Ionic liquids (ILs) are molten salts with melting point close to or below room temperature and are entirely composed of ions. Properties of ILs can be modified by varying alkyl chain length or by changing cations/anions. ILs possess unusual properties; the most striking property is their negligible vapor pressure. Nowadays, presence of colored dyes, heavy metals and organic contaminants in water is a major issue of concern. Increasing level of these contaminants encouraged the researchers to develop eco-friendly methods for removal of these contaminants from water. Present review focuses on applications of ILs in environmental remediation. We have presented an overview of extraction of water contaminants such as dyes, heavy metals and organic compounds. Use of ILs for extraction process of these contaminants is an excellent method over conventional methods, especially from environment point of view. One can recycle ILs after their use in extraction processes by using specific solvent.
INTRODUCTION

In recent years interest in Ionic liquids (ILs) have steadily grown due to their remarkable characteristics such as (1) non-measurable vapor pressure, which means they do not produce atmospheric volatile organic compounds (VOCs) and can be used in low-pressure (vacuum) environments; (2) nonflammability, hence are safer to use; (3) good solvents for a wide variety of organic, inorganic and organometallic compounds; (4) broad liquid temperature range; (5) high ionic conductivity; (6) moderate to high viscosity; (7) hampered self-diffusion; (8) thermal and chemical stability; (9) large electrochemical window (10) possibility of recycling (11) low nucleophilicity and capability of providing weekly coordinating or non-coordinating environment. These characteristics render them promising replacements for VOCs, which are a source of environmental problems, that provides the possibility for clean manufacturing in chemical industry[1-3]. Another important feature of ILs is their designability: miscibility with water or organic solvents can be tuned through side chain lengths on the cation and choice of anion. Because of their properties, ILs attract great attention in number of applications[4-20] (scheme 1). In addition, their non-volatility results in low impact on the environment and human health, and they are recognized as solvents for "green chemistry". To date, there is a significant number of high-class reviews on room temperature ionic liquid (RTIL) research activities, from the early ones that generally focused on catalysis,[21-29] to current detailed descriptions of characteristics and thermodynamic properties,[30-32] solvent properties,[33] review on greenness of ILs[34] and specified applications such as in analytical chemistry,[35,36] coordination chemistry,[37] fluorine chemistry,[38] polymer materials[39] and nanotechnology,[14] electrochemical sensing systems,[40,41] dissolution of cellulose with ionic liquids,[19] supercritical fluid applications[42] and in the chemical industry[43]. All these reviews contribute largely to the rapid rise and incentive of research interest on RTILs. In the proposed review we have made an attempt to compile the environment related applications of ILs mainly use of these solvents in environmental remediation, specifically removal of water contaminants, i.e. dyes, heavy metals and organic entities such as phenols etc.

Scheme 1. Applications of ionic liquids in various fields

![Scheme 1. Applications of ionic liquids in various fields](Image)
EXTRACTION OF WATER CONTAMINANTS: Water contaminants such as dyes, heavy metals and phenols are significant pollutants, causing environmental and health problems to human beings and aquatic animals [44-46]. There are number of conventional ways [47-49] for the removal of these contaminants from water. But there is a need to develop environment friendly and economic method for the extraction process. Recently, ILs are being used for extraction of water contaminants [50].

Extraction of dyes from aqueous solutions. One of the main classes of the pollutants is dyes. Once dyes enter in the water, then it becomes difficult to treat as these have a complex molecular structure and synthetic origin that makes them more stable and harder to be biodegraded [51]. Wastewaters from industries like textile, dying, printing, cosmetics, food coloring, papermaking, etc. are the major contributors of colored effluents [52]. However, textile industries consume large amount of water and different types of dyes imparting color to effluents. The dyes and colors are toxic and major pollutant, causing environmental and health problems to human beings and aquatic animals [53,54]. Hence, in order to avoid these issues due to the discharge of these dyes into the ecosystem, there is a need to eradicate the residual dyes from the large volume of aqueous effluent. ILs are found to be best extractant for the extraction of dyes from their aqueous solutions. The main findings of literature showing removal of dyes using various ILs are summarized in Table 1. Vijayaraghavan et al [55] studied the extraction and recovery of commonly used azo dyes namely Navy 5RE, an acid blue dye (1-[4-(3-phenylsulfonic acid)azo-1-naphthylazo]-4-anilino naphthene-5-sulfonic acid, disodium salt) and acid red dye (1-[2-tolyl-4-(2-tolylazo)-azo]-2-hydroxy-3,6-disulfonic acid, disodium salt) using neutral hydrophobic IL, 1-butyl-1-methylpyrrolidinum bis(trifluoromethylsulfonyl)imide [p14][tf2N], with an extraction efficiency of 98% to provide a method for controlling pollution of waste-waters. On the addition of IL to the dyes, decrease in concentration of dyes in aqueous phase w.r.t the time have been observed and for determining the separation of dyes in IL, UV–vis spectroscopy have been used.

<table>
<thead>
<tr>
<th>Dyes</th>
<th>ILs</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid blue Dye, Acid Red Dye</td>
<td>[p14][tf2N]</td>
<td>[55]</td>
</tr>
<tr>
<td>Methyl Orange, Orange G, Eosin Yellow</td>
<td>[Cn+mim][PF6], n=4,6,8, [Cn+mim][BF4]</td>
<td>[56]</td>
</tr>
<tr>
<td>AO, MB, NB, SO, NR, PC</td>
<td>[Cn+mim][PF6], [Cn+mim][Br], [Cn+mim][BF4], [Cn+mim][Tf2N]</td>
<td>[57]</td>
</tr>
<tr>
<td>CR</td>
<td>[Cn+mim][Tf2N]</td>
<td>[58]</td>
</tr>
<tr>
<td>Acid Yellow RN, Reactive Yellow M-5R,</td>
<td>[Cn+mim][PF6]</td>
<td>[59]</td>
</tr>
<tr>
<td>Reactive Black KN-G2RC, Weak Acid Blue</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Brilliant Blue RAW</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acid Brilliant Red B, Acid Yellow RN</td>
<td>[Cn+mim][PF6]</td>
<td>[60]</td>
</tr>
<tr>
<td>Sudan I, PAN, PAR, MR, NPAR</td>
<td>[Cn+mim][PF6], n=4,6,8 [Cn+mim][BF4], [Cn+mim][BF4]</td>
<td>[61]</td>
</tr>
<tr>
<td>Thymol blue</td>
<td>[Cn+mim][PF6], n=4,6,8,10</td>
<td>[62]</td>
</tr>
<tr>
<td>MO, MB</td>
<td>[N1888][SCN], [N1888][DCA], [N1888][BA], [N1888][Hex]</td>
<td>[63]</td>
</tr>
</tbody>
</table>
To check selectivity of the method, the dyes from real tanning effluent dye samples have also extracted using this IL. The results show that for the effluent sample, in the first extraction, 26% of the red dye have been extracted and after subsequent extractions (four times) with fresh IL, almost 98% of extraction can be reached using [p14][tf2N], in spite of the presence of other components. Also, the IL used for the extraction of dyes form water, has been separated from dye by washing the IL/dye extracts, with a mixture of iso-propyl alcohol and water (1:1 by volume), therefore, separated IL can be reused. In this study, authors have suggested that the hydrophobicity of the IL plays an important role in the extraction process.

In a study[56], imidazolium based ILs; 1-butyl-3-methylimidazolium hexafluorophosphate ([C₄mim][PF₆]), 1-hexyl-3-methylimidazolium hexafluorophosphate ([C₆mim][PF₆]), 1-hexyl-3-methylimidazolium tetrafluoroborate ([C₆mim][BF₄]) and 1-octyl-3-methylimidazolium hexafluorophosphate ([C₈mim][PF₆]) have been used for the removal of anionic dyes; methyl orange, eosin yellow, and orange G from their aqueous solutions. The results show that the phase volume ratio has no noticeable impact on the extraction efficiency of these dyes but pH of aqueous phase has a significant effect on the extraction efficiencies of dyes. In case of hydrophobic ILs, with increase in the hydrophobicity of IL, extraction efficiency of dyes increases. Furthermore, the effect of temperature has also been studied, which confirmed that the increase in temperature leads to increase in extraction efficiency of dyes. Also, in this report, it has been assumed that in the extraction process, the dye transfers from the aqueous phase to IL. So, Gibbs energy $\Delta G_T^0$, enthalpy $\Delta H_T^0$, and entropy $\Delta S_T^0$ for this transfer has been calculated and it was found that all values of $\Delta G_T^0$ are negative, whereas, for both $\Delta H_T^0$ and $\Delta S_T^0$ all values are positive. This thermodynamic data indicated that, extraction process is spontaneous and hydrophobic interactions are responsible for the extraction of dyes using IL. To check the selectivity of extraction process, the partition coefficient of methyl orange have been estimated in the presence of KCl, which was found to be enhanced. Form this study, it has been concluded that, for the studied water samples under the optimized pH conditions, extraction efficiencies of methyl orange, eosin yellows and orange G are found to be 85-99%, ~ 100% and 69% respectively.

Ali et al.[57] have demonstrated that ILs; 1-butyl-3-methylimidazolium hexafluorophosphate (bmimPF₆), 1-butyl-3-methylimidazolium tetrafluoroborate (bmimBF₄), 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)trifluoromethylsulfonyl) imide (bmimTf₂N), and 1-hexyl-3-methylimidazolium bromide (hmimBr) are perfect solvents in extracting cationic dyes from their aqueous solutions. In their work, acridine orange (AO), methylene blue (MB), nile blue A (NB), safranine O (SO), neutral red (NR), pinacyanol chloride (PC) dyes have extracted using ILs. The results show that the addition of ~1.7 wt% (~0.06 M) of used ILs to 1.5 mM of aqueous dye solutions resulted in almost complete removal these dyes (figure 1(a)). The identity of the precipitated dyes, ¹H NMR spectra as well as UV-Vis molecular absorbance spectra (figure 1 (b)) of the extracted solid dyes compared with the dyes from the stock, which are found to be identical. Also the authors suggested that the hydrophobicity of the IL does not play any role in deciding the efficiency of the dye precipitation process, as bmimBF₄ is hydrophilic in nature while the other ILs are hydrophobic and the precipitation efficiency of the all the six studied dyes with all the four ILs is almost comparable.
Gharehbaghi et al.\textsuperscript{[58]} have reported an IL-based dispersive liquid–liquid extraction (IL-DLLE) method to extract an azo dye, Congo Red (CR) [1-naphthalene sulfonic acid, 3,30-(4,40-biphenylenebis) bis(4-amino-)disodium salt] from their aqueous solutions. Firstly, authors studied the effect of cation and anion of IL on the extraction efficiencies of CR. It has been concluded that keeping the anion same and increasing the length of alkyl substituent on the cation of ILs, partition coefficients of CR in the ILs/aqueous systems increases, which follows the order:

\[
\frac{P_{[\text{Emim}][\text{Tf}_2\text{N}]/W}}{P_{[\text{Hmim}][\text{Tf}_2\text{N}]/W}} < \frac{P_{[\text{Hmim}][\text{BF}_4]/W}}{P_{[\text{Hmim}][\text{Tf}_2\text{N}]/W}}
\]

From these results, authors have concluded that, [Hmim] can be the best cation for the extraction process. Whereas, by keeping the cation same and changing the anion, partition coefficients of CR in the ILs/aqueous systems follows the order:

\[
\frac{P_{[\text{Hmim}][\text{BF}_4]/W}}{P_{[\text{Hmim}][\text{BF}_4]/W}} < \frac{P_{[\text{Hmim}][\text{Tf}_2\text{N}]/W}}{P_{[\text{Hmim}][\text{Tf}_2\text{N}]/W}}
\]

These results show that [Hmim][Tf\text{N}] has the best extraction efficiency of CR, hence this IL has been selected for the extraction process. Results indicate that at pH of 5.0, [Hmim][Tf\text{N}] showed the maximum removal of CR. A quantitative extraction $>$95\%, of the dye could be attained by using 90–400 mg/10 mL of IL for the initial concentrations of CR in the range of 40–250 mgL$^{-1}$. It has suggested that, out of two studied dispersant, ethanol and acetone, acetone can be selected as better dispersant due to its better miscibility with the IL. The selectivity of the method has been tested by using NaNO$_3$ along with the dye sample, and it has been found that extraction efficiency slightly increases in the presence of NaNO$_3$. The schematic view of IL-DLLE experimental setup is given in scheme 2. The used IL has also been recovered by applying a reverse dispersive liquid–liquid extraction using acidic stripping solutions, as according to their results, in acidic media, CR prefers the aqueous phase than the IL phase.
Li et al.\textsuperscript{[59]} have explored the liquid–liquid extraction (LLE) of acid dyes and reactive dyes from water solution by using hydrophobic IL, [BMIM][PF\textsubscript{6}] as an extraction phase. The effects of extraction phase ratio, pH of the aqueous phase, and concentration of dicyclohexyl-18-crown-6 (DCH-18C6) in the organic phase have been studied. Authors have concluded that acid dyes can be extracted quantitatively by using [BMIM][PF\textsubscript{6}] whereas the removal of reactive dyes is low (approx. 5.4–31.5\%) by using IL only. The removal of reactive dyes has been enhanced approximately up to 82\% by the addition of DCH-18C6. The pH value has a great impact on the removal of both the acid as well as reactive dye. It has been suggested that for the acid dyes anion-exchange method is responsible for the extraction process and the soluble part of the [BMIM][PF\textsubscript{6}] plays an important role as counter-ions. For the reactive dyes the formation of hydrogen bonds between the dyes and DCH-18C6 increase the removal efficiency. In another study, LLE of azo dyes; Acid Yellow RN and Acid Brilliant Red B by using hydrophobic IL; [BMIM][PF\textsubscript{6}] as an extraction phase have also reported.\textsuperscript{[60]} The effects of extraction phase ratio, pH of the aqueous phase, concentration of salt have been assured. Results demonstrated that acid dyes can be quantitatively extracted with [BMIM][PF\textsubscript{6}], however, the mechanisms of the extraction process depends upon the charge on the structure of dye molecules. In case of acid yellow RN, the anion-exchange extraction process is accountable for the extraction where as for the Acid Brilliant Red B, the ion-pair process is responsible.

Fan and co-workers\textsuperscript{[61]} have examined the extraction of azo dyes; 1-(phenylazo)-2-naphthol (Sudan I), 1-(2-pyridylazo)-2-naphthol (PAN), 4-(nitrophenylazo) resorcinol (NPAR), 4-(2-pyridylazo) resorcinol (PAR), and 2-(4-dimethylaminophenylazo) benzoic acid (methyl red, MR) by using RTILs; [C\textsubscript{4}mim][PF\textsubscript{6}], [C\textsubscript{6}mim][PF\textsubscript{6}], [C\textsubscript{8}mim][PF\textsubscript{6}], [C\textsubscript{6}mim][BF\textsubscript{4}] and [C\textsubscript{8}mim][BF\textsubscript{4}] from their aqueous solutions. The extraction process has determined by means of UV-vis spectrophotometry at 25°C. The factors which affect the extraction process such as extraction time, phase volume ratios, pH of water phase, chemical structure of the ILs, have been studied. The results suggested that the IL/water distribution ratios (D) of the azo dyes increases generally with increasing alkyl chain length of the ILs, and the extraction efficiency the ILs with [BF\textsubscript{4}] anion was much higher than those with [PF\textsubscript{6}] and these D values are remarkably
influenced by the water phase pH. The interactions between ILs and dyes are complex in aqueous media. Authors have concluded that the hydrophobic interaction was the main driving force for the extraction of the molecular form of the dyes, whereas electrostatic interactions were the main driving force for the extraction of cationic or anionic forms of the dyes from aqueous solutions. An ion-exchange mechanism has been suggested for the ILs based extraction of the azo dyes at extreme pH conditions. Visser and coworkers\cite{62} have explored the pH-dependent partitioning of an indicator dye, thymol blue using a series of hydrophobic ILs; 1-alkyl-3-methylimidazolium hexafluorophosphates ([Cₙmim][PF₆]), n = 4, 6, 8 and 10. Figure 2 illustrates the qualitative partitioning of thymol blue in its three forms between aqueous (top) and [bmim][PF₆] (bottom) phases, as aqueous phase pH is changed from very acidic to very basic. The results demonstrate that in acidic medium, thymol blue exists in its red form as a neutral zwitterion which prefers the RTIL phase and in basic medium thymol blue exists in its blue form and partitions quantitatively to the aqueous phase.

\textbf{Figure 2. The phase preference of the three forms of thymol blue in [bmim][PF₆]}

Chen et al.\cite{63} have extracted methyl orange (anionic dye) and methylene blue (cationic dye) from water using non-fluorine hydrophobic quaternary ammonium-based ILs, i.e., tricaprylmethylammonium thiocyanate ([N\textsubscript{1888}][SCN]), tricaprylmethylammonium dicyanoamide ([N\textsubscript{1888}][DCA]), tricaprylmethylammonium benzoate ([N\textsubscript{1888}][BA]), and tricaprylmethylammonium hexanoate ([N\textsubscript{1888}][Hex]). Various factors which affect the extraction efficiency including extraction time, temperature, salt effect, and pH have been investigated. Results suggested that with the increase in temperature extraction efficiencies of methyl orange increases whereas, of methylene blue decreases with all the four ILs. Also, pH has a significant effect on the extraction efficiency of methyl orange, in contrast to this, no significant effect was found on the extraction efficiency of methylene blue. Out of four used ILs, [N\textsubscript{1888}][SCN] exhibited best ability for extracting both of the dyes with extraction efficiencies of 89.09% and 64.14% for methyl orange and methylene blue, respectively. It has also been shown that extraction efficiencies can be improved by adding NaCl in the extraction system, except for extraction of methyl orange with [N\textsubscript{1888}][SCN].

\textbf{Extraction of heavy metals from aqueous solutions.} Most of the industrial manufacturing
processes produce wastewater containing heavy metals. The improper treatment of this wastewater prior to discharge is found to be detrimental for environment, human and aquatic species\[64-66\]. Hence, efficient removal of toxic metals from wastewater is an important matter. Hydrophobic ILs can be used as an extractant in order to remove metal ions from the aqueous phase, as they form complexes with the metal ions and hence increase the hydrophobicity of metal. Table 2 gives the literature showing metal ions removal from waste water using ILs. A hydrophobic RTIL, \([\text{Camim}]\text{PF}_6\) have been used for the mercury preconcentration and determination in different water samples by Martinis et al.\[67\]. Hg has been extracted quantitatively from Hg-2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (Hg-5-Br-PADAP) complex using \([\text{C}_4\text{mim}]\text{PF}_6\) via LLE procedure. The back extraction of analyte from RTIL has also been achieved by using hydrochloric acid. The heavy alkali metal ions (Ag\(^+\) and Pb\(^{2+}\)) extraction form aqueous solution have carried out with 1-alkyl-3-ethylimidazolium hexafluorophosphates and bis\{trifluoromethyl)sulfonyl\}imidates by Dománska and Rękawek.\[68\] Results reveal that the increase in hydrophobic character of IL leads to higher extraction efficiency of these metal ions. In contrast to this, the increase in alkyl chain length of IL from ethyl to hexyl decreases the extraction efficiency. It has been concluded that 1-ethyl-3-ethylimidazolium bis\{trifluoromethyl)sulfonyl\}imide, having a highest hydrophobic character among the other IL used, shows maximum extraction efficiency. Copper, mercury, silver, and palladium ions have been selectively extracted from water\[69\] using hydrophobic ILs containing cations 1-octyl-4-methylpyridinium, 1-methyl-1-octylpyrroldinium, or 1-methyl-1-octylpiperidinium and anions tetrafluoroborate, trifluoromethyl sulfonate, or nonafluorobutyl sulfonate. It has been concluded that mercury ions can be efficiently extracted by using IL containing pyridinium cation. For the selective extraction of metal ions, a disulfide functional group, show an efficient and selective extraction for mercury and copper ions, while silver and palladium metal ions have been efficiently and selectively extracted by a nitrile functional group. Other than the above-mentioned metal ions, the radioactive metal, uranium has also been extracted from water using hydrophobic ILs; tricapryl-methylammonium methionate, \([\text{A336}]\text{[Met]}\), tricapryl methylammonium thiocyanate, \([\text{A336}]\text{[SCN]}\) and tricapryl methylammonium thiosalicylate, \([\text{A336}]\text{[TS]}\)\[70\]. The results show that from 10 µL artificial uranyl nitrate solution containing 36 µg of uranium, almost complete extraction of uranium can be achieved with 200 mg of \([\text{A336}]\text{[TS]}\) and \([\text{A336}]\text{[SCN]}\). Where as, with the \([\text{A336}]\text{[Met]}\), for the significant uranium extraction, a higher content of IL is needed. The selectivity of the method have been checked out by using natural water sample, for which \([\text{A336}]\text{[SCN]}\) shows a poor extraction efficiency. It has been concluded that \([\text{A336}]\text{[TS]}\), proves to be best extractant for uranium from natural water samples containing calcium as well as magnesium along with uranium. The extracted uranium can also be separated form IL by using 2 M HNO\(_3\) solution. Fischer et al.\[71\] have applied liquid-liquid extraction (LLE) method for the removal of metaloids; Ag, As, Cd, Cr, Cu, Hg, Ni, Pb, Pt, Sn, Zn and the cancerostatic platinum compounds cisplatin and carboplatin form sewage waste water using ILs. For this process quaternary ammonium and phosphonium cations based and thiol-, thioether-, hydroxyl-, carboxylate- and thiocyanate functionalized anions based ILs have been used.
Table 2. Literature showing the metal ion removal using ILs

<table>
<thead>
<tr>
<th>Metal ions</th>
<th>ILs</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hg²⁺</td>
<td>[C₄mim][PF₆], [4MOPYR][BF₄], [4MOPYR][TfO], [4MOPYR][NfO], [C₄mim][PF₆], n=4,8,12</td>
<td>[67]</td>
</tr>
<tr>
<td>²³⁰U</td>
<td>[A336][TS]</td>
<td>[70]</td>
</tr>
<tr>
<td>Ag, Cu, Hg and Pt</td>
<td>[A336][TS], [A336][MTBA], [A336][SCN], [PR₄][TS], [PR₄][MTBA]</td>
<td>[71]</td>
</tr>
<tr>
<td>Zn</td>
<td>[A336][SCN], [HPy][PF₆]</td>
<td>[71], [73]</td>
</tr>
<tr>
<td>Ag⁺, Pb²⁺</td>
<td>[EEIM][NTf₂], [BEIM][NTf₂], [HEIM][NTf₂], [BEIM][PF₆], [HEIM][PF₆]</td>
<td>[68]</td>
</tr>
<tr>
<td>Cd</td>
<td>[A336][TS]</td>
<td>[74]</td>
</tr>
<tr>
<td>Ag, Pd, Au</td>
<td>[MPS•PYRRO][Tf₂N]⁺, [MPS•PIP][Tf₂N]⁺, [MBCNPYRRO][Tf₂N]⁺, [4MBCNPyR][Tf₂N]⁻</td>
<td>[75]</td>
</tr>
</tbody>
</table>

It has been suggested that by using tricaprylmethylammonium thiosalicylate, [A336][TS], tricaprylmethylammonium 2- (methylthio) benzoate, [A336][MTBA], trihexyl(tetradecyl) phosphonium thiosalicylate, [PR₄][TS] and trihexyl(tetradecyl) phosphonium 2- (methylthio) benzoate, [PR₄][MTBA] ILs, 95% extraction efficiency can be achieved for Ag, Cu, Hg and Pt, whereas, for other metals, extraction is low with all these ILs. However, [PR₄][TS] IL and [A336][SCN] show high extraction efficiencies for monoaquacisplatin and Zn contamination.

Germani et al.[72] have investigated hydrophobic ILs [C₄mim][PF₆], n=4,8,12 as extracting agents for mercury from aqueous solutions. Their results indicate that the alkyl chain length and the hydrophilic features of the whole system affect the metal ion association and the extraction process. In another study,[73] liquid-liquid based microextraction method have been used for the preconcentration of zinc in water and milk samples with hydrophobic IL; 1-hexylpyridinium hexafluorophosphate. Kogelnig et al.[74] have described almost complete (>99.9%) extraction of cadmium by using [A336][TS] from a natural river matrix. They have also performed the extraction process with tricaprylmethylammonium benzoate, [A336][BA] and tricaprylmethylammonium hexanoate, [A336][Hex]. But the maximum removal have been shown by [A336][TS] only.Lee[75] has used ILs containing pyridinium, pyrrolidinium and piperidinium cations with anion bis(trifluoromethylsulfonyl)imid in the extraction of silver, palladium, or gold metal ions from water at room temperature. Results conclude that for silver or palladium ions extraction, a disulfide or nitrile group containing IL exhibit good extraction efficiency. Gold ions are efficiently and selectively extracted with these ILs.

**Extraction of other organic contaminants form aqueous solutions.**

Phenolic compounds produced by various industries[76,77] are pollutants of major concern, because of extensive use, high toxicity and potential accumulation in the environment.[78] Therefore, it is vital to remove these compounds from water, prior to the release of water into the environment. Literature showing extraction of organic compounds from waste water using ILs is collected in table 3. Deng et al.[79] made an attempt to extract these compounds from aqueous solution using an hydrophobic magnetic room temperature ionic liquid, trihexyltetradecylphosphonium tetrachloroferrate (III)).
Table 3. Extraction of organic components form water using ILs.

<table>
<thead>
<tr>
<th>Organic component</th>
<th>ILs</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenols</td>
<td>[3][C4PCl4][FeCl4]</td>
<td>[79]</td>
</tr>
<tr>
<td>Phenol, Tyrosol, p-hydroxybenzoic acid</td>
<td>[C6mim][BF4], [C8mim][BF4] (n=6, 8, 10)</td>
<td>[80]</td>
</tr>
<tr>
<td>Phenol, o-cresol, hydroquinone, 2-nitrophenol</td>
<td>[C8mim][BF4]</td>
<td>[81]</td>
</tr>
<tr>
<td>Butanol</td>
<td>[OIm][TEIM]</td>
<td>[82]</td>
</tr>
<tr>
<td>PAHs</td>
<td>[C6mim][PF6]</td>
<td>[83]</td>
</tr>
<tr>
<td>1,3-propanediol</td>
<td>[Im4,1][CF3SO3], [Im4,1][N(CN)2]−, [Im4,1][SCN], [Im4,1][CH3SO3], [Mo6,1][CF3SO3], [Pl4,1][CF3SO3], [Im2,1][CF3SO3]−, [Im201,1][CF3SO3]−</td>
<td>[84]</td>
</tr>
<tr>
<td>Amino acids</td>
<td>[C8mim][PF6], [C8mim][PF6], [C8mim][BF4], [C8mim][BF4]</td>
<td>[85]</td>
</tr>
<tr>
<td>Caprolactam</td>
<td>[C6mim][PF6]; (n = 4, 6, 8), [C8mim][BF4], [C8mim][NTf2], [86]</td>
<td></td>
</tr>
</tbody>
</table>

Vidal et al.[80] investigated LLE of phenol, tyrosol, and p-hydroxybenzoic acid using [C6mim][BF4] and [C8mim][BF4] (n=6, 8, 10). Results reveal that, [C6mim][BF4] shows almost double extraction efficiency than [C8mim][PF6].

Wan et al.[81] have studied the extraction of phenolic compounds; phenol, o-cresol, hydroquinone and 2-nitrophenol using 1-octyl-3-methylimidazolium tetrafluoroborate ([C8mim][BF4]). The results demonstrate that with increasing extraction temperature or decreasing the volume ratio of [C8mim][BF4] to aqueous, the distribution coefficient decreases gradually.

Ha et al.[82] have studied the recovery of butanol from aqueous solutions with imidazolium ILs by LLE method. The results confirm that hydrophobicity of IL plays an important role in the extraction of butanol. Among the other ILs used, hydrophobic IL, 1-octyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide shows a maximum extraction efficiency (74%) at 323.15 K. Similarly, in a study,[83] dispersive LLE method has been used for the extraction of 18 polycyclic aromatic hydrocarbons (PAHs) (Naph, acenaphthene (Ace), fluorene (Flu), phenanthrene (Phe), Anth, Flt, pyrene (Pyr), benz[a]anthracene (B[a]A), chrysene (Chry), 5-methylchrysene (5-MC), benzo[e]pyrene (B[e]P), B[b]F, B[k]F, B[a]P, dibenzo[a,l]pyrene (DB[a,l]P), dibenz[a,h]anthracene (DB[a,h]A), B[g,h,i]P and I[1,2,3-c,d]P from water samples. The extraction yields for the different compounds ranged from 90.3% to 103.8%. Out of all used imidazolium ILs, [C8mim][PF6] proves to be best extractant.

Müller and Görak[84] have investigated the 1,3-propanediol extraction form aqueous solutions by using a series of water miscible ILs; 1-butyln-3-methylimidazolium trifluoromethansulfonate ([Im4,1][CF3SO3]−), 1-butyln-3-methylimidazolium dicyanamide ([Im4,1][N(CN)2]−), 1-butyln-3-methylimidazolium thiocyanate ([Im4,1][SCN]−), 1-butyln-3-methylimidazolium methysulfate ([Im4,1][CH3SO3]−), 1-butyln-3-methylmorpholinium trifluoromethansulfonate ([Mo6,1][CF3SO3]−), 1-butyln-3-methylpyrrolidinium trifluoromethansulfonate ([Pl4,1][CF3SO3]−), 1-ethyl-3-methylimidazolium trifluoromethansulfonate ([Im2,1][CF3SO3]−), 1-methoxyethyl-3-methylimidazolium trifluoromethansulfonate ([Im201,1][CF3SO3]−). For the extraction,
aqueous two-phase system method has been adopted. Their results indicate that the distribution coefficient of 1,3-propanediol depends on the polarity or hydrogen-bond accepting strength of the anion or cation. Imidazolium based ILs [C₄mim][PF₆], [C₆mim][PF₆], [C₆mim][BF₄] and [C₈mim][BF₄] have also been used for the recovery of amino acids from aqueous media[85]. Results show that hydrophobicity of amino acids plays the main driving force for their partition into a particular ionic liquid. IL with BF₄⁻ anion gives better extraction performance than PF₆⁻ anion. The increase in alkyl substituent chain length on the cation of the IL leads to decrease in extraction degree of the amino acids. On the other hand, extraction efficiency increases with increasing solubility of water in IL phases.

Chen et al.[86] have investigated LLE of caprolactam from aqueous solution using [C₄mim][PF₆] (n = 4, 6, 8), [C₆mim][BF₄] and [C₆mim][NTf₂]. It has been suggested that chemical structures of the ILs, ILs cation and anion structure and concentration of ammonium sulfate solution influence the distribution ratio of caprolactam significantly. [C₄mim][PF₆] showed high value of the distribution ratio; hence this IL is found best solvent for caprolactam extraction from aqueous solutions.

In conclusion, ILs represents new class of organic solvents which are used for environmental remediation. These solvents can be used in the replacement of conventional VOCs due to their unique physical properties. The use of ILs in the extraction of water contaminants provides new opportunities to the researchers to explore their use in the area of environmental protection. The hydrophobicity of IL plays an important role in the removal of water contaminants, specially dyes and heavy metals. The most interesting feature of ILs, is the recyclability of these solvent after their use in the extraction process. This property makes them economic to use. For using ILs for extraction process, one has to be careful about the proper choice of specific IL. There are reports in literature exploring the use of ILs in the direction of environmental remediation, but this field has further to be explored.

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