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# Ionic Liquids:
# Methods of Degradation and Recovery

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## 1. Introduction

In recent years ionic liquids (ILs) have attracted considerable attention owing to their potential use in a diversified range of applications. It is believed that ILs can successfully replace volatile organic media in a wide range of chemical processes. They have been studied and applied in organometallic catalysis, organocatalysis and biocatalysis, where they provide unique reaction media offering better selectivity, faster rates and greater catalyst or enzyme stability in comparison to conventional solvents (Buszewski & Studzińska, 2008; Dupont et al., 2002; Liu et al., 2010; Mathews et al., 2000; Minami, 2009; Welton, 1999). The applications of ILs also include areas such as electrochemical transformation, fuel cells, solar cells, sensors and nanochemistry. They are emerging as lubricants, modifiers of mobile and stationary phases in the separation sciences, and are candidates for the dissolution of cellulose, starch and wood (Wassersheid & Welton, 2003).

ILs are characterized by properties such as negligible vapour pressure and non-flammability under ambient conditions, high thermal conductivity, a wide electrochemical window and high polarity. They also have the ability to dissolve a wide diversity of materials, including salts, fats, proteins, amino acids, surfactants, sugars, polysaccharides and organic solvents. However, the most important attribute of ILs is the possibility of designing their properties to order. Thanks to the enormous number of cation and anion combinations, ILs can possess a wide spectrum of physical and chemical properties (solubility, polarity, viscosity or solvent miscibility), and they are already recognized by the chemical industry as new, target-oriented reaction media.

The properties of ILs can be used for developing new processes that are technologically, environmentally and economically advantageous. Listed benefits include the possibilities of reusing and relatively easily recovering ILs, which effectively reduces the amount of waste generated during technological operations. It is, however, important to remember that ILs are still quite expensive media, and their recycling after regeneration or recovery makes such a technology economically all the more justified. Among available technologies, conventional processes such as distillation, membrane separation and extraction can be

applied (Fernandez et al., 2010). Distillation in mild conditions may be the first choice for the separation of volatile products owing to the negligible vapour pressure of ILs. For separating non-volatile products, extraction and membrane processes such as nanofiltration and evaporation can be used. The operations to recover ILs from aqueous solutions described in this chapter are classified as phase addition (for example, salting-out), force field (gravity settling) and barrier (membrane separation).

Since the recovery of ILs on a large industrial scale will consume a great amount of energy, or if they are to be recovered from very dilute solutions where either investment or operational costs can be so high that they make the recovery operation not feasible, effective treatment is needed prior to the final application. Most ILs are not readily biodegradable, so advanced oxidation processes (AOPs) are frequently suggested as effective processes (Siedlecka et al., 2010 Stolte et al., 2010). The AOPs used for IL degradation, as well as a few examples of biological degradation and adsorption removal processes, are described in this chapter. The possibilities of reducing the amount of industrial waste containing ILs as well as potential sources of environmental release are illustrated in Figure 1.
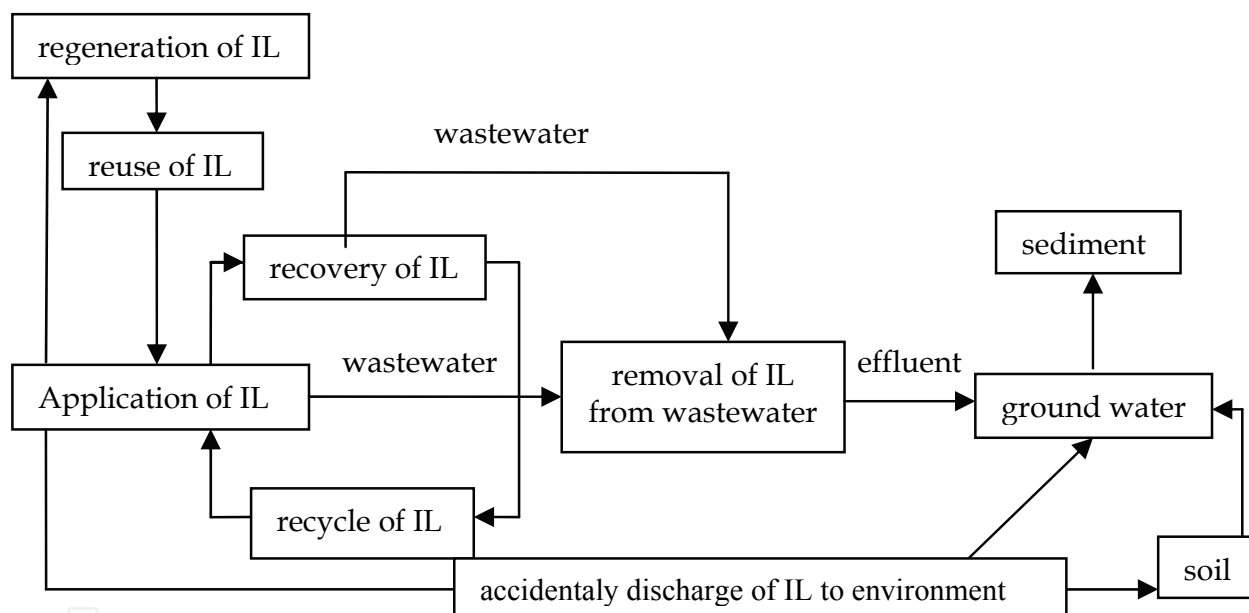
Fig. 1. Reduction of wastes containing ionic liquids in industrial applications, and potential sources of ILs released to the environment.

The non-measurable vapour pressure is a reason why ILs are frequently uncritically regarded as inherently environmentally friendly compounds. The loss of ILs is low, so a potential source of air pollution or inhalation is eliminated. Nevertheless, if one does classify ILs as "green" chemicals, questions such toxicity and persistence in the environment must also be addressed. The application of ILs on an industrial scale may pose an environmental hazard as a result of their transport, storage, technical breakdown, discharge in wastewaters etc. Therefore, in order to responsibly apply ILs in industrial processes, investigations of their fate and behaviour in the relevant environmental compartments (degradation, sorption etc.) and a proper risk assessment of ILs in the soil and aquatic environment (toxicity) must be undertaken and taken into consideration. The biodegradability of ILs, their toxicity and sorption in the environment are also briefly discussed in this chapter.

## 2. Behaviour of ionic liquids in water

Knowledge of the impact of structural variations of ionic liquids on their solubilities in water is of significance in relation to future applications, selecting the appropriate wastewater treatment process, and understanding their environmental fate. The loss of ILs into the aqueous phase may be an important factor in estimating the costs of recycling and water treatment.

Studies on the behavior of ILs in water have been taken by some research groups. Studies in which the cation and/or anion were changed were carried out by Freire et al. (Freire et al., 2007; Freire et al., 2008). They demonstrate unequivocally that the size of ILs, hydrophobicity and hydrogen bonding ability of both cation and anion are the most important factor regarding the solubility of ILs in water. However the nature of the anions largely determines the behaviour of IL-water mixture (Freire et al., 2008). Furthermore, ILs possessing long aliphatic substituents have been reported to undergo micellization (Anouti et al., 2009, Jungnickel et al., 2008, Łuczak et al., 2008; Łuczak et al., 2009). The formation of micelles in aquatic solution is due to the nature of the ions making up the ILs, which generally contain hydrophobic and hydrophilic domains. Hence the aggregation tendency of surfactant-like ILs is dependent on the relative size of these domains (Łuczak et al., 2008, Siriex-Plener et al., 2004) – the larger the hydrophobic domain, the greater the tendency to aggregate. Moreover, this tendency to aggregate increases in the presence of inorganic entities (Rickert et al., 2007), which is of significance for industrial wastewater treatment.

Several examples of IL hydrolysis are described in the literature. It is mainly the anions used in ILs that undergo hydrolysis – when reacting with water they generate mineral acids, e.g. sulphuric acid, phosphoric acid and hydrofluoric acid) (Islam & Ohsaka, 2008, Swatlowski, 2003). Hydrolysis of ILs can cause corrosion by these acids: it has been reported that carbon steel and stainless steel are corroded as a result of the dilution of ILs in water. A negative effect is exerted by anions such as tosylate, dimethylphosphate, hexafluorophosphate etc. (Uerdingen et al., 2005). Therefore, investigations into the recovery and removal of ILs from wastewaters and the environmental fate of ILs should take the influence of both cation and anion species into consideration.

## 3. Recovery operations of ionic liquids

According to the waste hierarchy developed by the European Union Directive 2008/98/EC (European Union, 2008), the effort priorities for dealing with spent material are expressed as "Re-duce, Re-use, Re-cycle". This means that only minimum amounts of substances should be used in a process. If possible, the substance should then be reused and reincorporated into the system and eventually recovered from the waste stream. Different operations are required in order to comply with the regulations.

Regeneration is often necessary if a substance cannot be reused directly. For the recycling of waste, recovery operations are applicable. Removal operations are then the final step to prevent a negative impact on the environment or human health when the final waste is disposed of.

This procedure is also valid for ILs, not just for legislative reasons, but also because of their relatively high production costs. However, the continual reuse of ILs will lead to a concentration of contaminants. Regeneration can then enhance the reusability of the IL and prolong its lifetime by separating it from the suspected contaminant. This was the first operation to be used and developed. An overview is given in Fernandez et al. (2010).
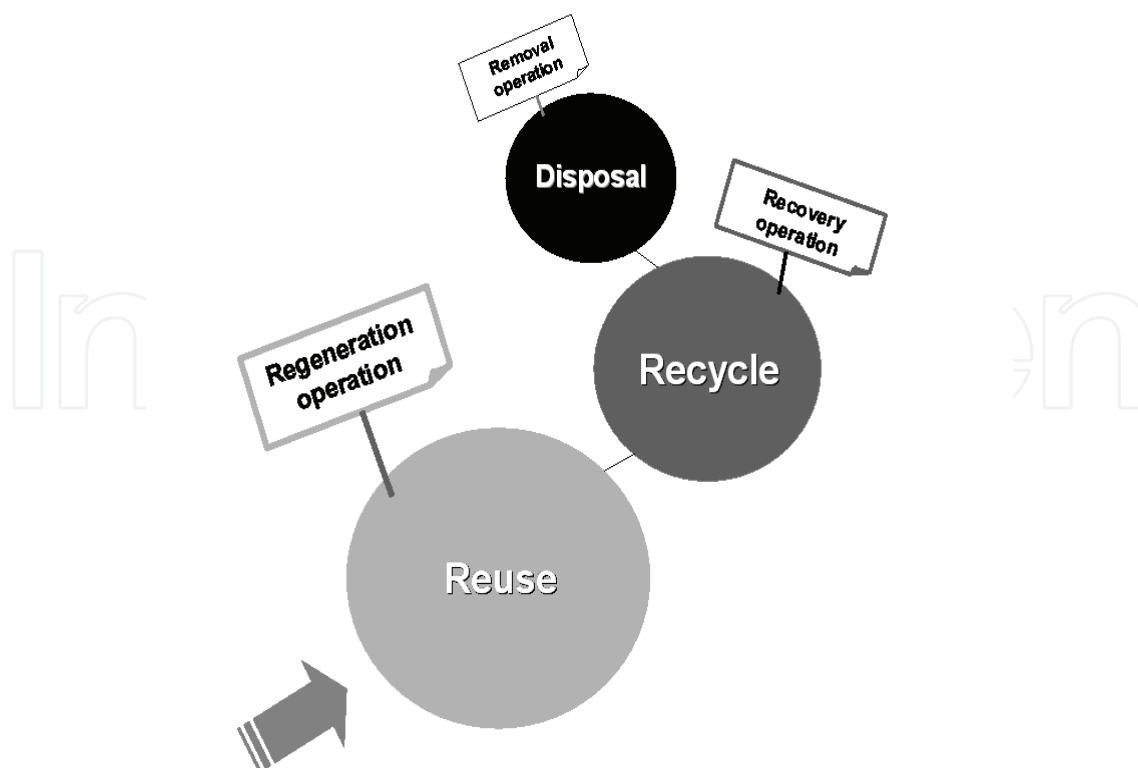
Fig. 2. Scheme of the effort priorities for dealing with spent ionic liquids. The spheres starting with "reuse" are the overall treatment purposes requiring different technical operations (in rectangles).

However, these regeneration processes are limited to the threshold concentration of contaminants that make ILs unusable for a given purpose and turns them into IL waste. Recovery operations of IL waste are then of special interest.

In view of the physicochemical properties and applications of ILs, the recovery of IL wastes focuses mostly on wastewater streams. ILs adsorbed on solid surfaces can also enter the waste stream; but most solid waste is treated thermally, and IL recovery from such waste has not yet been undertaken.

Wastewater streams containing ILs are of concern when it comes to environmental aspects on the one hand, e.g. (eco)toxicity and biodegradability, and technical aspects on the other hand, e.g. operating costs for replenishing ILs lost from a process. The amounts of ILs that can be expected in wastewater streams are roughly equivalent to their solubilities. Even though hydrophobic ILs are poorly soluble in water, concentrations in water can be relatively high. In this case, attempts should be made either to replace the IL used with a less soluble substance or to develop processes to recover them from wastewater, preferably in a closed system where recovery can be carefully controlled (McFarlane et al., 2005).

In this chapter the recovery operations of ILs from aqueous solutions are explained and classified by their separation mechanism: (1) phase addition, (2) force field and (3) barrier.

### 3.1 Recovery by phase addition

Simple salting-out processes have been investigated for separating ILs from water. Distillation, as applied to regeneration (Mathews et al., 2000), has not yet been applied to recovery, probably because of the low IL concentration in wastewater in contrast to the regeneration of spent ILs contaminated with water.

The principle of salting out is relatively simple, although its mechanism is not completely known, yet. To salt out an IL from an aqueous solution, an electrolyte is added as a solid or as a saturated aqueous solution. The electrolyte withdraws some of the water present, forming a second phase that can be removed by decantation; the energy penalty incurred by the evaporation of the water is thus avoided. As the electrolyte used as the mass-separation agent is not usually recoverable, its cost is an important factor to be taken into account. An example has been given by Gutowski et al. (2003) of how this recovery operation works in practice: a homogeneous mixture of 1-butyl-3-methylimidazolium chloride and water is turned into a biphasic system when a concentrated solution of potassium phosphate is added: (1) the upper phase – rich in IL; (2) the lower phase – rich in potassium phosphate. Further studies on the recovery of ILs by the addition of other kosmotropic salts and carbon dioxide were reported and reviewed by Fernandez et al. (2010). There is, however, still a lack of information on which to base a definition of these phase systems before they can be implemented in new technologies (Bridges et al., 2007).

## 3.2 Recovery using a force field
The standard use of a force field for the recovery of ILs is gravity settling, e.g. enhanced by a centrifugal contactor. It has been applied with success to a dispersion of a hydrophobic IL with common salt and with water (Birdwell et al., 2006).
When IL cations such as 1-butyl-3-methylimidazolium are coupled with an iron-containing anion, e.g. tetrachloridoferrate, they show a strong magnetic response, which can be used for their recovery (Hayashi & Hamaguchi, 2004; Lee et al., 2007). A magnetic field is thereby induced on a biphasic system consisting of an IL-rich phase and water-rich phase, which can then be separated easily. Together with other methods, e.g. ultracentrifugation, separation could possibly be improved, although this might be impracticable in an industrial situation.

## 3.3 Recovery using a barrier
Besides the separation of ILs and water by phase addition and force field, membrane filtration has been studied as a promising technology. The first report on the application of nanofiltration to separate mixtures containing ILs was published in 2003 by Kröckel et al. Retentions of ILs of up to 82% and 95% were obtained for 1-butyl-3-methylimidazolium tetrafluoroborate and 1-butyl-3-methylimidazolium sulphate, respectively, using commercial Desal membranes. In a more recent study, lower retention values of only 60% for 1-butyl-3-methylimidazolium tetrafluoroborate and 67% for 1-butyl-3-methyl-imidazolium bromide as maximum values were obtained (Wu et al., 2009). Own experiences, published in 2008 by Fernández et al., are reaching up to 99 % of ILs retention from aqueous solutions. This means that depending on the initial concentration of the IL in waste water the residual concentrations could still be too high for biological processes during waste water treatment why the removal of ILs from waste water is then of great importance. In general, the use of membrane technology for IL recovery is regarded as advantageous in comparison to the other two separation methods described. In membrane technology no auxiliary substance as required for phase addition needs to be added, and it can be applied to a variety of ILs, whereas separation by force field is limited to magnetic ILs.
Although membrane technology is an important step towards the effective recovery of ILs from waste water, not all technological potentials have been fully tapped and research has so far been based mainly on phase separation, barrier and forced field technologies. Further

research is still going on to reduce IL waste. However, if ILs are not reusable and recoverable any more, the removal of ILs can be applied as the final treatment step. Though the last step in a series of treatment steps, it needs to be considered, because no infinitely applicable regeneration and recovery techniques are available at the moment; up till now, every product has eventually become waste.

## 4. Removal of ILs

### 4.1 Physicochemical removal

Adsorption is an important technology that is widely used to remove organic pollutants from water. The effectiveness of sorption depends fundamentally on the characteristics of the substance to be adsorbed and on the type of adsorbent. In addition, operational requirements may lead to contact times that are too short to ensure equilibration.

Adsorbents such as activated carbon (Palomar et al., 2009), ion-exchange resin, activated sludge and fermentation waste (Vijayaraghavan et al., 2009) have all been used to remove ILs from aqueous solutions. The ion-exchange resin exhibits the best sorption efficiency (98%) but the process is relatively slow (180 min.). Activated carbon gives a faster rate of sorption (15 min.), but the affinity of ILs for this sorbent is much poorer compared to ion-exchange resin. Adsorption on activated sludge and fermentation waste is insignificant (Vijayaraghavan et al., 2009).

The affinity of ILs for activated carbon is the result of diverse intermolecular interactions (polar, π-π, van der Waals and hydrogen bonding). Ion exchange is minimal at acidic and neutral pH, but is significantly enhanced at basic pH values, where deprotonation and the generation of negatively charged functional groups takes place on the carbon surface (Vijayaraghavan et al., 2009). There is a rise in the adsorption capacity of activated carbon as imidazolium-based ILs are composed of hydrophobic cations (1-methyl-3-octyl-imidazolium and 1-hexyl-3-methylimidazolium cations) and/or hydrophobic anions (bis[(trifluoromethyl)sulphonyl]amide, hexafluorophosphate) (Palomar et al., 2009). The role of van der Waals interactions between the non-polar groups of the cation and the organic matter has also been investigated using soil and sediments (Beaulieu et al., 2008; Matzke et al., 2009; Mrozik et al., 2008a; Mrozik et al., 2008b; Stepnowski, 2005; Stepnowski et al., 2007; Studzińska et al., 2009). Physical adsorption phenomena have been effectively used for the immobilization of hydrophobic ILs on other solid supports (Liu et al., 2010).

The results obtained on different activated carbons demonstrate that adsorbent porosity is also an important factor in IL sorption. The higher average pore diameter in activated carbon facilitates the comparatively easy diffusion of ILs into the pore structure, enhancing its sorption (Vijayaraghavan et al., 2009).

### 4.2 Degradation methods

It is known that ILs are thermally, electrochemically and chemically relatively stable (Siedlecka et al., 2010), but they will eventually decompose during technological operations. In recent years numerous investigations have been carried out into IL toxicity and biodegradability (Bailey et al., 2008; Bernot et al., 2005a; Bernot et al., 2005b; Docherty et al., 2006; Gathergood et al., 2004; Gathergood et al., 2006; Gathergood & Scammells, 2002; Garcia et al., 2005; Latała et al., 2005; Latała et al., 2009a; Latała et al., 2009b; Latała et al., 2010; Pernak et al., 2003; Pham et al., 2010; Renke et al., 2003; Składanowski et al., 2005; Stasiewicz et al., 2008; Stepnowski et al., 2004; Stock et al., 2005; Stolte et al., 2008; Swatlowski et al., 2004).
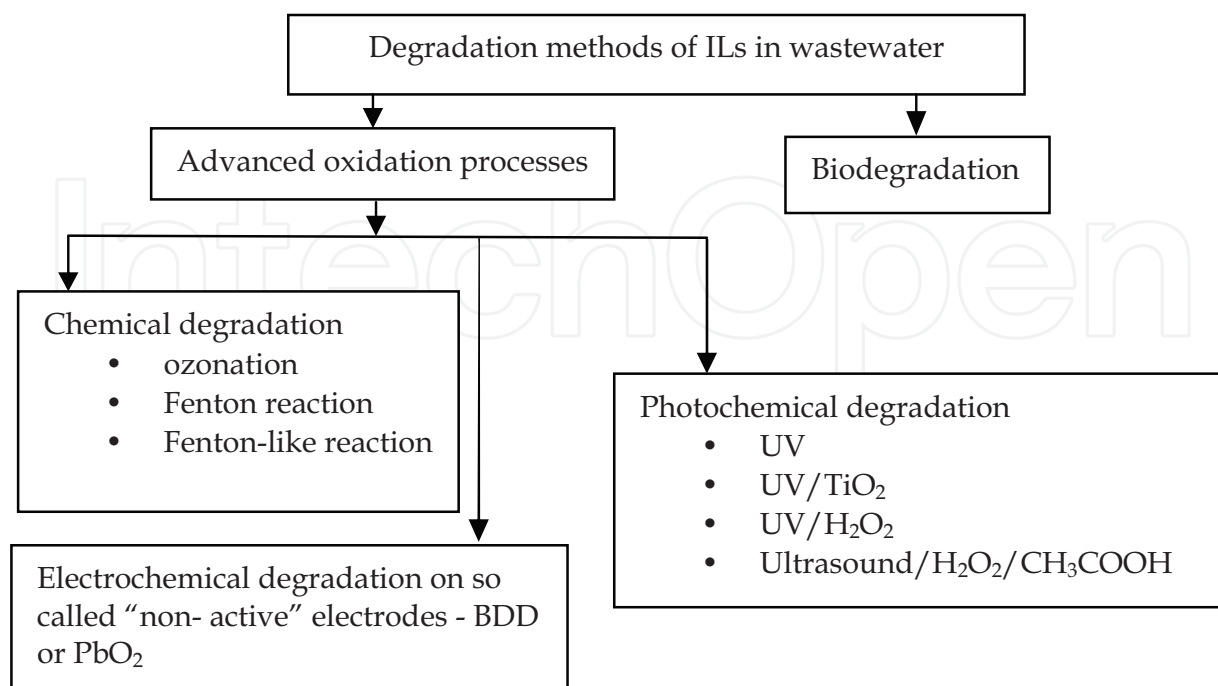
Fig. 3. ILs degradation methods proposed in literature

However, the toxicity and environmental resistance of their decomposition products is totally unknown. For this reason, chemical, photochemical or electrochemical oxidation have been put forward as processes for removing from wastewater both non-recoverable ILs and their degradation products (Czerwicka et al., 2009; Li et al., 2007; Pernak & Branicka, 2004; Siedlecka et al., 2008; Stepnowski & Zalewska, 2005; Stolte et al., 2008) (Fig.2.). Biological wastewater treatment is regarded as environmentally very friendly, and some examples of this process are given in this chapter.

### 4.2.1 Chemical degradation

The chemical oxidation of aqueous solutions of ILs has been investigated. Information is available on ozonation (Pernak & Branicka, 2004), the Fenton reaction and Fenton-like reactions (Siedlecka et al., 2008a; Siedlecka et al., 2008b; Siedlecka et al., 2009).

Ozonation of 1-(alkoxymethyl)-3-hydroxypyridinium, 1-(alkoxythiomethyl)-3-hydroxy-pyridinium and 1-(alkoxymethyl)-3-(dimethylamino)pyridinium chlorides was found to be rapid and effective. In this process small amounts of decomposition products were generated, with the drop in pH indicating that some of them could be organic acids. Additionally, the ozonation products of 1-(tetradecyloxy)methylpyridinium chlorides substituted by a hydroxyl group in position 3 or 5 or containing a dimethylamino group in position 3, demonstrated no bacteriostatic or mycostatic effects. (Pernak & Branicka, 2004). These authors conclude that the products formed are less harmful than parent pyridinium compounds. The fact that pyridinium ILs without a hydroxyl group substituted at the pyridinium head group do not lend themselves to ozonation confirms that ozone itself is a highly selective oxidant (Hoigne et al., 1989).

In Fenton ($H_2O_2/Fe^{2+}$) and Fenton-like ($H_2O_2/Fe^{2+}$) systems the hydroxyl radical ($\bullet OH$) with a very strong oxidative potential ($E_0=+2,8V$) degrades non-biodegradable and recalcitrant organic pollutants. In contrast to ozone, the hydroxyl radical is a non-selective oxidant. Furthermore, the modification of Fenton-like reactions by the addition of a large dose of $H_2O_2$ promotes a series of propagation reactions that produce a perhydroxyl radical, a superoxide anion, and a peroxide anion in addition to the hydroxyl radical (Walling, 1975). These radicals can lead to different pathways of IL degradation, products and display different transformation kinetics (Siedlecka et al., 2009; Siedlecka & Stepnowski, 2009). Fenton and Fenton-like systems are very effective in the degradation of 1-alkyl-3-methylimidazolium ILs. It was demonstrated that the efficiency of oxidation is structurally dependent. The lengthening of the alkyl chain from four to eight carbons in the 1-alkyl-3-methylimidazolium cation significantly lowered the rate of degradation (Siedlecka & Stepnowski, 2009). A comparative study of three 1-butyl-3-methylimidazolium salts leads to the conclusion that anions can inhibit degradation by competition with cations for hydroxyl radicals, or by undergoing complex reactions with ferric and ferrous ions (Siedlecka et al., 2009). Moreover, the 1-butyl-3-methylimidazolium cation degradation rate was retarded with the lengthening of the alkyl chain in the perfluorocarboxylic anions present in a solution of 1-butyl-3-methylimidazolium chloride (Siedlecka et al., 2009). A high dose of $H_2O_2$ in a Fenton-like system accelerates the degradation of imidazolium-based ILs, especially 1-butyl-3-methylimidazolium chloride, but slows down the degradation of 1-butyl-3-methylpyridinium chloride. The authors conclude that increasing the $H_2O_2$ dose in Fenton-like systems changes the mechanism of IL degradation (Siedlecka et al., 2008a; Siedlecka et al., 2008b; Siedlecka & Stepnowski, 2009).

Analysis of mixtures oxidized by Fenton-like systems shows that mono-, di- and amino-carboxylic acids are probably degradation products. Effective degradation of the imidazolium ring is achieved only for 1-butyl-3-methylimidazolium chloride (Siedlecka et al., 2008b; Siedlecka & Stepnowski, 2009). ^{1}H-NMR spectra and GC-MS results showed that radical attack is non-specific, with any one of the carbon atoms in the ring and the alkyl chain being susceptible to attack. The products with some hydroxyl groups substituted at different sites in the parent compounds are rather unstable and decomposed by two pathways: the first is oxidative ring opening, the second is cleavage of the N-C bond in the *N*-alkyl side chain. Unfortunately, all these chemical degradation investigations were limited to imidazolium-based ILs, where a great number of pyridinium-, pyrrolidinium-, phosphonium- or ammonium-based ILs are commercially available.

It seems that a hybrid system consisting of a Fenton-like process and a biological stage should be considered for IL degradation, thereby accelerating the mineralization of ILs. Therefore, systematic investigations of the toxicity and biodegradability of post-oxidation mixtures should be conducted.

### 4.2.2 Photochemical degradation
In one of the first studies, Stepnowski & Zaleska compared the effectiveness of three methods: UV photodegradation, UV photolysis of hydrogen peroxide, and photocatalysis on UV-irradiated $TiO_2$. For these investigations imidazolium ILs with different alkyl chain length were chosen (1-butyl-, 1-hexyl-3-methylimidazolium, 1-methyl-3-octylimidazolium, 1-ethyl-3-ethylimidazolium chloride or tetrafluoroborate, methyl imidazole as reference). The stability of these compounds with respect to all the photodegradation methods used

appeared to be structure-related. The process that was most effective with all the compounds was oxidation based on the UV/$H_2O_2$ system, the degradation efficiency decreasing in the order: 1-butyl-3-methylimidazolium<1-hexyl-3-methylimidazolium< 1-methyl-3-octylimidazolium<1-ethyl-3-ethylimidazolium cations. The 1-ethyl-3-ethyl-imidazolium cation turned out to be the most stable compound, although in the case of direct photolysis, the octyl- and hexyl- alkyl side chain cations were the least degradable (Stepnowski & Zaleska, 2005). For confirmation of the results, the AOP degradation products had to be identified. For these investigations 1-ethyl-, 1-butyl-, 1-hexyl-3-methyl-imidazolium and 1-methyl-3-octylimidazolium chlorides were treated with the UV/$H_2O_2$ system. Identification was based on LC-MS/MS measurements. It was found that modification (at least in the first stage of oxidation) occurred in the imidazolium ring, not in the alkyl chain of the molecule. The longer the alkylated cation, the greater the probability of oxidation of the alkyl chain (Czerwicka et al., 2009). The results tallied with those obtained using a Fenton-like system (Siedlecka et al., 2008b) or after biodegradation (Stolte et al., 2008). Nevertheless, the toxicity and biodegradability of the degradation products still need to be analysed. The major objective of the work of Morawski et al. was to investigate photocatalysis as a method of degrading different types of ILs (imidazolium, ammonium, phosphonium, pyridinium). For that purpose those authors used UV light in the presence of $TiO_2$. They concluded that the lower the molar mass, the greater the IL stability, and also that degradability depends upon the cation and anion, although to different degrees. Phosphonium ILs were shown to be the most susceptible to this type of degradation (Morawski et al., 2005).

Itakura et al. studied the efficacy of the photocatalytic decomposition of ILs using platinized $TiO_2$ (Pt/$TiO_2$) and bare $TiO_2$, but unlike other authors, they also took anion degradation into account. They tested three ILs: 1-ethyl-3-methylimidazolium bromide, 1-ethyl-3-methyl-imidazolium hexafluorophosphate, 1-butyl-3-methylimidazolium tetrafluoroborate. There was no significant difference between the degradation efficiencies obtained with $TiO_2$ or Pt/$TiO_2$. It appears to be a perfect method for cation degradation, but it is unsuitable for anions. To degrade these (especially hexafluorophosphate and tetrafluoroborate), another method was needed: hydrothermal treatment with Ca(OH)$_2$ mineralizer could serve this purpose (Itakura et al., 2009).

Katoh & Takahashi studied photochemical degradation under pulsed laser irradiation in order to examine the decomposition behaviour of 1-methyl-3-butylimidazolium bis[(trifluoromethyl)sulphonyl]amide and iodide. They concluded that the excited state 1-butyl-3-methylimidazolium cation ([BMIM$^+$]$^*$) underwent degradation efficiently and suggested that the neutral 1-butyl-3-methylimidazolium radical ([BMIM]$^\bullet$) was relatively stable (Katoh & Takahashi, 2009). The majority of studies have looked at the photodegradation of imidazolium-based ILs. Nevertheless, there is some information on the photochemical transformations of pyridinium salts, which could be a good starting point for later IL degradation studies (Damiano et al., 2007).

It seemed interesting to use the ultrasonic chemical oxidative degradation method proposed for 1,3-dialkylimidazolium ILs with different anions (chloride, bromide, hexafluorophosphate and tetrafluoroborate). The oxidative decomposition of ILs was carried out in aqueous hydrogen peroxide/acetic acid assisted by ultrasonic chemical irradiation. Li et al. in 2007 achieved a high efficiency of degradation (93% after 12h, and 99% after 72h). The degradation products were monitored using GC-MS. They demonstrated that hydrogen atoms in the imidazolium ring are oxidized first, and that fragmentation leads to ring

opening. This is in agreement with the results obtained by other authors (Czerwicka et al., 2009; Li et al., 2007). They also found that there was no significant influence of either alkyl chain length or anion type on the degradation pathway. The high degree of degradation augurs well for this method (Li et al., 2007). Also the direct influence of sonification on pure imidazolium based ILs decomposition was analysed. The first sign of degradation was the darkening of their colour to an amber shade. It was shown that ultrasonic treatment led to the decomposition of organic ILs. GC-MS, IR spectroscopy, and NMR spectroscopy were used for monitoring the degradation process (Oxley et al., 2003).

### 4.2.3 Electrochemical degradation

ILs are thought to be electrochemically stable. They possess large electrochemical potential windows from 2V to 6V, but these data are the result of rather short cyclic voltammetry experiments (Galiński et al., 2006). It has been demonstrated that different reaction products can be found when longer electrolysis experiments are performed (Kroon et al., 2006). The differences in the electrochemical stabilities of ILs results from the presence of impurities. In the presence of water the potential window of ILs narrows dramatically (Islam & Ohsata, 2008; Welton, 1999). Moreover, some reactions, e.g. the generation of a superoxide ion or a hydroxide radical, which limits the chemical stability of ILs, may be affected by the presence of water in ILs (Barnes et al., 2008).

Therefore, a very promising disposal strategy for toxic and recalcitrant ILs in aqueous solutions is electrolysis using "non-active" anodes such as boron-doped diamond (BDD) or PbO$_2$. These anodes have the ability to generate quasi-free hydroxyl radicals during the electrolysis of water, which are capable of efficiently oxidizing ILs. The electrochemical oxidation of imidazolium ILs was carried out for the first time by Stolte et al. in 2008. Almost complete degradation of 1-butyl-3-methylimidazolium chloride was achieved on a bipolar BDD anode. The positively charged imidazolium core, responsible for the non-biodegradability of imidazolium-based ILs, was completely destroyed after 4h of electrolysis. In addition, the biodegradability improved in comparison to that of the parent compound solution (Stolte et al., 2008). Further investigations carried out by our research group indicate that another "non-active" anode – PbO$_2$ – also successfully degrades imidazolium- and pyridinium-based ILs (data not published).

### 4.2.4 Other degradation methods

Thermal degradation could be an alternative method for degrading ILs, in spite of their excellent thermal stability. Very promising is the fact that, despite their tolerance to short-term high temperature treatment, longer exposure to such temperatures could induce decomposition. Kroon et al. predicted the susceptibility of ILs to thermal degradation on the basis of quantum chemical calculations. These authors stated that long-term thermal stability depends on the cation type (imidazolium and phosphonium cations were found to be the most stable), that the effect of alkyl chain length is not significant, and that highly proton-abstracting anions (halides) are more susceptible, whereas poorly proton-abstracting ones like bis[(trifluoromethyl)sulphonyl]amide are more resistant to high temperature decomposition (Kroon et al., 2007). These conclusions are comparable with published experimental data. The thermal degradation of some ILs is relatively easy, for example, that of a water-HAN (80 wt. %, hydroxylammonium nitrate) mixture. The experiment was performed using a dynamic reactor with mass spectrometry. The critical temperature had

earlier been established as 120°C, but in this study a temperature of 200°C was used, at which NO, $NO_2$, $N_2O$, $N_2$ or $O_2$ were produced (Amariei et al., 2007). The thermal decomposition behaviour of readily investigated imidazolium-based ILs was studied by Ohtani et al. The thermal degradation products of 1-alkyl-3-methylimidazolium ILs (with trifluoromethylsulphonate, hexafluorophosphate and tetrafluoroborate, chloride, or bromide anions) were detected with Py-GC coupled to different analysers (FID, Nr-ECD, NPD, MS). It was concluded that in the case of halides, the corresponding haloalkanes and 1-alkylimidazoles were mainly formed, that from ILs containing the tetrafluoroborate anion, the corresponding alkenes with smaller amounts of haloalkanes and 1-alkylimidazoles were formed, that from 1-butyl-3-methylimidazolium trifluoromethylsulphonate, butene, 1-methyl- and 1-butylimidazole, a few haloalkanes and $CF_3H$ and $SO_2$ were formed, that in the case of the hexafluorophosphate anion, the products were similar to those obtained from the tetrafluoroborate anion (additionally some phosphorus-containing compounds were observed), and that the imidazole ring decomposed very little under the experimental conditions at around 550°C (Ohtani et al., 2008).

The high-temperature decomposition of some ILs could be very dangerous. The problem lies in the degradation products of, for example, cyano-containing ILs. Wooster et al. examined the thermal degradation of different ILs with dicyanamide or tricyanomethide anions using pyrolysis + GC-MS. They showed that under the influence of temperature products were formed whose structure was strongly dependent on cation type. They found that polymerization occurred in the case of cyano-containing anions and N-based cations (N-butyl, N-methyl-pyrrolidinium, N-methyl, N-propyl-pyrrolidinium), whereas the presence of the phosphonium cation (trihexyltetradecylphosphonium) led to complete decomposition to volatile compounds (Wooster et al., 2006). All investigations involving the thermal decomposition of ILs need to be supplemented by mass spectrometric analysis of the degradation products in order to identify these products and to evaluate their toxicity. On the other hand, if we take into consideration the matrix and the examples just mentioned, thermal degradation does not appear to be a very suitable method for decomposing ILs from wastewater.

There are rather few investigations covering the complete degradation of ILs, that is, both cation and anion. Itakura et al. reported that a combination of two methods was needed to achieve success. They investigated the combination of hydrothermal mineralization (HM) and photocatalytic degradation (PD) to decompose 1-ethyl-3-methylimidazolium bromide or hexafluorophosphate and 1-butyl-3-methylimidazolium tetrafluoroborate. As already mentioned, PD did not decompose the anions to a sufficient extent. On the other hand, hydrothermal treatment used on its own did not completely degrade the cations either. Only the combination of both methods led to the detoxification of water contaminated by the ILs being tested (Itakura et al., 2009).

### 4.3 Biological methods

The use of living organisms, especially microorganisms, for degrading ILs seems a natural and obvious approach, one that appears at least potentially to be more friendly to the environment. The results of primary biodegradation (using bacteria) studies using different IL cations were very interesting. 27 ILs with different head groups (e.g. imidazolium, pyridinium) and side chains were tested. LC-MS was used to identify the primary biodegradation products. It was shown that the more toxic ILs with longer side-chains were more susceptible to biodegradation. It was found that lipophilicity was the factor

responsible for the increasing tendency towards toxicity and biodegradability, but unfortunately it creates a conflict of interests in looking for biological degradable ILs (Stolte et al. 2008). Markiewicz et al. showed that a level of 0.2mM 1-methyl-3-octylimidazolium chloride is the terminal concentration threshold for primary biodegradation. Higher concentrations led to sorption onto the sewage sludge flocs, although inhibition of cell function as a consequence of decreased dehydrogenase activity was observed (Markiewicz et al., 2009). This indicates that the toxicity of ILs towards activated-sludge microorganisms should be taken into consideration. To predict this effect quantitative structure–property relationship modelling could be helpful (Couling et al., 2006). Besides bacteria, fungi can also be used for IL degradation. To this end, Esquivel-Viveros et al. tested *Fusarium* sp., and demonstrated that 1-butyl-3-methylimidazolium hexafluorophosphate could be degraded by these fungi. The results were obtained using a membrane-accelerated biofilm reactor as well as tests on Petri dishes and in Erlenmeyer flasks (Esquivel-Viveros et al., 2009). Minimal or zero degradation of 1-butyl-3-methylimidazolium-based ILs was confirmed by Gathergood and co-workers ((Garcia et al., 2005; Gathergood et al., 2004; Gathergood et al., 2006).

Comparative studies have also been carried out regarding the differences between the biodegradabilities of various ILs. The biodegradability of ILs containing imidazolium and pyridinium cations by an activated sludge microbial community were investigated by Docherty et al. and Pham et al. (Docherty et al., 2007; Pham et al., 2007). They came to the same conclusions, namely, that alkylpyridinium ILs are more rapidly biodegraded than imidazolium ILs. It was also found that ILs with a pyridinium head group are less toxic (Pham et al., 2007) and that the longer the alkyl chain, the faster the biodegradation (Docherty et al., 2007). Only one of all the tested ILs – 3-methyl-1-octylpyridinium bromide – fitted the criteria for DOC Die-Away, and could be designated as readily biodegradable (Docherty et al., 2007). Excellent biodegradability is also shown by pyridinium cations bearing an ester containing a substituent at positions 1 or 3 (Stolte et al., 2008).

From the toxicity point of view, the identification of products formed during biodegradation is very important, because the toxic effect could interrupt the biodegradation process. For this purpose, Pham et al. first studied the biodegradation pathway of 1-butyl-3-methylpyridinium bromide, including the identification by LC-MS of the metabolites formed. They found two pathways of degradation, one leading to 1-(2-hydroxybutyl)-3-methylpyridinium and the other to 1-(2-hydroxyethyl)-3-methylpyridinium (Pham et al., 2009). Unlike Pham et al., however, Docherty et al. found 1-butyl-3-methylpyridinium bromide to be very poorly biodegradable: responsible for this was the different IL concentration, another parameter to be taken into account when testing (Docherty et al., 2007; Pham et al., 2009). Apart from imidazolium- and pyridinium-based ILs, alkylammonium salts were also tested in the context of biodegradation in activated sludge. The problem is that many quaternary ammonium salts possess biocidic properties. Nishiyama et al. found the salt form of trimethylamine, dimethylamine and methylamine as a result of biodegradation in the presence of activated sludge. They noticed that the biochemical oxygen consumption needed for the degradation of alkylammonium salts with long alkyl chains could reduce the antimicrobial activity. Despite this, however, the removal of dissolved organic matter was almost complete (Nishiyama et al., 1995). The influence of UV/$H_2O_2$ peroxidation on the biodegradability of quaternary ammonium salts was also tested. Adams et al. found this pretreatment to be very effective only in the case of alkyldimethylbenzyl ammonium chlorides, whereas with dioctyldimethyl ammonium

chloride there was no significant influence on biodegradability (Adams et al., 2000). It was shown that perfluorinated IL ions were more susceptible to biodegradation than halides (Gathergood & Scammells, 2002). Garcia et al. investigated the influence of imidazolium-based IL anions on their biodegradation. They found that the octyl sulphate anion was better biodegradable than hexafluorophosphate, bromide, tetrafluoroborate, and bis[(trifluoromethyl)sulphonyl]amide (Garcia et al., 2005). This was in agreement with the results of Gathergood et al. (Gathergood et al., 2006) but contradicted the results obtained in the same research group by Hartjani et al. These authors tested pyridinium ILs and did not find any significant influence of the octyl sulphate anion on IL biodegradability (Hartjani et al., 2008). It could be concluded that the anion on its own influences the biodegradability of ILs to a minimal degree, but if combined with some other cations may alter the susceptibility to biodegradation (Stolte et al., 2010). The results of comprehensive IL biodegradability studies are collated in several valuable papers and reviews (Gathergood et al., 2004; Garcia et al., 2005; Gathergood et al., 2006; Coleman & Gathergood, 2010; Stolte et al., 2010).

## 5. The fate and degradation of ILs in the environment

So far, the majority of ILs have been used in research laboratories, but before long they are going to be utilized in industry. Because of their potential toxicity, their behaviour and possibility to degradation in the environment are very important factors in risk assessments concerning their introduction as new industrial chemicals on to the market. Non-volatile ILs will inevitably pollute the soil, sediments and ground waters as a result of accidental spills, leaching of landfill sites or via effluents. Therefore, the sorption, biodegradability and (eco)toxicity of ILs play a very important role in their environmental fate.

Sorption has a critical effect on the transport, reactivity and bioavailability of organic compounds in the environment. Up till now, sorption studies have focused mainly on imidazolium-based salts. Several experiments have examined sorption to a variety of soils and sediments, indicating that these compounds are relatively strongly adsorbed (Matzke et al., 2009; Mrozik et al., 2009; Stepnowski, 2005; Stepnowski et al., 2007). The sorption ability and mobility of ILs in soil have been investigated in two ways: by batch testing or column leaching experiments. Using batch tests, the interactions of ILs involved in sorption, the strength of these interactions and the sorption capacity were studied on selected soils. The column leaching experiments investigated both the sorption and transport of ILs (Studziński et al., 2009). All the studies confirmed that the sorption mechanism is a combination of electrostatic interaction and physical sorption. However, the major type of interaction between soil and ILs is electrostatic. The highly negatively charged moieties on the surfaces of particles, e.g. of clay minerals, or on ionized carboxylic functional groups in biomolecules, are able to interact with the positively charged head group of ILs. However, van der Waals forces also play a significant role in sorption process. The content of clay, and to a small extent that of organic matter, elevates the sorption capacity of ILs in soil (Matzke et al., 2009; Stepnowski et al., 2007).

Lipophilicity and the side chain length of ILs are the main factors determining the rate of their transport through the soil matrix. Elongating the alkyl chain increases affinity for soil or sediment. Further, double layer sorption has been observed in the more hydrophobic, long-chain ILs. In contrast, the presence of a hydroxyl group in the alkyl chain causes the sorption ability of these ILs to be relatively poor (Mrozik et al., 2009).

Desorption of ILs is inversely correlated with sorption strength: strongly bound long-chain ILs are desorbed to a lesser extent than short-chain ones (Matzke et al., 2009; Stepnowski et al., 2007). This means that the transport of ILs in the environment will be strongly related to their hydrophilicity. Hydrophobic ILs in aquatic systems will be attenuated by sediments. In contrast, more mobile, hydrophilic contaminants released into the environment are likely to enter aquatic ecosystems. However, the anions present in the aqueous phase, with which certain cations form ion pairs, also affect phase transfer (Matzke et al., 2009; Stepnowski et al., 2007).

The presence of ILs in ground water will have an influence on living organisms, from bacteria to human beings. Therefore, the tests that investigate IL toxicity towards microorganisms, cells and animals, as well as their inhibitory effects upon enzymes, are of particular interest. IL toxicity towards aquatic organisms – *Lemna minor* (Larson et al., 2008), algae (Latała et al., 2005), the fresh water crustacean *Daphnia magna* (Bernot et al., 2005a), the fresh water snail *Physa acuta* (Bernot et al., 2005b), the zebra fish *Danio rerio* (Pretti et al., 2006) and the reef sponge (Kelman et al., 2001) – are discussed in detail by Pharm et al. (Pham et al., 2010). The results suggest that toxicity is correlated with the hydrophobicity of pyridinium-, imidazolium- and quaternary ammonium-based ILs. Moreover, pyridinium and imidazolium cations containing nitrogen-bearing rings are more toxic than quaternary ammonium cations (Couling et al., 2006).

The toxic effects of ILs on microorganisms in particular would limit their biodegradability. Studies analysing the biodegradability of ILs were reviewed in the previous chapter (Coleman & Gathergood, 2010; Gathergood et al., 2004; Gathergood et al., 2006; Garcia et al., 2005; Romero et al., 2008; Stolte et al., 2008).

Imidazolium-based ILs can also be partially degraded in aerobic aqueous solution inoculated with soil-bacteria (Kumar et al., 2006). Analysed by GC-MS, the breakdown products found after the 12-day degradation of 1-butyl-3-methylimidazolium tetrafluoroborate, degradation were m/z=97 and m/z=124.

The poor biodegradability and (eco)toxicity of some ILs are reasons why we should prevent leakages of ILs to the environment by searching for effective means of removing and recovering them from wastewater and minimizing their presence in waste streams.

## 6. Conclusion

ILs are a very promising class of organic solvent, potentially useful in many different areas of the chemical industry. However, in view of their toxicity and poor biodegradability, they have so far played a marginal role in commercial technologies. We therefore need to look for such a technology using ILs that fulfils the criteria for a sustainable process. One of the aims of sustainable processes is the minimization of waste – in the case of ILs, this can be achieved by regenerating and recycling them after having been used in various processes, operations that extend their whole life cycle. More attention must therefore be paid to the recovery of ILs from wastewaters. Investigations should focus on searching for quick, simple, cost acceptable and effective methods. At the same time, there should be progress in wastewater treatment: advanced oxidative processes appear promising in this respect. However, oxidation studies have been carried out only with aqueous solutions of ILs, which are a much simpler matrix than an industrial effluent. In addition, more information on the transformation pathways during chemical, photochemical, electrochemical and biochemical

degradation processes is needed. The biodegradability and toxicity of the post-oxidation products of ILs are still unknown.

Regardless of the application, method of recovery and restoration of ILs, to the system, some of these compounds will sooner or later get into the environment as a result of uncontrolled leakage. The discharge of ILs into environment may cause soil and groundwater contamination. Therefore, the risk to human health and living organisms should be precisely assessed before ILs are used by industry. The growing number of studies of the biodegradability and (eco)toxicity of ILs indicates that they will probably be the first class of chemicals to have been thoroughly investigated from the ecological point of view prior to their application on an industrial scale. The study of the fate and behaviour of chemicals used by industry should be a basic criterion of environmental friendly processes. Additionally, this knowledge and the possibility of designing IL properties by changing the cation and/or anion, makes it possible to select less toxic and more biodegradable ILs for application.

## 7. Acknowledgments

## 8. References

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