white solution. This is extruded through a nozzle into an ionotropic gelling solution of $CaCl_2$. The beads obtained are kept in the coagulation bath overnight before being rinsed with HCl solution. In order to avoid the degradation of the composite biopolymer matrix, the obtained capsules are stored in 0.1 M HCl solution [10, 21, 33–35]. Zhang et al. also used the encapsulation method for the immobilization of ILs. They introduced PVA into the alginate solid support to enhance the strength and durability of the beads. Before the extrusion step, they blended the PVA alginate solution with the IL ([A336][MTBA]) for 6 h at 500 rpm and 30°C [36].

Shanthana Lakshmi et al. [61] immobilized Cyphos IL-101 in polymer microspheres using the phase-inversion technique. In the first step a Phase I is obtained, a casting solution to form the microspheres, which contain the polymer and the IL dissolved in N,N-dimethylformamide. The microspheres pass through a second oil phase (dodecane) and then into a coagulation bath (Phase III—a mixture of ethanol and double-distilled water). In the coagulation bath, the phase inversion is induced by exchange across the interface of the solvent from the polymer solution with a non-solvent [61].

Qian et al. immobilized a tropine-type chiral ionic liquid with proline anion on silica gel by a chemical bonding method. In the first step, they activated the surface of the silica gel, mixed the tropine 3-iodopropyl trimethoxysilane and potassium iodide in ethanol, and then mixed all the reagents and left the reaction to perform at 110°C. The compound which resulted was added to a mixture of l-proline and sodium hydroxide solution and stirred continuously for 48 h [52].

Other researchers immobilized ILs onto magnetic nanoparticle surfaces by free radical copolymerization [42, 43]. The reaction is performed under a nitrogen atmosphere and each of the papers mentions different times taken for the reaction (6–24 h) and different temperatures (70–110°C). Liu and co-workers used the sol-gel method for the immobilization of the IL onto silica-based materials [53, 54].

The use of chemical processes to immobilize the IL onto a suitable solid support involves the use of a lot of reagents which limit their application from the economical point of view. Therefore, physical processes are most widely used. The physical method which has been tested most is the dry method of impregnation because researchers consider that through this process the stability of the extractant on the solid support is increased [24, 25, 27, 28, 57–59]. The schematic process of ILs immobilization onto a solid support, using the dry method of impregnation, is presented in **Figure 2**.

Some researchers activate the surface of the solid supports before impregnation [27, 28]. Also the ionic liquid is dissolved in a volatile diluent (ketone, methanol and ethanol). The two components are kept in contact for at least 24 h. Subsequently, the diluent is evaporated and pure ionic liquid remains inside the pores of the support. The evaporation of the diluent is achieved through drying in an oven at 50°C for 24 h or by using roto-vapour.

Because the immobilization of the IL by the dry method of impregnation involves a lot of time for contact between the IL and the solid support, some researchers used the stirring method [20, 29, 41, 46–50]. They stirred these two phases (the IL dissolved in a diluent and the solid support), different stirring times are reported, and then filtered, washed and dried the solid support immobilized with the IL in order to evaporate the diluent. The total time taken for the immobilization of the IL on a solid support using the stirring method depends on how much treatment is carried out on the solid support before impregnation, and how many steps of the washing there are before the final product is obtained.
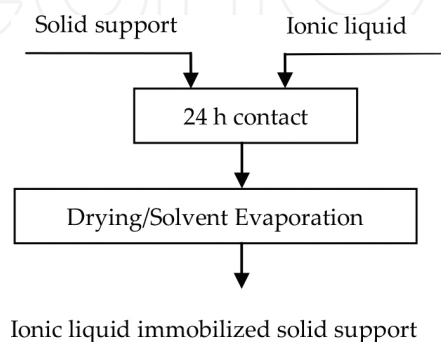
Figure 2. The obtaining of ionic liquid immobilized on a solid support using the dry method of impregnation.

Negrea et al. studied the influence of the impregnation method on the adsorption capacity of the resulting materials. For the immobilization of Cyphos IL-101 on Florisil and Silica solid supports, the methods they used for impregnation were: the dry method, the stirring method, the dynamic column method and the ultrasound method. The materials obtained were used in the removal of Cs^+ ions from aqueous solutions [62]. The materials obtained through the various methods they studied were characterized using FTIR, BET, SEM and EDX analysis. It was observed that the method used for the impregnation of the IL onto the solid support influences the surface morphology of the product obtained. This led to the materials having different adsorption capacities in the removal of Cs^+ ions from aqueous solutions. The most efficient method of impregnation proved to be the ultrasound method with which the distribution of the ILs particles onto the surface of the studied solid supports was uniform. This method also resulted in the highest adsorption capacity of Cs^+ [62].

Other researchers used the ultrasonication method for the immobilization of the ionic liquid onto a solid support because it is an economic alternative process, which is not so time-consuming [30, 37–40, 45, 60].

The research group of Lupa, Negrea and co-workers studied the influence of the ultrasonication conditions (amplitude and time of ultrasonication) upon the immobilization of Cyphos IL-101, $OmimBF_4$ and $BmimPF_6$ onto Florisil. It was observed that in order to obtain a stable and homogenous impregnation of the solid support with the studied IL, it is not necessary to increase the ultrasonication time, but a higher amplitude should be used. Increasing the ultrasonication time leads to the conglomeration of the IL particles on the solid support affecting in this way the reproducibility of the adsorption experiments [63]. Increasing the amplitude of sonication assures an easier transmission of the IL particles through the liquid

media until it reaches the cavities of the solid support. Through this process, instead of the 24 h of impregnation needed in case of the dry method, the immobilization is achieved in 10 min. After the immobilization of the IL onto the solid support through ultrasonication, the suspension is dried for 24 h at 50°C for solvent evaporation. This time could be minimized if the evaporation of the solvent is carried out using a roto-vapour. The same group of researchers studied the possibility of IL immobilization using the process of pellicular vacuum solvent vaporization using a roto-vapour. They studied the influence of the impregnation conditions: stirring time and temperature in the case of the immobilization of the 1-n-hexyl-3-methyl imidazolium chloride on Florisil. The material obtained was used in the removal of Tl ions from aqueous solutions [66]. It was observed that to improve the adsorption capacity of the obtained ionic-liquid impregnated material, it is not necessary to increase the stirring time during the impregnation process, but it is necessary to increase the temperature. The temperature increase led to a large quantity of ionic liquid being impregnated onto the solid support and to a shorter time for solvent evaporation [66].

4. Use of ionic liquid immobilized solid supports for the removal of metal ions from aqueous solutions

Ionic liquid immobilized solid supports were used for the removal of different metal ions from various samples such as: wastewater, sea water and hydrochloric acid solution. The adsorption efficiency of the studied materials was determined using the mass balance equation:

$$q = \frac{(C_0 - C_e) \cdot V}{m} \tag{1}$$

where C_0 and C_e represent the initial and equilibrium concentration of the studied metal ion [mg/L]; V is the volume of the aqueous solution sample containing the metal ion [L] and m represents the mass of the used ionic liquid immobilized solid support [g].

This section presents the results of studies on the adsorption efficiency obtained by various ionic liquid immobilized solid supports used in the removal of metal ions from different samples. Identifying the adsorbent with the greatest capacity of adsorption is difficult as the experimental conditions vary from one study to another. However, in most of the adsorption studies, the following were analyzed to find their influence on adsorption capacity: pH, contact time between the adsorbent and adsorbate, and initial concentration of the metal ions. With some exceptions, when more models are tested, the equilibrium data were fitted with Langmuir and Freundlich isotherms and the kinetic data were discussed using the pseudo-first order and pseudo-second order kinetic models.

Gallardo et al. studied zinc (II) extraction from HCl acid solutions using Amberlite XAD7 impregnated with Cyphos IL-101 through the dry method. They studied the influence of the HCl concentration, the content of the Cyphos IL-101 upon the uptake efficiency and sorption isotherms [27]. Compared to the raw Amberlite XAD7, the adsorption capacity was 10 times

higher when resin impregnated with Cyphos IL-101 was used in the removal of Zn(II) from acidic solutions. They reported that the impregnated materials could be regenerated after adsorption using Na_2SO_4, H_2SO_4 or HNO_3. Also sorption and desorption efficiencies were maintained almost constantly over five sorption/desorption cycles [27]. The removal of lead ions was studied by Sun et al. [40] through adsorption onto graphene oxide and magnetic chitosan ionic-liquid and by Tokalioglu et al. [47] using carbon nanospheres coated with an ionic liquid. In the first case, an adsorption capacity of 85 mg/g was obtained, while the carbon nanospheres coated with ionic liquid gave an adsorption capacity of 50.3 mg/g.

A lot of studies were made on the removal of Cr ions from aqueous solutions. Chromium compounds are widely applied in many industries (pigments, metallurgy, electroplating, leather tanning, stainless steel production, steel, photography) giving rise to huge quantities of wastewater containing chromium [20, 53]. The discharged chromium exists in two important states of oxidation, Cr(III) and Cr(VI). Cr(VI) is more toxic than Cr(III) because of its ability to oxidize other substances. In **Table 2**, there is a summary of the adsorption capacities of different ionic liquid immobilized solid supports in the removal of Cr(VI) from aqueous solutions. It can be observed from the data presented in **Table 2** that the highest adsorption capacity was given by the Dowex 1 x 8 in the removal process of Cr(VI) from aqueous solutions. This could be explained by the fact that Dowex is known to be a good ion exchanger and so it may be that the success in this removal process results from a combination between adsorption and ion

Solid support	Ionic liquid	Immobilization method	q_m, mg/g	Work conditions	References
Amberlite XAD-7	Cyphos IL-104	Stirring method 0.25 g of IL/1 g of SS	44.85	S:L = 4 g/L; t = 60 min; T = 298 K; pH = not mentioned (n.m.)	[19]
Amberlite XAD-7	Aliquat 336	Stirring method 2 g of IL/1 g of SS	50.44	S:L = 1.6 g/L; t = 24 h; T = 298 K; pH = 6	[29]
Dowex 1 x 8	Aliquat 336	Ultrasonication 6 mL of IL/1 g of SS	230.9	S:L = 10 g/L; t = 30 min, T = 300 K; pH = 3.5-4	[30]
Cellulose	MeTOACl	Ultrasonication	38.94	S:L = 10 g/L; t = n.m., T = room temp.; pH = 2	[37]
Magnetic chitosan/ graphene oxide	N-(3-Aminopropyl)- imidazole	Ultrasonication 1 g IL/1 g SS	107.99	S:L = 1g/L; t = 60 min, T = 303 K; pH = 2	[38]
Magnetic chitosan/ graphene oxide	Tetraoctylammonium bromide	Ultrasonication 1 g IL/1 g SS	145.35	S:L = 1g/L; t = 40 min, T = 303 K; pH = 3	[39]
Silica	Cyphos IL-104	Sol-gel method	19.31	S:L = 4 g/L; t = 4 h; T = 298 K; pH = 6	[53]
Silica	[A336][C272]	Sol-gel method	15.29	S:L = 4 g/L; t = 4 h; T = 298 K; pH = 6	[53]

Table 2. The adsorption capacities developed by ionic liquid immobilized solid support in the removal process of Cr(VI) from aqueous solutions.

exchange. Also high adsorption capacities were obtained by magnetic chitosan/graphene oxide immobilized with different ionic liquids. The mixture between an organic solid support (chitosan) and an inorganic one (Fe_3O_4) leads to the enhancement of the adsorption capacity of the obtained product. The lowest adsorption capacity was obtained by the silica impregnated with the studied ILs using the sol-gel method of impregnation. The materials obtained through the impregnation of the IL onto the solid supports by ultrasonication presented the highest efficiency in the removal process of Cr(VI) from aqueous solutions.

Ionic liquids immobilized through encapsulation in biopolymer capsules were used in the removal of some precious metals such as: Au, Pd, Hg, Pt. The work conditions and the obtained adsorption capacities of the ionic liquid immobilized biopolymers are presented in **Table 3**. It can be observed that the Cyphos IL-101 immobilized in microcapsules of gelatin and alginate composite were efficient in removing Hg, Pd, Bi, Au, Pt ions from acid solutions. Adsorption capacities of over 100 mg/g were obtained. [A336][MTBA] immobilized through encapsulation in alginate beads functionalized with PVA developed a smaller adsorption capacity for the removal of Hg(II) ions from aqueous solutions. A higher adsorption capacity for the removal of Hg(II) from aqueous solutions resulted from using TOMATS impregnated onto palm shell activated carbon. In this case, equilibrium is achieved after 3 h of shaking.

Solid support	Ionic liquid	Immobilization method	Removed metal	q_m, mg/g	Work conditions	References
Composite polymer (gelatin and alginate)	Cyphos IL-101	Encapsulation	Hg	150	S:L = 0.2 g/L; t = 96 h; T = 298 K; In the presence of HCl solution	[10]
			Pd	130-145	S:L = 0.6 g/L; t = 72 h; T = 298 K; In the presence of HCl solution	[21]
			Bi	110-130	S:L = 0.25 g/L; t = 96 h; T = 298 K; In the presence of HCl solution	[33]
			Au	140	S:L = 0.6 g/L; t = 96h; T = 298 K; In the presence of HCl solution	[34]
			Pt	177	S:L = 0.6 g/L; t = 48–72 h; T = 298 K; In the presence of HCl solution	[35]
PVA alginate gel beads	[A336][MTBA]	Encapsulation	Hg	49.89	S:L = 1 g/L; t = 24 h; T = 298 K; pH = 6	[36]
Palm shell activated carbon	TOMATS	Orbital shacking	Hg	83.33	S:L = 20 g/L; t = 3 h; T = 308 K; pH = 8	[46]

Table 3. The efficiency of the IL immobilized in biopolymer capsules in the removal process of metal ions from aqueous solutions.

Ionic liquid impregnated solid supports were also used as adsorbent materials in the removal of some radionuclides from aqueous solutions. It can be observed from **Table 4** that ionic liquid impregnated solid support can be used for the removal of radionuclides from aqueous solutions containing trace amounts. The materials impregnated with the studied ionic liquid developed a higher efficiency when the ultrasonication is used for the impregnation of the IL onto the solid support. The inorganic materials presented a higher efficiency than the organic materials as solid support for the impregnation of the IL.

Solid support	Ionic liquid	Immobilization method	Removed metal	q_m, mg/g	Work conditions	References
Diatomite	1-ethyl-3-methylimidazolium chloride	Stirring method	U(VI)	88	S:L = 1 g/L; t = n.m.; T = 298 K; pH = 4.2	[49]
Florisil	Cyphos IL-101	Dry method	Cs(I)	3.086	S:L = 4 g/L; t = 2 h; T = 298 K; pH = 8	[59]
Silica	Cyphos IL-101	Dry method	Cs(I)	1.48	S:L = 4 g/L; t = 2 h T = 298 K; pH = 8	[57]
Florisil	Cyphos IL-101	Ultrasound	Cs(I)	2.95	S:L = 4 g/L; t = 1 h, T = 298 K; pH = 3.5	[63]
Florisil	OmimBF$_4$	Ultrasound	Cs(I)	2.27	S:L = 4 g/L; t = 1 h, T = 298 K; pH = 3.5	[64]
Florisil	BmimPF$_6$	Ultrasound	Cs(I)	1.6	S:L = 4 g/L; t = 1 h, T = 298 K; pH = 3.5	[65]
Florisil	Cyphos IL-101	Dry method	Sr(II)	2.94	S:L = 4 g/L; t = 2 h; T = 298 K; pH = 6	[58]
Silica	Cyphos IL-101	Dry method	Sr(II)	3.97	S:L = 4 g/L; t = 2 h; T = 298 K; pH = 6	[58]
Functionalized styrene divinylbenzene	OmimBF$_4$	Ultrasonication	Sr(II)	15.6	S:L = 4 g/L; t = 2 h; T = 298 K; pH = 3.5	[32]
Functionalized styrene divinylbenzene	BmimPF$_6$	Ultrasonication	Sr(II)	13.7	S:L = 4 g/L; t = 2 h; T = 298 K; pH = 3.5	[32]
Functionalized styrene	Cyphos IL-101	Ultrasonication	Sr(II)	8.13	S:L = 4 g/L; t = 2 h; T = 298	[32]

Solid support	Ionic liquid	Immobilization method	Removed metal	q_m, mg/g	Work conditions	References
divinylbenzene					K; pH = 3.5	
Functionalized styrene divinylbenzene	OmimBF$_4$	Ultrasonication	Tl(I)	4.83	S:L = 4 g/L; t = 2 h; T = 298 K; pH = 3.5	[32]
Functionalized styrene divinylbenzene	BmimPF$_6$	Ultrasonication	Tl(I)	3.92	S:L = 4 g/L; t = 2 h; T = 298 K; pH = 3.5	[32]
Functionalized styrene divinylbenzene	Cyphos IL-101	Ultrasonication	Tl(I)	2.94	S:L = 4 g/L; t = 2 h; T = 298 K; pH = 3.5	[32]
Florisil	OmimBF$_4$	Ultrasonication	Tl(I)	8.48	S:L = 2 g/L; t = 2 h; T = 298 K; pH = 3.5	[60]
Florisil	BmimPF$_6$	Ultrasonication	Tl(I)	7.97	S:L = 2 g/L; t = 2 h; T = 298 K; pH = 3.5	[60]
Florisil	Cyphos IL-101	Ultrasonication	Tl(I)	11.1	S:L = 2 g/L; t = 2 h; T = 298 K; pH = 3.5	[60]
Florisil	1-hexyl-3-methylimidazolium chloride	Pellicular vacuum solvent vaporization	Tl(I)	2.95	S:L = 40 g/L; t = 2 h; T = 298 K; pH = 3.5	[66]

Table 4. The adsorption capacities developed by ionic liquid immobilized solid support in the removal process of different radionuclides from aqueous solutions.

5. Conclusion

Ionic liquids could be used in the solid-liquid separation processes by their immobilization in suitable solid supports. In this way, the loss of ILs into the aqueous phase is avoided, and a smaller amount of IL is used. The ionic liquid immobilized solid supports could be efficiently used for metal ions removal from aqueous solutions even from dilute samples. Through the immobilization of IL onto different solid supports, the adsorption performance of the materials is enhanced because of the combination of the advantages of the IL and the properties of the solid support. The type of materials used as solid support for ILs immobilization, and the method used for the immobilization process influences the adsorption efficiency of the product obtained. Regarding to the materials, silica and Amberlite XAD-7 have been the most tested as solid supports. The most immobilized ionic liquids were quaternary phosphonium ionic liquid and imidazolium type. The immobilization of the ILs in biopolymers was performed through encapsulation. Between the chemical and physical methods used for the immobiliza-

tion of ILs, the second one proved to be more advantageous. The materials obtained through the impregnation of the IL onto the solid supports by ultrasonication presented the highest efficiency in the removal process of metal ions from aqueous solutions. Even if the results are very promising, a wider combination of solid supports and ILs can be tested, opening the door to explore new challenges.

Acknowledgements

Author details

Lavinia Lupa[1*], Petru Negrea[1] and Adriana Popa[2]

*Address all correspondence to: lavinia.lupa@upt.ro

1 Faculty of Industrial Chemistry and Environmental Engineering, Politehnica University of Timisoara, Timisoara, Romania

2 Institute of Chemistry Timisoara of Romanian Academy, Romanian Academy, Timisoara, Romania

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