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REVIEW

Ionic liquids to remove toxic metal pollution

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Abstract
Pollution by toxic, non-degradable metals is a rising health concern in the context of increasing industrialization and metal demand. Diseases may include brain damage, cardiovascular problems, gastrointestinal disorders and cancer, calling for advanced methods to clean soil, water, wastewater and air. Here, we review the use of ionic liquids, which are considered as eco-friendly solvents, to remove metals. Ionic liquids have unique properties such as no vapor emission, good solvation ability, higher thermal stability and tunability. Ionic liquids separate efficiently metal ions from aqueous solutions by electrostatic, Van der Waals and ion–pair interactions. Ionic liquids can be recovered by stripping, then reused several times for liquid–liquid extraction, adsorption and membrane separation. Ionic liquids improve membrane stability in membrane separation, and they act as surfactant for adsorption.

Keywords Heavy metals · Ionic liquids · Liquid–liquid extraction · Adsorption · Membrane separation process

Introduction

Heavy metals refer to any metal and metalloids that have a relatively high density in the range of 3.5–7 g cm^{-3} (Gautam et al. 2014; Bashir et al. 2018). They are existing elements by nature usually present throughout the earth's crust; however, they are considered as one of the serious environmental contaminants due to their high toxicity and non-biodegradability (Maximous et al. 2010). These metals are unique and placed under the important class of human carcinogens. They are releasing into the natural surroundings from various sources such as geogenic, industrial, agro, medicinal, and domestic effluents (Tchounwou et al. 2012; Sivarajasekar et al. 2018). Usually, these metals occur only in trace and ultra-trace levels in accordance with geological composition of the catchment basin. Heavy metals are present in water usually in the form of colloidal, granular, and solubilized states. The standard concentration of heavy metals to be present in drinking water as per the Environmental Protection Agency (Gautam et al. 2014) is tabulated in Table 1.

Heavy metals such as Cr, Fe, Mn, Ni, Cu, Co, and Zn are necessary micronutrients needed for chlorophyll synthesis as well as enzyme activation in plants and also stimulate an immune activity and normal growth in humans (Chen et al. 2013; Sreekanth 2010). These metals are predominantly used in pigments, electroplating, alloy and battery manufacturing industries (Pospiech 2015a, b; Sivarajasekar et al. 2018). But the same metals turn into a highly toxic materials, when they discharge into the environment at higher concentrations exceeding the permitted levels. They are highly soluble in the aquatic environment due to which they can get easily accumulated in living organisms either directly or indirectly when they are consumed, but they consume a lot of time before they are broken down, i.e., metabolized or excreted (Chen et al. 2013; Sreekanth 2010). Because of high toxicity, heavy metals induce serious health disorders in human beings such as edema of the eyelids, tumor, damage the reproductive and central nervous systems, genetic disorder and may promote the cells to instigate the cancer too (Dubey et al. 2018; Bashir et al. 2018). The number of environmental legislations and regulations are increased during recent years and more specific regulations have been put forth for the treatment of contaminated water for a safer environment (Mahurpawar 2015). Table 2 presents the list of permissible limits for the discharge concentration of heavy metals (mg/l) from various industrial effluents as per the

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Table 1 Standard concentration of heavy metals in drinking water

Metals	Drinking water standards (mg/l)
Lead	0.1
Nickel	0.1
Chromium	0.05
Copper	1.0
Zinc	5
Cadmium	0.005
Mercury	0.002
Arsenic	0.004

Environment (Protection) Act, 1986 reported by the Central Pollution Control Board in April 2018.

Therefore, exploring a selective, cost-efficient and eco-friendly metal-extracting compounds, separation methods are of great interest worldwide. An appropriate solvent for metal removal in separation technique is chosen based on the factors like solvating capacity, volatility, thermal stability, flammability, and toxicity. However, traditional volatile organic compounds (VOCs) create unfavorable factors when used, resulting in environmental and health safety issues (Ríos et al. 2012). So, it is mandatory to protect the environment by minimizing the usage of these conventional VOCs or explore for novel alternative solvents (Francisco 2013). The fundamental principle of green chemistry is to avoid the usage of toxic solvents and the waste generation (Krishnan et al. 2020). By obeying the green chemistry principles, ionic liquids have received a great attention as an excellent solvent media in the recovery or separation of various metal ions with an expectation of high yields.

Ionic Liquids

Ionic liquids are represented as fluid, semi-organic salts comprising a bulky asymmetric organic cations such as imidazolium, phosphonium, sulfonium, ammonium, pyridinium, piperidinium, pyrrolidinium, morpholinium and weakly coordinating organic or inorganic anions like Halides, Tetrafluoroborate, hexafluorophosphate, triflate, bis(trifluoromethylsulfonyl) imide, dicyanamide) at or near room temperature (Aspects NEW 2013; Chung 2015). There are numerous synonyms being used for ionic liquid such as ionic fluid, molten salt, liquid organic salt, fused salt, and neoteric solvent (Francisco 2013).

It is relatively a recent magical compound that is preferred because of its fascinating properties like higher thermal stability, good dissolving ability, higher ionic conductivity, wide electrochemical windows, high polarity, negligible vapor pressure, non-flammability, and non-volatility (Vergara et al. 2014; Chung 2015; Krishnan et al. 2020). Their unique properties make it an ideal green media to experiment the new processes for reducing the metal pollution so as to provide feasibilities include

- Fast reaction rate
- Recoverability with ease
- Higher selectivity
- Better reliability, and
- Reuse of spent solvent (Hajipour and Rafiee 2009)

Ionic liquids are complex and multifaceted solvents, having a great potential to interact with the molecules through hydrogen bonding, ion pair, Van der Waals, coulombic, and electrostatic interactions. These interactions can be fine-tuned by altering the ionic liquids' cation or anion achieving in increased separation efficiency compared to conventional solvents. Such tuning may help to predict the ionic liquids with required physicochemical properties such as density, viscosity, polarity, refractive index, and mutual solubility with co-solvents for specific applications (Wang et al. 2016). This remains the predominant reason attributed to its implementation as solvent systems in separations, chemical sensing, tissue preservation, lubricants, electro-analytical applications, pharmaceutical drug delivery, and extractions of thermally sensitive species. They further serve as a electrolyte in batteries, metal plating, solar panels and as an excellent medium in solubilizing gases such as carbon dioxide, oxygen, hydrogen, and carbon monoxide. They have high ionic conductivity that boost up the reaction rates to a

Table 2 List of permissible limits for the discharge concentration of heavy metals (mg/l) from various industrial effluents as per Environment (Protection) Act, 1986 reported by Central Pollution Control Board on April 2018

Industries	Concentration of heavy metals in mg/l						
	Pb	Cr	Hg	Zn	Ni	Cu	Cd
Petroleum oil refinery	0.1	2.0	0.01	5.0	1.0	1.0	–
Pharmaceuticals	0.1	0.1	0.01	–	–	–	–
Paint	0.1	–	–	–	–	–	–
Leather	–	2.0	–	–	–	–	–
Dye and dye intermediate	0.1	2.0	0.01	5.0	3.0	2.0	0.2
Organic chemical manufacture	0.1	1.0	0.01	5.0	2.0	2.0	–
Battery manufacturing industry	0.1	–	0.02	5	–	–	–

great extent in a number of reactions such as microwave-assisted, polymerization, and multiphasic reactions (Chung 2015). When compared to conventional solvents, ionic liquids can be regenerated with the help of recycling-enabled metal stripping agents in separation techniques. Due to its multifaceted applications, ionic liquids gained the attention not only in academia, but also in industries (Francisco 2013).

Ionic liquids can be hydrophilic or hydrophobic in nature based on combination of its cations and anions. The anion of ionic liquid is the key component to predict the miscibility/solubility of water. For example, ionic liquids containing imidazolium cation with halide, acetate, and nitrate anions are completely soluble in water, whereas ionic liquids based on imidazolium cation with hexafluorophosphate and bis(trifluoromethanesulfonyl)amide anions are water-insoluble. Some ionic liquids are partially soluble based on the substituents of the anions. Dialkylimidazolium tetrafluoroborate or trifluoromethane sulfonate ionic liquids are under this category (Kärkkäinen 2007). Wide range of ionic liquids were tested by using it as solvents or catalysts in different reactions such as Diels–Alder, Friedel–Crafts, alkylation, allylation, hydro-formulation, esterification, and dimerization(Hajipour and Rafiee 2009). They have been employed in several industrial applications. BASF was the first company utilized ionic liquids in the name of biphasic acid scavenging utilizing ionic liquid (BASIL) process in which 1-methylimidazole was used as a base for the synthesis of diethoxyphenyl phosphine. The ionic liquid, 1-butyl-3-methyl-imidazolium chloride [BMIM][Cl] was obtained as a by-product. 1-methylimidazole was reformed by reacting these ionic liquid with NaOH. Another company named IFP used chloroaluminate anion based ionic liquids as a solvent for the conversion of butane to octene in the process called Difasol (Kärkkäinen 2007).

Treatment technologies

Figure 1 shows the treatment technologies like liquid–liquid extraction, adsorption, and membrane system used for metal removal from wastewater using ionic liquids.

Liquid–Liquid Extraction

Liquid–liquid extraction is the process of separating components in the solution based on its distribution between two immiscible liquid phases. The extraction process is a simple procedure executed under mild operating conditions and it does not require additional separation unit for the recovery and reuse of the solvent spent (Dietz 2006). The extraction efficiency is strongly dependent on the solvent and its physiochemical properties. So far in this method, organic solvents were used which not only contaminate the aquatic environment but also difficult to recover the solvent spent. To overcome this difficulty, ionic liquids the so-called green alternatives were used by researchers in recent years in liquid–liquid extraction method for the removal of metal. Generally, extraction experiment is carried out by shaking a known volume of aqueous solution at known metal concentration and ionic liquids in a mechanical shaker at known

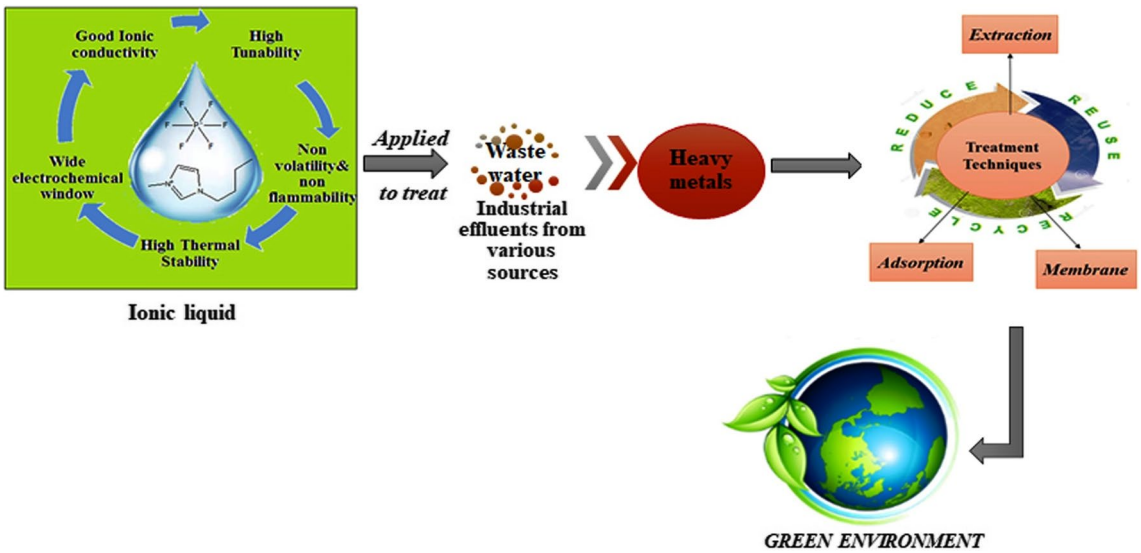

Fig. 1 Treatment technologies such as liquid–liquid extraction, adsorption, and membrane processes used for the removal of heavy metals from wastewater using ionic liquid for creating the aquatic environment cleaner and greener. Ionic liquids play a vital role in the removal of pollutants due to their extraordinary properties like non-volatility, high thermal stability, high tunability, good ionic conductivity, and excellent solvation ability

rpm. After extraction, the two phases (aqueous and organic phases) are separated in a separating funnel which is assisted by centrifugation at known agitation speed. The sample of an aqueous phase is taken and analyzed by spectroscopy. The sample of ionic liquids phase, i.e., organic phase containing metal ions is calculated by mass balance equation (Vergara et al. 2014). After the completion of experiments, the ionic liquids are recovered using a suitable stripping agent and reused for extraction process. The flowchart as shown in Fig. 2 depicts the overall process of extraction and stripping for metal removal from wastewater.

During solvent extraction, the coordination bond between the metal ion and ionic liquid plays a dynamic role in the determination of the extraction efficiency. They exhibit a strong ability to interact with heavy metals through ion pair, electrostatic and hydrogen bond interactions. Usually the transfer of metal ions from the aqueous solution to the ionic liquid phase by different mechanisms include ion exchange (cationic or anionic) mechanism and neutral or solvation mechanism. In an ion exchange mechanism, the transport properties are highly dependent on the hydrophobicity of ionic liquids that decide the distribution coefficient, selectivity, and performance index in liquid–liquid extraction (Ren et al. 2011). The hydrophobic anions of ionic liquids have a great tendency to stimulate the ion exchange and its vice versa for hydrophobic cations of ionic liquids (Rout and Binnemans 2014), i.e., Using the ionic liquids containing hydrophilic cations in the extraction process, efficiency of metal ions are higher than that of using ionic liquids containing more hydrophobic cations. Unlike the organic solvents, both cations and anions of ionic liquids can be transferred to aqueous phase by ion exchange mechanism. Cation exchange mechanism implies that the metal ion (M^+) in aqueous solution is exchanged with cations of ionic liquids for charge neutrality. In case of neutral mechanism, no cations of ionic liquids is transferred to the aqueous phase. Metal complexes from aqueous solution move toward the ionic liquid phase due to the solvation ability and nano-heterogeneity in ionic liquids (Janssen et al. 2016). Because of weakly coordinating anions in ionic liquids, metal ions in the aqueous solution are less soluble in ionic liquid so that it requires chelating agents to chelate with metal ions to form metal complexes. Chelators or ligands are normally used to improve the metal selectivity and hydrophobicity in ionic liquids. The solvating capability of chelating agents in ionic liquids are more thermodynamically favored than toxic organic compounds for the separation of metal ions from aqueous solution.

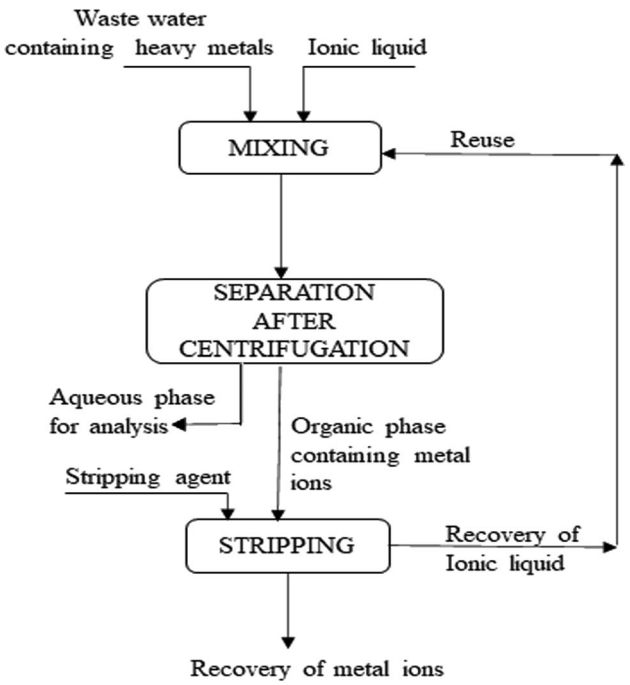

Fig. 2 Flowchart representing the removal of heavy metals from aqueous solution using ionic liquid by liquid–liquid extraction technique. Ionic liquid and metal ions from organic phase are recovered using stripping agent in stripping process. Recovered ionic liquids are recycled and reused

Few studies were conducted earlier using ionic liquids with chelating agents to remove metals from wastewaters. Martinis et al. (2009) developed the analytical methodology to determine the mercury in different water samples (mineral, tap, river and sea waters) and achieved more than 95% extraction efficiency. As proved by Regel-Rosocka (2009), trihexyl (tetradecyl) phosphonium chloride/toluene mixture could be an effective extractant (95%) for the removal of zinc(II) than individual trihexyl (tetradecyl) phosphonium chloride in chloride media. Lertlapwasin et al. (2010) described that the extraction of nickel, copper, and lead in aminothiophenol/1-butyl-3-methylimidazolium hexafluorophosphate medium was easier than chloroform in aqueous solution. Raimondo Germani et al. (2011), studied the removal of Cu^{2+} from aqueous solution using Imidazolium-based ionic liquids/lipophilic polyamine (TE14DT) complexes. In anion exchange mechanism, common β-diketone ligand 2-theonyl trifluoroacetate, Htta is generally used. In extraction process, metal ion, M^+ in the aqueous solution combines with ligand to form metal complexes, $[M\ (tta)]^-$. Then, $[M\ (tta)]^-$ is exchanged with hydrophobic sites of ionic liquid to form weak ion pairs and anions of ionic liquid is transferred into the aqueous phase for the reason of charge balance (Chen and Zhang 2019).

Usually, the problems occurred by the use of chelating agents or ligands in extraction process are: the loss of ionic liquids or ligands in the aqueous phase and decreasing the number of possible extraction cycles making their process application economically unattractive (Technology 2014; Stojanovic et al. 2017). Task-specific ionic liquids or extractant-functionalized ionic liquids have been proposed as a promising extracting agent formed by incorporating the

functional groups like thiourea, thioether, phosphate, phosphine, etc. directly within cations of ionic liquids (Olivier et al. 2009; Mehdi et al. 2010; Di Profio and Germani 2013). Using this functionalized ionic liquids, the affinity (coordination ability) of ionic liquids toward metal extraction increases in turn increasing the extraction efficiency. Papaiconomou et al. 2008 experimentally investigated the extraction of Cu^{2+}, Hg^{2+}, Pd^{2+}, and Ag^{+} ions from water using hydrophobic task-specific ionic liquids containing disulfide and nitrile functional groups. Furthermore, they reported that the ionic liquids having disulfide functional group were an effective extractant for mercury and copper, whereas for silver and palladium, ionic liquids containing nitrile functional group were the best. Most of the functionalized ionic liquids are ammonium based, for the separation of metal ions from aqueous solutions. Trioctylmethylammonium salicylate was synthesized and studied by Egorov et al. (2010) for the extraction of Cu^{2+} and Hg^{2+} from aqueous solution with an efficiency of more than 90%. Rajendran et al. (2011) synthesized the nine ammonium-based ionic liquids functionalized carboxylic, tricarboxylic, and anthranilic groups and proved as an potential extractor for the removal of metal ions like Zn^{2+}, Ni^{2+}, Pb^{2+}, Fe^{2+}, and Cu^{2+} from the tannery effluents. Another ammonium-based task-specific ionic liquid which was halogen-free water immiscible was studied by Vergara et al. (2014) for the extraction of nickel, copper, lead, zinc, and cobalt from aqueous solutions. Leyma et al. (2016) synthesized phosphonium and ammonium-based ionic liquids comprising thio and thioether functionalities for the extraction of Cu^{2+}, Cd^{2+}, and Zn^{2+} with an efficiency of 94%. However, the drawback of functionalized ionic liquids is hard to synthesize in most cases, fairly expensive and high viscosities.

According to the literature, ionic liquids were used without chelating agents for the sequestration of metals from aqueous solution. Reyna-gonzález et al. (2012) reported the extraction of copper(II) (E = 82.6%) from aqueous solution using 3-butylpyridinium bis(trifluoromethanesulfonyl)imide ([3-BuPyr][NTf_2]) without the addition of a chelating agent or pH control of the aqueous phase. Di Profio and Germani (2013) experimentally studied the complete extraction of Hg ions (E ≥ 90%) from aqueous solution using hydrophobic ionic liquids such as 1-octyl-3-methylimidazolium tetrafluoroborate ([C_8MIM][BF_4]) and 1-octyl-3-methylimidazolium bis(trifluoromethyl)sulfonyl imide ([C_8MIM][TF_2N]) without the addition of chelating agents. It was also suggested that the addition of inorganic salts such as sodium chloride or sodium bromide to the aqueous solution completely removes the mercuric ions within few hours at low temperature which is suitable for industrial applications. A summary of liquid–liquid extraction based on ionic liquids for the removal of metal ion in the year 2008–2018 is tabulated in Table 3.

The leaching behavior of hydrophobic ionic liquids in aqueous solution is analyzed through Total dissolved Organic Carbon (TOC) measurement, whereas the halide impurities are predicted by dissolving the ionic liquids in ethanol/water solution and then analyzing it using conductivity meter (Platzer et al. 2017). During solvent extraction, two-phase solvent solutions can be converted into a homogeneous phase by changing the temperature. In the homogeneous phase, a fast reaction takes place between the metal ion and ionic liquids in the presence of temperature. By cooling, the phase separation is formed by the moving of metal complex to ionic liquid phase. This method is called homogenous liquid–liquid extraction (or) coalescence extraction (or) phase transition extraction. For the first time, Vander Hoogerstrate et al. (2013) reported the homogenous liquid–liquid extraction of metal ions (Cu^{2+},Sc^{3+},Ni^{2+}, Ag^{+}, Zn^{2+}, Mg^{2+}, In^{3+}, Ga^{3+}) using carboxyl-functionalized ionic liquid, betainium bis-(trifluoromethylsulfonyl)imide[Hbet][Tf_2N] and zwitterionic betaine as the extractant. It was found that the ionic liquid formed a homogenous solution with water above the Upper Critical Solution Temperature (UCST) at 55 °C. Furthermore, Sc^{3+}, In^{3+}, and Ga^{3+} were extracted in the ionic liquid phase.

Halogenation-free ionic liquids were also participated in the extraction process to separate metals from aqueous solution. The studies conducted earlier reported the usage of ionic liquids such as Trioctylmethyl ammonium camphorate and Trioctylmethyl ammonium dodecanedioate in the extraction of Cd^{2+}, Cu^{2+} and Pb^{2+} from aqueous solutions (Valdés Vergara et al. 2014). Ionic liquids like 1-butylimidazolium di(2-ethylhexyl) phosphate[BIm^{+}][$D2EHP^{-}$] and 1-methylimidazolium di(2-ethylhexyl) phosphate[MIm^{+}][$D2EHP^{-}$] were used to remove mercury ion (E = 100%) which was investigated by Guezzen and Amine Didi (2016). Few studies were only conducted which deployed other types of ionic liquids like morpholinium and pyridinium-based ionic liquids for the separation of heavy metals. Hydrophobic quaternary 3-pyridinium ketoximes such as 3-[1-(hydroxyimino)undecyl]-1-propylpyridinim chloride and 3-[1-(hydroxyimino)undecyl]-1-propylpyridinim bromide dissolved in toluene were used for the extraction of Zn(II) from chloride solutions was studied by Wieszczycka et al. (2013). Wojciechowska et al. (2017a, b, c) experimentally investigated that the extraction of Cu(II) from the real leachate solutions using ionic liquids like 3-[1-(hydroxyimine) undecyl]-1-propylpyridinim chloride [OX-3PC10-PrCl], 1-(3-pyridyl) undecan-1-one [K-3PC10], 1-propyl-3-undecanoylpyridinium bromide [K-3PC10-PrBr], 1-propyl-3-undecanoylpyridinium chloride [K-3PC10-PrCl], and 1-(3-pyridyl) undecan-1-one oxime ([x-3PC10], 3-[1-(hydroxyimine)undecyl]-1-propylpyridinium bromide [Ox-3PC10-PrBr] dissolved in toluene with an efficiency of 97%. Using 1-(3-pyridyl) undecan-1-one oxime,

Table 3 Removal of heavy metals from aqueous solution using liquid–liquid extraction based on ionic liquids with extraction Efficiency, reported from the year 2008 to 2018

Ionic liquid used	Extracted Metal ion	Metal Concentration used (ppm)	Extraction Efficiency	Remarks	Paper
Tricaprylmethylammonium thiosalicylate, [A336][TS], Tricaprylmethylammonium benzoate,[A336][BA] Tricaprylmethylammonium hexanoate, [A336][Hex]	Cd^{2+}	4	99.9%	The extraction efficiency of ionic liquids for Cd(II) from ultra-pure water and natural river water follows the order [A336][TS] > [A336][Hex] > [A336][BA]	Kogelnig et al. (2008)
1-octyl-3-methylimidazolium tetrafluoroborate [OMIM][BF_4], 1-octyl-3-methylpyridinium tetrafluoroborate [3MOPYR][BF_4], 1-octyl-4-methylpyridinium tetrafluoroborate [4MOPYR][BF_4] 1-octyl-4-methylpyridinium trifluoromethylsulfonate [4MOPYR][TfO], 1-octyl-4-methylpyridinium nonafluorobutylsulfonate [4MOPYR][NfO], 1-octyl-4-methylpyridinium bis(trifluoromethyl)sulfonylimide [4MOPYR][Tf_2N], 1-butyronitrile-4-methylpyridinium bis(trifluoromethyl) sulfonylimide [4MPYRCN][Tf_2N], 1-methyl-1-butyronitrilepiperidinium bis(trifluoromethyl) sulfonylimide [MPIPCN][Tf2N], 1-methyl-1-[4,5-bis(methylsulfide)]pentylpiperidinium bis(trifluoromethyl)sulfonylimide [4MPIPS2][Tf_2N] 1-methyl-1-[4,5-bis(methylsulfide)] pentylpyrrolidinium bis(trifluoromethyl) sulfonylimide [4MPYRROS2][Tf_2N]	Cu^{2+},Hg^{2+},Na^{+}, K^{+}, Mg^{2+}, Co^{2+},Fe^{3+},Ni^{2+},Tl^{+},Pb^{2+},Sn^{4+},Ba^{2+}, Zn^{2+},Cd^{2+}	50–500		Ionic liquids based on sulfide functional groups were highly efficient for the extraction of Hg(II) and Cu(II) while ionic liquids based on nitrile functional groups for silver and palladium ions	Papaiconomou et al. (2008)

Table 3 (continued)

Ionic liquid used	Extracted Metal ion	Metal Concentration used (ppm)	Extraction Efficiency	Remarks	Paper
1-Alkyl-3-ethylimidazolium hexafluorophosphate 1-Alkyl-3-ethylimidazolium bis{(trifluoromethyl)sulfonyl} imide	Pb^{2+},Ag^{+}	30–80	Tap water—< 98% River water—96–99% Sea water—< 95% Mineral water—< 98%	Increase in alkyl chain length from ethyl to hexyl decreases the extraction efficiency [EMIM][NTF_2] has better extractor for Pb^{2+} removal than [EMIM] [PF_6]	Domanska and Rekawek (2009)
Trihexyl(tetradecyl)phosphonium chloride (Cyphos IL 101) Trihexyl(tetradecyl) phosphonium bis(trifluoromethylsulfonyl) imide (Cyphos IL 109)	Zn^{2+}	5000	95%	Zn(II) extraction was endothermic in nature which was predicted by thermodynamic analysis Cyphos IL 109 was not effective for Zn(II) extraction	Regel-Rosocka (2009)
Trioctylmethylammonium salicylate (TOMAS)	Cu^{2+}, Fe^{3+}	55–65	Cu^{2+}—89% Fe^{3+}—99%	Reported that extraction efficiency was directly related to stability constant of salicylate complexes Metals were stripped using Trioctyl methyl ammonium salicylate modified electrodes	Egorov et al. (2010)
Trihexyl(tetradecyl)phosphonium chloride (Cyphos IL 101)	Fe^{3+}	58	> 99%	Reported that extracted Fe(III) as tetrachloroferrate complex in the organic ionic liquid and can be recovered using 0.5 M HCl solutions	Kogelnig et al. (2010)
1-butyl-3-methylimidazolium hexafluorophosphate [BMIM] [PF_6]z	Cu^{2+},Ni^{2+},Pb^{2+}	5	Cu^{2+}—76% Ni^{2+}—57% Pb^{2+}—20%	The extraction efficiency of all metal ions with the ligand in the ionic liquid was higher than that obtained in chloroform using the same conditions	Lertlapwasin et al. (2010)
1-hexyl-3-methylimidazolium hexafluorophosphate ([C_6MIM] [PF_6]), 1-octyl-3-methylimidazolium hexafluorophosphate ([C_8MIM][PF_6]), 1-octyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl] imide ([C_8MIM] [Tf_2N])	Cu^{2+}	670	44%	Mentioned that the alkyl chain length of imidazolium ring (cation of ionic liquid) played a relevant role to determine the extraction efficiency Metal-ion partition was strongly dependent on nature of the solvent and working temperature	Germani et al. (2011)

Table 3 (continued)

Ionic liquid used	Extracted Metal ion	Metal Concentration used (ppm)	Extraction Efficiency	Remarks	Paper
Trihexyl(tetradecyl)phosphonium chloride (Cyphos IL 101), Trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl) phosphinate (Cyphos IL 104)	Pd^{2+}	270	99%	The selectivity of Pd^{2+} extraction over Pb, Fe, Pt depends upon the acidity of aqueous solution and with increasing HCl concentration, selectivity decreases	Cieszynska and Wisniewski (2011)
Trihexyl(tetradecyl)phosphonium chloride (Cyphos IL 101)	Zn^{2+}	500	100%	The highest purity of Zn(II) over Fe(III) was achieved where the separation factor was 30 Zn(II) was greatly extracted from low-concentrated feed solutions	Regel-Rosocka and Wisniewski (2011)
Tetrapropylammonium benzoate (ILA), Tetrapropylammonium salicylate (ILB), Tetrapropylammonium anthranilate (ILC), Tetrabutylammonium benzoate (ILD), Tetrabutylammonium salicylate (ILE), Tetrabutylammonium anthranilate (ILF), Tricaprylmethylammonium benzoate (ILG), Tricaprylmethylammonium salicylate (ILH), and Tricaprylmethylammonium anthranilate (ILI)	Cu^{2+},Ni^{2+},Pb^{2+}, Fe^{2+},Zn^{2+}	–	Cu^{2+}—11.7–47.5% Ni^{2+}—53.4–84.7% Pb^{2+}—44.1–88.2% Fe^{2+}—40.4–94.2% Zn^{2+}—12.9–93.3%	Proven as ionic liquids an excellent extractor of heavy metals like Zn, Ni, Pb, Fe, and Cu from the tannery effluents	Rajendran et al. (2011)

Table 3 (continued)

Ionic liquid used	Extracted Metal ion	Metal Concentration used (ppm)	Extraction Efficiency	Remarks	Paper
1-octyl-3-methylimidazolium tetrafluoroborate [omim$^+$][BF_4^-], 1-butyl-3-methylimidazolium hexafluorophosphate [bmim$^+$][PF_6^-], 1-octyl-3-methylimidazolium hexafluorophosphate [omim$^+$][PF_6^-], 1-butyl-3-methylimidazolium bis{(trifluoromethyl)sulfonyl} imide, [bmim$^+$][NTf_2^-], 1-octyl-3-methylimidazolium bis{(trifluoromethyl)sulfonyl} imide, [omim$^+$][NTf_2^-], Methyl trioctylammonium chloride, [MTOA$^+$][Cl$^-$]	Fe^{3+},Zn^{2+},Cd^{2+}, Cu^{2+}	100	Fe^{3+}—90% Zn^{2+}—100% Cd^{2+}—100% Cu^{2+}—80%	Increased metal ion concentration results decreasing the extraction rate [omim$^+$][BF_4^-] gave the selective separation of Zn(II), Cd(II) over Fe(III) and Cu(II) [MTOA$^+$][Cl$^-$] gave a maximum extraction rate than other ionic liquids	Ríos et al. (2012)
2-butylpyridinum bis(trifluoromethanesulfonyl) amide, [mimSBu][NTf_2],	Cu^{2+}	120	82.6%	Extraction process was studied without the addition of a complexing agent and pH control of the aqueous phase Ionic liquids were recovered using a strong acid	Reyna-González et al. (2012)
1-butyl-3-methylimidazolium hexafluorophosphate [bmim$^+$][PF_6^-]	Li^{2+}	–	99.60%	Reported that the conjunction with ionic liquids gave an extraordinary results	Cristóvão et al. (2012)
1-hexadecyl-3-methylimidazolium chloride ([C_{16}MIM][Cl])	Au^+	50	100%	Anion exchange mechanism was proposed for gold extraction and was confirmed by method of continuous variation and infrared spectrum analysis Oxalic acid was used as a stripping agent	Tong et al. (2013)

Table 3 (continued)

Ionic liquid used	Extracted Metal ion	Metal Concentration used (ppm)	Extraction Efficiency	Remarks	Paper
1-octyl-3-methylimidazolium hexafluorophosphate [C_8MIM][PF_6], 1-octyl-3-methylimidazolium tetrafluoroborate [C_8MIM][BF_4] 1-octyl-3-methylimidazolium bis[trifluoromethyl)sulfonyl] imide [C_8MIM][Tf_2N]	Hg^{2+}	500	>90%	Addition of inorganic salts such as NaCl or NaBr to the aqueous phase resulting increased extraction rate Cation exchange mechanism was proposed for the nature of extraction	Di Profio and Germani (2013)
3-[1-(hydroxyimino)undecyl]-1-propylpyridinim chloride 3-[1-(hydroxyimino)undecyl]-1-propylpyridinim bromide	Zn^{2+}	5000	12–28%	Zn^{2+} extraction was increased with increasing the length of alkyl chain of pyridinium anion Phase ratio assists the reduction of Zn(II) ion concentration which was represented by Mc-Cabe—Thiele diagram	Wieszczycka et al. (2013)
Trihexylmethylammoniumcarbonate, Trioctylmethylammonium carbonate, Trihexylmethylammoniumadipate, Trihexylmethylammonium salicylate, Trihexylmethylammoniumazelate, Trioctylmethylammonium dodecanedioate, Trihexylmethylammonium oxalate, Triotylmethylammoniumazelate	Cu^{2+},Pb^{2+} Zn^{2+},Co^{2+},Ni^{2+}	25	Cu^{2+}—100% Pb^{2+}—93–96% Ni^{2+}—96%	The reported ionic liquids were synthesized for the extraction of metal ions from aqueous solution and their results were compared with commercial ionic liquids	Vergara et al. (2014)
Trioctyl methyl ammonium camphorate Trioctyl methyl ammonium dodecanedioate	Cd^{2+},Cu^{2+},Pb^{2+}	50–100	76–81%	Recovery of ionic liquids was done using solvents with low polarity indexes The addition of sodium salt to the ionic liquid results loss of ionic liquid weight	Valdés Vergara et al. (2014)

Table 3 (continued)

Ionic liquid used	Extracted Metal ion	Metal Concentration used (ppm)	Extraction Efficiency	Remarks	Paper
Tetraoctyl phosphonium oleate $[P_{8888}][oleate]$	Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, In^{3+}, La^{3+}, Nd^{3+}, Sm^{3+}, Dy^{3+}, Er^{3+}, Yb^{3+}	1000	All metals expect K and Li—> 85% K^+—20% Li^+—60%	Liposome tests revealed that ionic liquids were very hydrophobic which limits its leakage toward the water phase Ionic liquids were regenerated using 0.1 M sodium oxalate	Parmentier et al. (2015)
Betaine {tri(n-butyl)[2-ethoxy-2-oxoethyl)ammonium dicyanamide, [BuGBOEt][Dca] Betaine {tri(n-butyl)[2-ethoxy-2-oxoethyl)ammonium-bis(trifluoromethylsulfonyl) imide [BuGBOEt][Tf_2N]	Cu^{2+},Cd^{2+},Ni^{2+}, Pb^{2+}	60–200	Cu^{2+}—98% Cd^{2+}—99% Ni^{2+}—95% Pb^{2+}—97%	Use of Dca^- anion greatly enhanced the extraction efficiency of ionic liquid phase toward metal ion extraction The metals were recovered using EDTA solutions	Zhou et al. (2015)
1-butyl-3-methylimidazolium hexafluorophosphate [$bmim^+$][PF_6^-]	Cu^{2+},Co^{2+},Ni^{2+}, Pb^{2+}	3	Cu^{2+}—40–50% Co^{2+}—50–60% Ni^{2+}—50–60% Pb^{2+}—30–40%	The number of ligands used in the metal complex, the extraction constant and stoichiometry of the extracted species were determined by slope analysis method	Fetouhi et al. (2016)
Aliquat 336	Au^+, Pt^{2+}, Pd^{2+}	200	Au(III)—100% Pt(IV)—19.6% Pd(II)—35.4%	Two-step stripping process was done for high purity of Au(III) using HCl and thiourea as a stripping agent	Wei et al. (2016)
1-butylimidazolium di(2-ethylhexyl)phosphate [BIm^+][$D2EHP^-$] 1-methylimidazolium di(2-ethylhexyl)phosphate [MIm^+][$D2EHP^-$]	Hg^{2+}	200	100%	Extraction rate was improved by the addition of sodium acetate to the aqueous solution Among 2 ionic liquids, [MIm^+][$D2EHP^-$] has strong extracting power for Hg(II)	Guezzen and Amine Didi (2016)
Cyphos IL 101 Aliquat 336	Cd^{2+}	36	99%	Extraction process was endothermic for both ionic liquids Mc-Cabe-Thiele plot showed the complete extraction of cadmium in two stages	Swain et al. (2016)

Table 3 (continued)

Ionic liquid used	Extracted Metal ion	Metal Concentration used (ppm)	Extraction Efficiency	Remarks	Paper
Tricaprylmethylammonium thiosalicylate [A336][TS] Trihexyl-tetradecylphosphonium thiosalicylate [PR_4][TS] Tricaprylmethylammonium methylthiosalicylate [A336][MTBA] Trihexyl-tetradecylphosphonium thiosalicylate [PR_4][MTBA] Trihexyl-tetradecylphosphonium 2-(propylthio)benzoate [P_{66614}][PTB] Trihexyl-tetradecylphosphonium 2-(benzylthio)benzoate [P_{66614}][BTB]	Cu^{2+},Cd^{2+} Zn^{2+}	Cu^{2+}—5 Cd^{2+}—4 Zn^{2+}—1	≥ 94%	[P_{66614}][PTB] was reported a better extractor of Cu(II) and Cd(II) but not Zn(II), whereas [P_{66614}][BTB] was the best for all metals	Leyma et al. (2016)
1-butyl-3-methylimidazolium hydrogen sulfate	Hg^{2+}	500–800	75-80%	Extraction was done in both monobasic and dibasic system Activated charcoal was used as a chelating agent for an effective removal	Sisodia and Khothari (2016)
N-octylpyridinium tetrafluoroborate ([OPy]$^+$) ([BF_4]$^-$ *N*-octylpyridinium(bis(trifluoromethylsulfonyl) imide (([OPy]$^+$) [Tf_2N]$^-$) *N*-octylpyridinium trifluoromethylsulfonate ([OPy])$^+$ ([TfO]$^-$) *N*-octylpyridiniumnonafluorobutylsulfonate ([OPy]$^+$ ([NfO]$^-$)	Hg^{2+}	1	Tap water—107% Pond water—83% Wastewater—95%	Among 4 ionic liquids, [OPy]$^+$[BF_4]$^-$ and [OPy]$^+$[TfO]$^-$ were found to be efficient extractant for Hg(II) extraction	Li et al. (2016)
N-methyl-*N*,*N*,*N*-trioctyl ammonium-bis-(2-ethylhexyl) phosphonate (MTOABEHP)	Gd(III)	60	>98.5%	Back extraction was effectively done using EDTA solutions and deionized water Stoichiometry of an extracted complex was found using log–log plot method	Dutta et al. (2016)

Table 3 (continued)

Ionic liquid used	Extracted Metal ion	Metal Concentration used (ppm)	Extraction Efficiency	Remarks	Paper
1-butyl-3-methyl-imidazolium bis (trifluoromethylsulfonyl) imide [bmim] [Tf2N], 1-octyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl) imide [omim][Tf_2N]	MO(VI)	480	90%	Addition of TBP to [bmim] [Tf2N] to avoid the third liquid phase formation Extraction was done using ionic liquids and was compared with kerosene to determine the efficiencies	Torres and Romero (2016)
Trihexyl(tetradecyl)phosphonium chloride (Cyphos IL 101), Trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl) phosphinate (Cyphos IL 104) Tributyl(tetradecyl)phosphonium chloride (Cyphos IL 167)	Ru(III), Rh(III)	25	Ru(III)—70% Rh(III)—50%	Cyphos IL 167 reported the better extractant of Ru(III) from single metal feeds extraction depends on the concentration of ionic liquid used	Wis and Regel-Rosocka (2017)
Methyltrioctylammonium *S*-hexyl thioglycolate [N_{1888}] [C_6SAc] Methyltrioctylphosphonium *S*-hexyl thioglycolate [P_{1888}] [C_6SAc]	Co^{2+},Ni^{2+}, Zn^{2+}	Co^{2+}— 5 Ni^{2+}—4 Zn^{2+}—1	Co^{2+}—20% Zn^{2+}—93%	90% of Zn(II) was removed within 2 h. Co(II) and Ni(II) were moderately removed Extraction depends on the stability of the metal–water cluster which was predicted by Quantum mechanical calculations	Platzer et al. (2017)
Tetrabutyl Phosphonium bis(2,4,4-trimethylpentyl) phosphinate ([P_{4444}] [BTMPP])	Li^{2+}	500	90%	From the thermodynamic analysis, change in standard "Gibb's energy, enthalpy, and entropy" was determined HCl solutions used as a stripping agent	Shi et al. (2017)
1-(3-Pyridyl)undecan-1-one oxime, 3-[1-(hydroxyimine)undecyl]-1-propylpyridinium chloride, 3-[1-(hydroxyimine)undecyl]-1-propylpyridinium bromide	Pb^{2+}	1000	70-75%	Among the three ionic liquids, [3PC10-PrCl] has better extractor toward lead removal from aqueous solution The extraction efficiency strongly dependent on chloride and extractant concentration and its structure	Wojciechowska et al. (2017a, b, c)

Table 3 (continued)

Ionic liquid used	Extracted Metal ion	Metal Concentration used (ppm)	Extraction Efficiency	Remarks	Paper
3-[1-(hydroxyimine) undecyl]-1-propylpyridinim chloride [OX-3PC10-PrCl], 1-(3-pyridyl) undecan-1-one [K-3PC10], 1-propyl-3-undecanoylpyridinium bromide [K-3PC10-PrBr], 1-propyl-3-undecanoylpyridinium chloride [K-3PC10-PrCl], 1-(3-pyridyl) undecan-1-one oxime ([x-3PC10], 3-[1-(hydroxyimine)undecyl]-1-propylpyridinium bromide [Ox-3PC10-PrBr]	Cu^{2+}	10	97%	Among 6 ionic liquids, [Ox-3PC10-PrBr] gave a maximum extraction rate of Cu(II) from the real leachate solutions containing Cu(II), Fe(II) and Fe(III)	Wojciechowska et al. (2017a, b, c)
Trioctyl(dodecyl) phosphonium chloride, $[P_{88812}][Cl]$	Pt(II), Pd(II), Rh(III)	100	{Pt(IV) Pd(II)}—> 80% Rh(III)—> 60%	The studied ionic liquids showed higher hydrophobicity and lower viscosity than commercial $[P_{66614}][Cl]$ Anion exchange mechanism was proposed	Firmansyah et al. (2018)
Trialkylmethylammonium chloride (Aliquat336)	Zn^{2+}	650	100%	Ionic liquid was mixed with trioctyl phosphine oxide showed the positive effect on Zn(II) extraction but with negative effect on ammonia stripping of zinc	Ding et al. (2018)
1-hexyl-3-methylimidazolium chloride $[C_6mim]Cl$, 1-hexyl-3-methylimidazolium bis((trifluoromethyl) sulfonyl) imide $[C_6mim][NTf_2]$, 1-hexyl-3-methylimidazolium Sodium diethyldithiocarbamate $[C_6mim][DDTC]$	Pt(II), Pd(II), Rh(III), Ru(III)	20–40	Pt(IV)—99% Pd(II), Rh(III), Ru(III)— < 10%	Both HCl, H^+, Cl^- showed a negative effect on extraction due to competition b/w HCl, ionic liquid and metal complexes Rh(III) remaining in aqueous phase was recovered as nano-scaled Rh_2S_3 using $(NH_4)S$	Yan et al. (2018)

Table 3 (continued)

Ionic liquid used	Extracted Metal ion	Metal Concentration used (ppm)	Extraction Efficiency	Remarks	Paper
1-butyl-1-methylmorpholinium butylphosphite (Mor_{1-4}-BP), 1-hexyl-1methylmorpholinium hexylphosphite(Mor_{1-6}-HP), 1-octyl-1-methylmorpholiumoctylphosphite (Mor_{1-8}-OP)	Ur(VI)	560	98.6%	Extraction reaction was developed through a neutral partition or an ionic exchange mechanism UO_2^{2+} ions were extracted from mixture containing transition metal ions at nitric acid concentration at 7 M	Zarrougui et al. (2018)

3-[1-(hydroxyimine) undecyl]-1-propylpyridinium bromide and 3-[1-(hydroxyimine) undecyl]-1-propylpyridinium chloride, lead(II) was extracted from chloride/nitrate solution in the study conducted by Wojciechowska et al. (2017a, b, c). Zarrougui et al. (2018) extracted and separated the uranium from concentrated nitric acid solutions comprising transition metals (Cu^{2+}, Fe^{3+}, Ni^{2+}, Co^{2+}, Zn^{2+} and Cd^{2+}) using 1-butyl-1-methylmorpholinium butylphosphite (Mor_{1-4}–BP), 1-hexyl-1methylmorpholinium hexylphosphite (Mor_{1-6}-HP) and 1-octyl-1-methylmorpholiumoctylphosphite (Mor_{1-8}-OP). Among the three ionic liquids, the researchers concluded that Mor_{1-8}-OP was the best extractant for the removal of uranium.

If one needs to predict the selectivity, distribution coefficient, and performance index of the potential ionic liquids from the available ionic liquids of more than 10^{18}, experimental realization process is a cost and time consuming one. The prescreening method, known as COnductor like Screening MOdel for Realistic Solvents (COSMO-RS), was first proposed by Klamt to predict the thermodynamic properties of ionic liquids and their suitability in particular application without any experimental data. Using this method, Zhao et al. (2018) proposed the molecular design of ionic liquids to extract lithium from aqueous solution. The screening results revealed that the structure of anion in ionic liquids plays a vital role in the affinity to Li ion, whereas cation for adjusting the hydrophobicity of ionic liquids to avoid loss during the water phase. The stoichiometry of extracting species is evaluated by slope analysis method (Shi et al. 2017; Zhao et al. 2018). As it can be observed, ionic liquids possess the better extracting characteristic especially in case of metal ion removal, when their alkyl chain is butyl or even longer to strengthen the hydrophobicity (Guezzen and Amine Didi 2016).

From the discussion of literatures, it was found that imidazolium, ammonium, and phosphonium-based ionic liquids were mostly used for the removal of metal ions from aqueous solution with good extraction efficiency, but few ionic liquids were not appropriate for extracting several metals. It is quite better to prescreen the ionic liquids using Solvation Model before doing the experimental part so as to predict the favorable ionic liquids for achieving high extraction efficiency of metal from aqueous solution.

Adsorption

Adsorption is a mass transfer process in which a specific solute from liquid solution is adsorbed on the surface of adsorbent. A number of adsorbents, such as activated carbon, nanoporous silica, zeolite, metal oxide, clays, chitin–chitosan, and activated alumina, play an essential role in getting rid of heavy metals from wastewater (Mi et al. 2013; Crini et al. 2018; De Vargas et al. 2020). In order to improve the

existing adsorbents with a wide range of pH value and high leaching ability, the ionic liquids can be used as a template, surfactant and crystal growth modifier. The advantages of ionic liquids in the adsorption process are:

- Small adsorbent requirement
- Avoidance of losing ionic liquids in the aqueous phase
- Low energy consumption
- Cost-effective process.

They form an extended hydrogen bond with the liquid solution to synthesize highly porous structured materials. During the adsorption process, ionic liquids can easily adsorb onto the fore-mentioned adsorbents through ion–pair interaction and may form a strongly structured interface at the surface of adsorbent. This interface may induce the adsorption of heavy metals in the wastewater by electrostatic and ion pair interactions resulting in higher adsorption capacity and separation rate (Ekka et al. 2017; Khulbe and Matsuura 2018) as shown in Fig. 3.

There are several analytical techniques such as Fourier Transform Infrared spectroscopy (FTIR), X-Ray powder Diffraction (XRD), Thermogravimetric analysis (TGA), N2 adsorption–desorption isotherm, Transmission Electron Microscopy (TEM), Field Emission Scanning Electron Microscopy (FESEM), and X-ray Photoelectron Spectroscopy (XPS) mainly used to analyze and characterize the functional groups, elemental composition, surface morphology, shape and phases of the adsorbed molecule as well as adsorbent. The main parameters to be considered, during the adsorption process are adsorbent capacity, selectivity, regenerability, lifetime, and adsorption kinetics. In the adsorption process, kinetic data are better described by first-order or second-order model and the value of activation energy suggests whether the adsorption process is physical sorption or chemical sorption by fitting with the experimental results (Lupa et al. 2017). The adsorption mechanism was explored and it was realized that the rate-controlling steps are chemical reaction and mass transport process (Kumar and Rajesh 2013). Another significant parameter is residence time which is used to estimate the adsorption capacity and equilibrium during the adsorption process. Therefore, equilibrium, kinetic and thermodynamic data are needed to determine the adsorbent capacity toward the separation of metals from aqueous solution (Sahmoune 2018; Crini et al. 2018). A summary of adsorption processes based on ionic liquids for metal ion removal in the year 2008–2018 is tabulated in Table 4.

The adsorption of ionic liquids onto polymeric support through impregnation is performed using ultrasonication method. On comparison with classical methods like dry method, column method, and wet method, this method requires only a short time period for impregnation. Using ultrasonication method, an efficient adsorption of hexavalent chromium was performed using tetraoctyl ammonium bromide-impregnated chitosan through three center (3c) cooperative mechanism in the study conducted by Santhana Krishna Kumar et al. (2012). This method was also used by Lavinia Lupa et al. (2014) in the adsorption of Ti(I) from aqueous solution using styrene-12% divinyl-benzene copolymer functionalized with amino-phosphonate groups and impregnated with trihexyl(tetradecyl)phosphonium chloride (Cyphos IL-101). In this study, the maximum adsorption capacity was obtained than other adsorbents such as Aspergillus Niger biomass or polyacrylamide-aluminosilicate composite. A number of authors investigated the removal of carcinogenic chromium from aqueous solution using different ionic liquids. The adsorption of Cr^{6+} was studied using synthesized *N*-Methylimidazolium-functionalized strongly basic anion exchange resins such as (RCl and R_2SO_4) (Zhu et al. 2009), Aliquat 336 impregnated Dowex 1×8 resin (Kalidhasan et al. 2012), poly(3-ethyl-1-vinyl imidazolium bis(trifluoromethanesulfonyl)imide) (Mi et al. 2013), 1-aminopropyl-3-methylimidazolium nitrate functionalized cellulose (ILFC) (Dong and Zhao 2018), and tetraoctyl ammonium bromide-impregnated amberlite XAD-4 polymeric matrix (Santhana Krishna Kumar et al. 2012). Furthermore, it was reported that their results were validated for electroplating and tannery effluent samples.

Several studies were conducted in the literature with regard to chemical modification of adsorbents for getting a maximum adsorption capacity and also to rectify the drawbacks ensued in conventional adsorbents for the separation of metal ions from aqueous solution. Chemical modification or functionalization of ionic liquids onto solid adsorbent is formed by sol–gel process through either doping or covalent grafting (Tian et al. 2010). Ionic liquids having functional groups such as amine, imidamide, oxime, and hydroxyl are commonly used to encapsulate or immobilize the adsorbents (Aksamitowski et al. 2019). Unlike conventional sorbents, chemically modified or functionalized silica material is an excellent sorbent for the removal of metal ions due to its numerous advantages like large porous structure, outstanding chemical, mechanical and thermal stabilities, capability to change the surface properties, etc. (Tian et al. 2010). In grafting technology, the ionic liquids are covalently bounded to the silica gel through electrostatic or ion pair interaction. However, the synthesis process is usually complicated and sometimes additional functional groups are acquired to accomplish a high metal selectivity and fast reaction rates (Yost et al. 2000; Liu et al. 2010b), whereas in doping of ionic liquids on silica material in sol gel process, the doped molecules can interact with positively charged metal ion in solution via electrostatic attraction (Ekka et al. 2015). In this process, ionic liquids can act as a porogens to prepare silica gel and as extractant to extract metal ions from aqueous

solution. Using this process, Turanov et al. (2016) studied the adsorption of Scandium and lanthanides from nitric acid solutions using silica gel doped with Trioctylmethyl ammonium 1-phenyl-3-methyl-4-benzoylpyrazol-5-benzoate ($[A336^+][L^-]$). Using synthesized mesoporous silica sorbents such as B104SGs and O104SGs doped with binary ionic liquids mixtures like ($[C_8mim^+][PF_6^-]$/Cyphos IL 104) or ($[C_4mim^+][PF_6^-]$/Cyphos IL 104), yttrium ion was separated reported by Liu et al. (2010b). For the adsorption of Chromium ions (Cr^{3+} and Cr^{6+}) from aqueous solution, the ionic liquids such as trialkylmethyl ammonium-bis 2, 4, 4-trimethylpentylphosphinate ([A336][C272]) and Cyphos IL 104 functionalized silica sorbents (SG-2 and SG-5) were used which was investigated by Liu et al. (2010a). Ekka et al. (2015) reported the adsorption of Pb^{2+} from aqueous solution using ionic liquids such as 1-butyl-3-methyl-imidazolium bromide ([BMIM][Br]), 1-octyl-3-methylimidazolium bromide ([OMIM][Br]) and 1-hexadecyl-3-methyl-imidazolium bromide ($[C_{16}MIM][Br]$)-impregnated mesoporous silica as these adsorbents possess higher adsorption capacity than clinoptilolite, montmorillonite, and kaolinite. Aksamitowski et al. (2019) studied the adsorption of Cu(II), Co(II), and Ni(II) using silica gel modified imidamide functional group of ionic liquids like *N′*-hydroxy-*N*,*N*-dioctylpyridine-3-carboximidamide (DO3PIA) and *N′*-hydroxy-*N*,*N*-dioctylpyridine-4-carboximidamide (DO4PIA). But the doping process faces some difficulties like slow diffusion of ionic liquids in silica gel resulting slow reaction kinetics consecutively low adsorption capacity of sol–gel adsorbents.

To overcome this, some additives like crown ether, Cyanex 923, etc. are added to stabilize the ionic liquids within the silica gel matrix. They act as a diffusion medium in the aqueous solution for sequestration of metal ions (Liu et al. 2007, 2010a). Using these additives in doping of ionic liquids on silica gel, a numerous studies were reported. Makote et al. (2008) studied the adsorption of Sr^{2+} ions from aqueous solution using synthesized ionic liquid, 1-ethyl-3-methylimidazolium bis (trifluoromethyl) sulfonamide ($[EtmeIM^+][Tf_2N^-]$) and silica gel doped with dicyclohexyl-18-crown-6 as an additive. For the adsorption of La^{3+} and Ba^{2+}, the ionic liquids, $[C_nmim][NTF_2]$ (n = 2,4,6,8,10) impregnated silica matrix doped with *N*,*N*,*N′*,*N′*-Tetra(*n*-octyl)diglycolamide were used which was described by Taylor et al. (2011). For the first time, Sun et al. (2016), experimentally demonstrated the adsorption of Pb(II) from water using a combination of trioctyl ammonium bromide, graphene oxide and magnetic chitosan with maximum adsorption capacity of 85 mg/g. Furthermore, it was reported that the addition of ionic liquids not only improved the dispersivity of the adsorbent, but also increased the adsorption sites. Various research works were conducted on metal adsorption using Trihexyl (tetradecyl) Phosphonium chloride (CYPHOS IL 101). The examples of reports include the adsorption of Zn^{2+},Cd^{2+} Hg^{2+} and Fe^{3+} using amberlite XAD-7 impregnated with CYPHOS IL 101

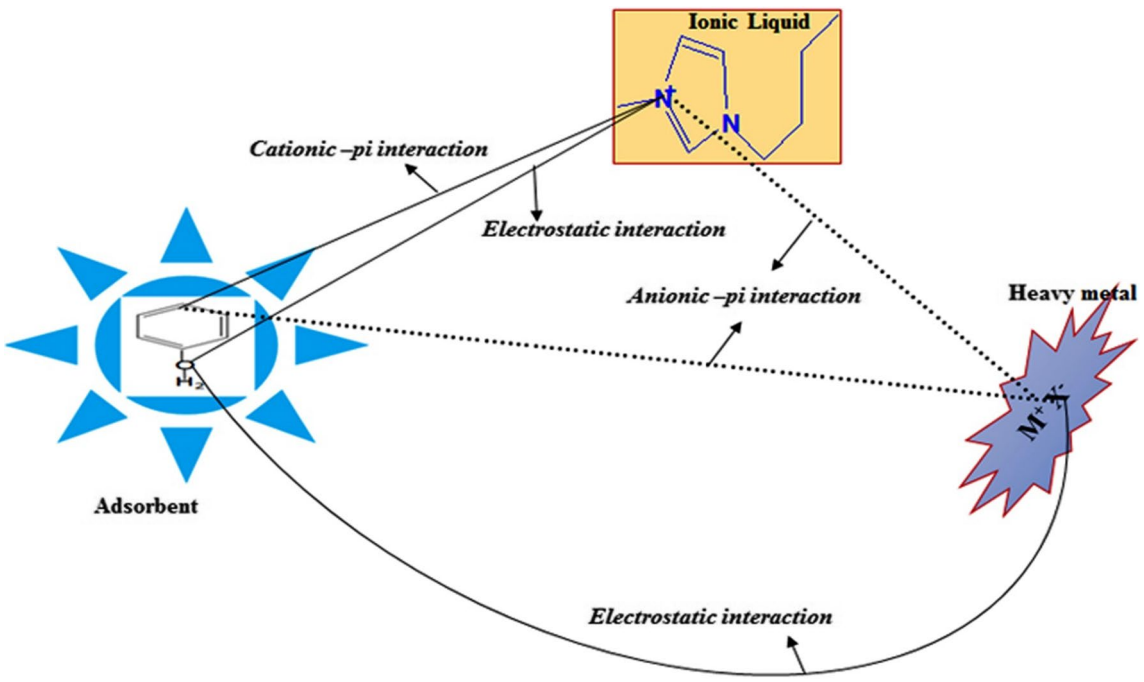

Fig. 3 Mechanism of heavy metal adsorption using adsorbent impregnated ionic liquids. Through electrostatic and ion pair (cationic or anionic-pi) interactions, the heavy metals are separated from aqueous solution in the adsorption process

Table 4 Removal of heavy metals from aqueous solution by adsorption based on ionic liquids with Maximum Adsorption Capacity, reported from the year 2008 to 2018

Ionic liquid used	Metal ion extracted	Maximum adsorption capacity (mg/g)	Remarks	Paper
Trihexyl(tetradecyl)phosphonium chloride (Cyphos IL 101)	Au^{+}	140	Sorption kinetics was governed by reaction rate of adsorption process at low concentration Gold can be recovered from ionic liquid impregnated resin using thiourea in HCl solution Sorption capacity was decreased by 30% with the recycling of the resin	Campos et al. (2008)
Trihexyl(tetradecyl)phosphonium chloride (Cyphos IL 101)	Zn^{2+}	20	Models based on film diffusion, chemical reaction did not fit with experimental data and model based on intraparticle diffusion, the equation was well-fitted with experimental data	Gallardo et al. (2008)
N-methylimidazolium chloride (RCl) *N*-methylimidazoliumsulfate (R_2SO_4)	Cr(VI)	132 and 125	RCl was easily regenerated and recycled for four cycles with no loss of adsorption capacities Resins used in the adsorption process with good chemical stability and high adsorption capacities	Zhu et al. (2009)
Trihexyl(tetradecyl)phosphonium chloride (Cyphos IL 101)	Cd(II)	0.50	Intra particle diffusivity linearly increased with sorbent dosage and interfacial area Reported that part of the ionic liquids s tightly bound to a polymer matrix did not react with metal ions which is predicted by sorption performance	Arias et al. (2011)
Methyltrioctylammonium chloride	Cr(VI)	230.9	Impregnation of ionic liquids in Dowex 1x8 resin was prepared using ultrasonication method for the adsorption of Cr(VI) Certified industrial wastewater effluent samples were successfully treated	Kalidhasan et al. (2012)
Trihexyl(tetradecyl)phosphonium thiosalicylate [PR4][TS], Trihexyl(tetradecyl)phosphonium 2-methylthio) benzoate [PR4][MTBA], Tricaprylylmethylammonium thiosalicylate [A336][TS], Tricaprylylmethylammonium 2-(methylthio) benzoate [A336][MTBA]	Cd^{2+}, Cr^{2+}, Cu^{2+}, Pb^{2+},Ni^{2+} Zn^{2+}	Cd^{2+}—0.005 Cr^{2+}—0.037 Cu^{2+}—0.028 Pb^{2+}—0.464 Ni^{2+}—0.029 Zn^{2+}—1.673	Removal efficiencies for metals was not effective for standard solutions but quite satisfactory for industrial effluents as well as activated sewage sludge wastes	Fürhacker (2012)
Tetraoctylammonium bromide	Cr(VI)	63.69	Interactions involving ion–pair, cation-π, electrostatic, Vander Waals played a vital role in the adsorption process Electroplating and Tannery effluents were treated using the procedure	Santhana Krishna Kumar et al. (2012)
Trihexyl(tetradecyl)phosphonium chloride (Cyphos IL 101)	Cs^{+}	3.086	Kinetic data in the adsorption process followed the pseudo-second-order model	Lupa et al. (2013)

Table 4 (continued)

Ionic liquid used	Metal ion extracted	Maximum adsorption capacity (mg/g)	Remarks	Paper
Trioctylmethyl ammonium thiosalicylate(TOMATS)	Hg^{2+}	83.33	By the analysis of thermodynamic parameter, adsorption process was endothermic and spontaneous in nature	Ismaiel et al. (2013)
Tricaprylmethylammonium chloride (Aliquat 336)	Cr(VI)	196.1	Tannery and electroplating effluents were treated for the removal of Cr(VI) Adsorbent was regenerated using the mixture of ascorbic acid and HCl mixtures with specific concentrations	Kalidhasan et al. (2013)
Poly(3-ethyl-1-vinylimidazolium bis(trifluoromethanesulfonyl)imide)	Cr(VI)	17.9	Experimental data were well-fitted with Langmuir adsorption isotherm Due to the electrostatic force and Vander Waals force of attraction, Cr(VI) was easily adsorbed on the amine on imidazole ring	Mi et al. (2013)
Tricaprylmethylammonium chloride (Aliquat-336)	Cr(VI)	285.71	Adsorption of Cr(VI) from tannery effluent sample was done using EGO—ionic liquid adsorbent	Kumar and Rajesh (2013)
Tetradecyl(trihexyl)phosphonium chloride (Cyphos IL 101)	Hg^{2+}	40	Reported that the sorption efficiency depends on the concentration of HCl and the ionic liquid loading Both nitric acid and thiourea were used as a desorbing agent, but Nitric acid has found out the best	Navarro et al. (2014)
1-Butyl-3-methylimidazolium bromide([BMIM][Br]), 1-octyl-3-methylimidazolium bromide([OMIM][Br]) 1-hexadecyl-3-methyl-imidazolium bromide([C_{16}MIM][Br])	Pb^{2+}	5.18	Adsorption process was feasible and endothermic in nature by the analysis of thermodynamic parameters Equilibrium data were well-fitted with Freundlich model	Ekka et al. (2015)
Tetra *n*-heptylammonium bromide	Cr(VI) and Cr(III)	85.83	Well-explained the interactions involved in the adsorption process Adsorption isotherm was studied to determine R_L value for the adsorption of Cr(VI)	Krishna Kumar et al. (2015)
1-Butyl-3-methylimidazoliumHexafluorophosphate [$Bmim^+$][PF_6^-]	Cs^+	1.6	Equilibrium data were best fitted with Langmuir adsorption isotherm and kinetics was controlled by pseudo-second-order reaction	Lupa et al. (2015)
Trihexyl(tetradecyl)phosphonium chloride (Cyphos IL 101), 1-octyl-3-methylimidazolium tetrafluoroborate [C_8MIM][BF_4], 1-butyl-3-methylimidazolium hexafluorophosphate [$bmim^+$][PF_6^-]	TI(I)	4.48	Ultrasonication method was used for adsorption process Equilibrium, kinetic and thermodynamic data were applied for the determination of adsorbent efficiency	Lupa et al. (2015)

Table 4 (continued)

Ionic liquid used	Metal ion extracted	Maximum adsorption capacity (mg/g)	Remarks	Paper
Aliquat-336	Pd(II)	187.6	Charge interaction and ion pair mechanism played an important role in the adsorption process Through the negative values of enthalpy, entropy, and free energy changes, the Pd(II) adsorption was exothermic and spontaneous in nature	Kumar et al. (2015)
1-methyl-3-(((3aS,5S,5aR,8aR,8bS)-2,2,7,7-tetramethyltetrahydro-3aHbis([1,3]dioxolo)[4,5-b:4′,5′-d]pyran-5-yl)methyl)-1H-imidazol-3-ium hexafluorophosphate(V)	Pb^{2+}	374.9	Langmuir adsorption isotherm and pseudo-second-order kinetic model were employed to understand the nature of adsorption 0.01 M HCl solution was used as a desorbing agent	Jayachandra et al. (2015)
Tetraoctyl ammonium bromide	Pb(II)	85	Combination of ionic liquids and magnetic composite bio-adsorbent was prepared in the first time for improving the dispersity of the adsorbent and adsorption capacity Langmuir adsorption isotherm was used to describe the equilibrium data	Sun et al. (2016)
Trihexyl(tetradecyl)phosphonium chloride (Cyphos IL 101)	Fe(III)	402	Sorption efficiency was controlled by metal speciation and ionic liquid loading in the Extractant impregnated resin (EIR) Experimental data were well-fitted with pseudo-second-order kinetics and Langmuir isotherm	Navarro et al. (2016)
Trihexyl(tetradecyl)phosphonium chloride (Cyphos IL 101)	TI(I)	0.59	Chemisorption mechanism was proposed to understand the nature of adsorption process Impregnation of the ionic liquid onto organic solid support was prepared through ultrasonication and vacuum drying	Lupa et al. (2017)
1-butyl-3-methylimidazolium chloride[BMIM][Cl]	Cr(VI)	285.7	Maximum adsorption capacity was obtained at the pH of 2 Kinetic data were best fitted with pseudo-second-order model and Langmuir adsorption isotherm	Nasrollahpour and Moradi (2017)
Ethyl hexadecyldimethyl ammonium bromide	Cd^{2+}, Hg^{2+}	Cd^{2+}—341.30 Hg^{2+}—43.43	Desorption was done using ammonium hydroxide solution and the regenerated EHDAIC was reused for 10 cycles Large sample volumes were tested using column extraction process	Shekhawat et al. (2017)
1-hexyl-3-methylimidazolium chloride([Hmim][Cl]), 1-hexyl-3-methylimidazolium bis{(trifluoromethyl)sulfonyl}imide, [$Hmim^+$][NTf_2^-]	Ag^+	–	Reported that there was no evident seen for a direct binding interaction between [Hmim] and silver ions	Beattie et al. (2018)

Table 4 (continued)

Ionic liquid used	Metal ion extracted	Maximum adsorption capacity (mg/g)	Remarks	Paper
3,3′-(hexyl)bis(3-methylimidazolium)bromide chloride([H(mim$_2$)[Br][Cl]), 1-hexyl-3-methylimidazolium chloride,([Hmim][Cl]), 1-octyl-3-mehyliiimidddazolium chloride ([Omim][Cl]),	Cd^{2+}	87.46 and 94.6	Among 3 ILs, [OMIM][Cl] had the highest adsorption capacities for Cd(II) removal Sips adsorption isotherm was the most appropriate fitting model with a high affinity for adsorption	Naderi et al. (2018)
3-Glycidyloxypropyltrimethoxysilane(GMA), Polyethyleneimine (PEI) 1H-pyrazole-1-carboxamidine hydrochloride lithium bis-trifluoromethane sulfonamide (Nft_2)	Au^{+}	120.56	Equilibrium data were well-described by Hill isotherm model Adsorption kinetics was controlled by pseudo-second-order model	Xiong et al. (2018)
1-aminopropyl-3-methylimidazolium nitrate	Cr(VI)	181.1	Ionic liquid functionalized cellulose was prepared through radiation grafting glycidyl methacrylate Adsorption properties were investigated in both batch and column experiments	Dong and Zhao (2018)

(Kumar et al. 2015; Arias et al. 2011; Navarro et al. 2014, 2016), adsorption of Ag^{+} using CYPHOS IL 101-impregnated biopolymer materials (Campos et al. 2008) and adsorption of Cs^{+} using florisil impregnated with CYPHOS IL 101 (Lupa et al. 2013). Only few studies reported in the literature related to pyridinium-based ionic liquids for the adsorption of metal ions from aqueous solutions. Wieszczycka et al. (2020) described the adsorption studies for the removal of Zn(II) from HCl and NaCl solutions using 1-propyl-3-undecanoylpyridinium chloride impregnated amberlite XAD-4. Wieszczycka (2020) studied the Zn (II) sorption from chloride solutions using ILs such as 1-propyl-3-undecanoylpyridinium chloride & 1-propyl-3-undecanoylpyridinium bromide encapsulated polymer sorbent (suspension copolymerization of styrene and divinylbenzene).

Membrane process

The membrane-based separation process is one of the effective methods for selective recovery of solutes from aqueous solution and has the ability to enrich some organic compounds such as amino acids, sugars, and herbicides (Wang et al. 2016). There are number of membranes used, which are supported liquid membranes, polymer inclusion membranes, bulk liquid membranes, and emulsion liquid membranes. Usually, these membranes containing carrier agents are selectively permeable, as it allows the specific solutes from aqueous solution to pass through. In these techniques, the carrier agent passed into the membranes, forms desired solute complexes easily with the host to extract. This process is called facilitated transport. However, it is limited on a large scale due to insufficient lifetime that requires frequent replacements, low stability of membranes, aging, and low selectivity for high fluidities. These effects might be due to the loss of ionic liquids or carrier agent either by evaporation or dissolution of metal ions in retentate (Jean et al. 2018). There is a possible strategy to overcome these difficulties is to improve the stability of the liquid membrane. It can be achieved by optimizing the carrier with the help of an ionic liquid. In this technology, ionic liquids can be stabilized either by infusing it inside the pores of the membrane as a carrier or through quasi-solidification of the ionic liquids to provide the membrane with greater permeability (Wang et al. 2016). They bring several benefits like high conductivity, viscosity, and also adjust the solubility by tuning the anion or cation of ionic liquids for improving the transport properties in carrier applications (Jean et al. 2018). A summary of the removal of heavy metals from aqueous solution/water by membrane separation processes based on ionic liquids in the year 2008–2018 is shown in Table 5.

From Table 5, it can be noted that phosphonium and ammonium-based ionic liquids were used as carriers in the liquid membranes such as polymer inclusion membrane and

supported liquid membrane for metal removal, were broadly described in the literature so far. The most promising ionic liquids used in the separation of heavy metals from aqueous solution are Tricaprylmethylammonium chloride, Trihexyl (tetradecyl)phosphonium chloride and Trihexyl (tetradecyl) phosphonium bis(2,4,4-trimethylpentyl)phosphinate. The reports discuss on the basis of Tricaprylmethylammonium chloride (Aliquat 336) to remove the metals such as Cr^{6+}(Kebiche-Senhadji et al. 2010), Fe^{3+}(Kogelnig et al. 2010; Regel-Rosocka et al. 2012), Cr^{3+} (Joanna Konczyk et al. 2010), Cd^{2+}(Peterson and Nghiem 2010; Sureyya Altin et al. 2011), Pb^{2+}, and Zn^{2+} (Kebiche-Senhadji et al. 2008; Regel-Rosocka et al. 2012), Co^{2+}(Kagaya et al. 2011) from aqueous solutions. Further, based on phosphonium-based ionic liquids such as Trihexyl (tetradecyl) phosphonium chloride and Trihexyl(tetradecyl)Phosphonium bis(2,4,4-trimethylpentyl)phosphinate 104 were used to remove the Pd^{2+}(Regel-Rosocka et al. 2015), Cu^{2+}(Castillo et al. 2014; Pospiech 2015a, b), Zn^{2+} (Baczynska et al. 2016; Mostazo et al. 2017), Cd^{2+} (Pospiech 2015a, 2015b), Fe^{2+} and Fe^{3+} (Baczynska et al. 2016) from aqueous solutions. Imidazolium-based ionic liquids were used in the removal of heavy metals based on membrane process, studied by few investigators. Jean et al. (2018) investigated the separation of Hg^{2+}, Cd^{2+}, and Cr^{3+} ions from acidic media using ionic liquid, isooctylmethylimidazolium bis-2-ethylhexylphosphate and transport across supported liquid membranes.

To overcome the stability problems related with supported liquid membrane, a novel technique used in liquid membrane known as "Pseudo-Emulsion based Hollow Fiber Strip Dispersion (PEHFSD)" is implemented for the extraction of metals from aqueous solution. In PEHFSD method, two tanks are generally used, one for aqueous solution containing metal ions to be extracted and other for pseudo-emulsion (both organic and stripping solutions). These solutions are stirred continuously throughout the experiments in the respective tanks (Alguacil and Lopez 2013). Two gear pumps are used for pumping the two solutions to the membrane through variable flows. The experiment is carried out by passing the aqueous solution through the tube side and pseudo-emulsion through the shell side (outer side) of membranes in a counter-current manner (Carvalho 2019). Thereafter, the organic solution readily wets the hydrophobic micropores, so that the metal ions from the aqueous solutions migrate toward the extractant through it (Wieszczycka et al. 2015). In general, high pressure is applied to the feed phase in order to maintain the interface at the pores. But at the same time, the differential pressure is always kept low to prevent the transportation of metal ions from the pseudo-emulsion to the aqueous phase side through the pores (Alguacil and Lopez 2013). Once the stirring is stopped in the pseudo-emulsion tank, the phase separation (i.e., recovery of metal ions) takes place between the organic and stripping solutions within a minute. The greatest benefits of using this technique are: both extraction and stripping process can be done simultaneously in a single membrane module, low consumption of ionic liquids and energy, large interfacial area for the transfer of mass in a hollow fibers (Chaturabul et al. 2015). Using this technique, Fe(III) was extracted with the efficiency of 82.7% using ionic liquid, RNH_3^+ HSO_4^- (ionic liquid is formed by the reaction of primary amine PRIMENE JMT and sulfuric acid dissolved in n-decane) reported by Alguacil et al. (2010). The same ionic liquid was utilized for the extraction of Cr(III) with 98% extraction efficiency which was studied by Alguacil and Lopez (2013). Furthermore, they reported that the mass transfer rate was controlled by diffusion in the micropores of the hollow fibers in PEHFSD method. Chaturabul et al. (2015) experimentally studied both the extraction and stripping of mercury ions from petroleum produced water using Aliquat 336. The extraction and stripping efficiencies of Hg(II) are 99.73% and 90.11%, respectively. By incorporating this method, Zn(II) was extracted from dilute solutions using synthesized task-specific ionic liquids like 3-[1-(hydroxyimine) undecyl]-1-propyl pyridinium bromide, 3PC10-PrBr and 3-[1-(hydroxyimine) undecyl]-1-propyl pyridinium chloride, 3PC10-PrCl as the carriers which was investigated by Wojciechowska et al. (2018).

Among various membrane separation techniques, the pressure-driven technique has a great capability to separate the solutes from the liquid solution based on the size. Usually, separation of solutes has been attained by applying pressure as a driving force with ionic liquid membrane acting as a semipermeable barrier. They have maximum flux compared with thermal and concentration-based separation processes. Using this technique, Hernández-Fernández et al. (2009) conducted a comparative study in the preparation of supported liquid membrane based on ionic liquids such as $[BMIM^+][Cl^-]$ and $[BMIM^+][BF_4]$ or $[BMIM^+][NTF_2^-]$ as the carriers using both pressure and vacuum-based techniques. It was found that the pressure-driven method contributed the maximum stability and higher amount of ionic liquids were getting immobilized within the respective membranes. Generally, the pertraction process in membrane technology, consisting of one or multiple membranes, occurs in a hollow fiber configuration so as to realize the maximum membrane surface per volume. The ionic liquid (extractant) thus flows down the inner side of hollow fiber and the wastewater containing metal ions is passed onto the outer side of hollow fiber. The pores of the membrane are then filled with extraction product. The metal ions diffuse from the wastewater, through membrane and to the extractant. The extractant can also be easily regenerated and reused. The greatest benefits of using pertraction process over normal extraction are acquiring a much lower quantity of extractant for the removal of pollutants, having high potential to separate the

Table 5 Removal of heavy metals from aqueous solution by membrane separation processes based on ionic liquids with higher extraction efficiency, reported from the year 2008 to 2018

Ionic liquid used	Type of membrane used	Metal ion extracted	Extraction efficiency (%)	Remarks	Paper
Tricaprylmethylammonium chloride (Aliquat 336)	Polymer Inclusion Membranes	Cd^{2+}, Pb^{2+}, Zn^{2+}	91.8	Results obtained was compared with Polymer Inclusion Membranes with D2EHPA Proved that Polymer Inclusion Membranes have a very good stability to transport metal ions even after 12 replicate measurements	Kebiche-Senhadji et al. (2008)
$RNH_3^+ HSO_4^-$	Polymer Emulsion Hollow Fiber Strip Dispersion	Fe^{3+}	82.7%	Mass transfer resistance of feed contributes nearly 17% to the overall resistance Interfacial mass transfer resistances are dominant due to the stripping reactions	Alguacil et al. (2010)
Tricaprylmethylammonium chloride (Aliquat 336)	Polymer Inclusion Membranes	Cr^{6+}	92.3	CTA and three different types of PVC were used as a polymer matrix to prepare Polymer Inclusion Membrane Recovery factor of Cr^{6+} was found at 92% using 0.1 M NaOH solutions	Kebiche-Senhadji et al. (2010)
Trihexyl(tetradecyl)phosphonium chloride (Cyphos IL 101)	Bulk liquid Membrane	Fe^{3+}	80	Transport of Fe(III) through Bulk liquid Membrane followed a non-steady kinetic regime with irreversible first-order rxns Stripping studies was achieved by 0.5 M HCl solutions	Kogelnig et al. (2010)
Tricaprylmethylammonium chloride (Aliquat 336)	Polymer Inclusion Membranes	Cr^{3+}	52	The transport process was controlled by chemical reaction which was predicted by activation energy using Arrhenius plot At pH 1, the % removal for Cr(IV) was more efficient than Cr(III) and vice versa for pH 4	Konczyk et al. (2010)
Tricaprylmethylammonium chloride (Aliquat 336)	Polymer Inclusion Membranes	Cd^{2+}	> 99	Metal selectivity can be controlled by presence of chloride concentration in aqueous solutions De-extraction was highly effective, if the stripping solution was acidic in nature	Peterson and Nghiem (2010)

Table 5 (continued)

Ionic liquid used	Type of membrane used	Metal ion extracted	Extraction efficiency (%)	Remarks	Paper
Trihexyl(tetradecyl)phosphonium chloride (Cyphos IL 101)	Polymer Inclusion Membranes	Zn^{2+}	> 80	Back extraction was successively achieved by 1 M sulfuric acid During pre-equilibration of membranes in water, a significant amount of ionic liquid was lost due to leaching, so that efficiency was decreased	Kogelnig et al. (2011)
Tricaprylmethylammonium chloride (Aliquat 336)	Supported liquid membranes	Cd^{2+}	82	Interface reactions were affected by feed and stripping solutions and the carrier properties EDTA was the best stripping solution to obtain high metal transport efficiency	Altin et al. (2011)
Tricaprylmethylammonium chloride (Aliquat 336)	Polymer Inclusion Membranes	Co^{2+}	–	TBP was used as a modifier and 2-nitro phenyl pentyl ether was used as a plasticizer to prepare Polymer Inclusion Membranes 1 M NH_3 + 1 M TEA were used as a stripping agents to recover metal	Kagaya et al. (2011)
Trihexyl(tetradecyl)phosphonium chloride (Cyphos IL 101) Trihexyl(tetradecyl) phosphonium bis(2,4,4-trimethylpentyl)phosphinate (Cyphos IL 104)	Polymer Inclusion Membranes	Zn^{2+}, Fe^{2+}, Fe^{3+}	100%	Ion exchange and addition mechanism was proposed Sulfuric acid was used as a stripping agent	Regel-Rosocka et al. (2012)
Methyltrioctylammonium chloride[$MTOA^+$][Cl^-]	Supported liquid membranes	Zn^{2+}, Cu^{2+},Cd^{2+}, Fe^{3+}	–	Pertraction method was used for the removal process Sodium carbonate was used as a stripping agent	Ríos et al. (2013)
RNH_3^+ HSO_4^-	Polymer Emulsion Hollow Fiber Strip Dispersion	Cr^{3+}	98%	The ionic liquid was formed by the reaction of the primary amine PRIMENE JMT and sulfuric acid dissolved in n-decane The mass transfer rate was controlled by the diffusion in the micropores of membrane module	Alguacil and Lopez (2013)

Table 5 (continued)

Ionic liquid used	Type of membrane used	Metal ion extracted	Extraction efficiency (%)	Remarks	Paper
Trihexyl(tetradecyl) phosphonium bis(2,4,4-trimethylpentyl)phosphinate (Cyphos IL 104), Tricaprylmethylammonium chloride (Aliquat 336), Trihexyl(tetradecyl)phosphonium chloride (Cyphos IL 101) Tributyl (tetradecyl) phosphonium chloride (Cyphos IL 3453)	Supported liquid membranes	Cu^{2+}	95	Liquid mining waste was treated under this procedure for Cu(II) extraction Fouling problem occurred at the membrane during stripping process after 4 Hrs of extraction process	Castillo et al. (2014)
Trihexyl(tetradecyl)phosphonium chloride (Cyphos IL101) Trihexyl(tetradecyl)phosphonium bromide(Cyphos IL 102) Trihexyl(tetradecyl) phosphonium bis(2,4,4-trimethylpentyl)phosphinate (Cyphos IL 104)	Polymer Inclusion Membranes	Pd^{2+}	84–90	Extraction Efficiency depends on the type of receiving phase Recovery factors of Pd(II) was found at < 60% using 0.5 M NH_4OH as a stripping agent	Regel-Rosocka et al. (2015)
Trihexyl(tetradecyl)phosphonium chloride (Cyphos IL 101) Trihexyl(tetradecyl) phosphonium bis(2,4,4-trimethylpentyl)phosphinate (Cyphos IL 104)	Polymer inclusion membranes	Cd^{2+}, Cu^{2+}	Cd^{2+}—99.9 Cu^{2+}—90.1	Selectivity of metal transport decreased with increasing the chloride concentration in neutral media	Pospiech (2015a, b)
Trihexyl(tetradecyl) phosphonium bis(2,4,4-trimethylpentyl)phosphinate (Cyphos IL 104)	Polymer inclusion membranes77	Cd^{2+}	99	CTA with CYPHOS IL 104 as carrier were used for Cd(II) removal from HCl and NaCl solutions, respectively The experimental results obtained were compared with conventional liquid liquid equilibrium data	Pospiech (2015a, b)
Tricaprylmethylammonium chloride (Aliquat 336)	Polymer Emulsion Hollow Fiber Strip Dispersion	Hg^{2+}	99.73%	Mathematical model was developed based on the combined flux (convection–diffusion-kinetic) principle The predicted results was in good agreement with experimental results with an average deviation of extraction was 1.5%	Chaturabul et al. (2015)

Table 5 (continued)

Ionic liquid used	Type of membrane used	Metal ion extracted	Extraction efficiency (%)	Remarks	Paper
Trihexyl(tetradecyl)phosphonium chloride (Cyphos IL 101), Trihexyl(tetradecyl) phosphonium bis(2,4,4-trimethylpentyl)phosphinate (Cyphos IL 104), Tributyl(tetradecyl) phosphonium chloride (Cyphos IL 167)	Polymer Inclusion Membranes and Supported liquid membranes	Zn^{2+}, Fe^{2+}, Fe^{3+}	Fe^{2+}—> 40 Zn^{2+} and Fe^{3+}-60–100	Zn(II) and Fe(III) were effectively transported through both Polymer inclusion membranes and Supported liquid membranes but not Fe(II) Separation effectiveness was increased in the following order for Zn(II) in Polymer Inclusion Membranes. CYPHOS IL104 < CYPHOS IL 101 < CYPHOS 167	Baczynska et al. (2016)
Trihexyl(tetradecyl) phosphonium bis(2,4,4-trimethylpentyl)phosphinate (Cyphos IL 104)	Polymer inclusion membranes	Zn^{2+}	–	Polymer Inclusion Membranes containing either D2EHPA (or) CYPHOS IL 104 have higher diffusional fluxes for Zn(II) ion in aqueous solutions than macrocycle Kryptofix 22DD	Mostazo et al. (2017)
Isooctylimidazolium bis-2-ethylhexylphosphate (omim D2EHP)	Supported liquid membranes	Cd^{2+}, Cr^{3+},Hg^{2+}	Cd^{2+}—35 Cr^{3+}—24 Hg^{2+}—31	Reported that absolute hardness and carrier solute complex stability are driving forces in the facilitated extraction process Mobile-site jumping extraction mechanism was studied by determining the stability constant and diffusion coefficient	Jean et al. (2018)
3-[1-(hydroxyimine) undecyl]-1-propyl pyridinium bromide (PC10-PrBr) 3-[1-(hydroxyimine) undecyl]-1-propyl pyridinium chloride (3PC10-PrCl)	Polymer Emulsion Hollow Fiber Strip Dispersion	Zn^{2+}	90–96%	Compared with 3PC10-PrCl, PC10-PrBr gave the better extraction results Recovery of Zn(II) was 70–80% during stripping solutions	Wojciechowska et al. (2018)

extractant and requiring lesser time. Installations are also very compact and consume little energy. This process was utilized by de los Ríos et al. (2013) for the selective extraction of iron, zinc, cadmium, and copper from aqueous solution using methyltrioctylammonium chloride as a carrier in supported liquid membrane. Hydrometallurgical process was studied by Pospiech (2015a, b) to extract Cadmium ion using Cyphos IL 104 as carrier and extractant from acidic and neutral chloride solutions across polymer inclusion membrane.

There are only a few papers exist which describe the extraction of metals using bulk liquid membrane containing ionic liquids as a carrier. Daniel Kogelnig et al. 2010 reported the separation of Fe(III) and Ni(II) from 6 M hydrochloride solution using trihexyl(tetradecyl)phosphonium chloride (Cyphos IL-101) as a carrier for liquid–liquid extraction and transport across bulk liquid Membrane. From the reports, it was concluded that the phosphonium-based ionic liquids were mostly handled as a carrier in both supported liquid membrane and polymer inclusion membrane for the removal of metals due to its unique dissolution ability, thermal and chemical stability. Therefore, phosphonium-based ionic liquids are highly recommended in the membrane process for getting the better results.

Conclusion

A number of reviews conducted earlier focused on various features of ionic liquids, whereas the current review is aimed at discussing the pollution, negative impacts to living organisms, and treatment technologies used for removal of heavy metals using ionic liquids. Also, the coordination bond between ionic liquids and metal ions present in the aqueous solution were discussed. Their purpose is to removal the heavy metals with ease from their sources to ensure the environmental sustainability as well as safeguard the living organisms. The extraordinary properties of ionic liquids make it an appropriate alternative for conventional solvents in separation technologies such as liquid–liquid extraction, adsorption, and membrane separation processes. By using this designer solvent in both technologies, one could achieve higher removal efficiency and possible recovery and reusability of ionic liquids which makes this process a cost-effective one in the separation of metal species from liquid media. To conclude, it can be said that the ionic liquids can be applied not only the removal of heavy metals but also other pollutants present in wastewater. In line with the green chemistry principles, ionic liquids provides a maximum support to create a cleaner and greener environment.

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Compliance with ethical standards

Conflict of interest There is no conflict of interest regarding this publication.

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