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Three degradation pathways of 1-octyl-3-methylimidazolium cation by activated sludge from wastewater treatment process

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ABSTRACT

The biodegradability and degradation pathways of 1-octyl-3-methylimidazolium cation $[OMIM]^+$ by microbial community of wastewater treatment plant in Jeonju city, Korea were investigated. It was found that $[OMIM]^+$ could be easily degraded by the microbial community. New degradation products and pathways of $[OMIM]^+$ were identified, which are partially different from previous results (Green Chem. 2008, 10, 214–224). For the analysis of the degradation pathways and intermediates, the mass peaks observed in the range m/z of 50–300 were screened by using a tandem mass spectrometer (MS), and their fragmentation patterns were investigated by MS/MS. Surprisingly, we found three different degradation pathways of $[OMIM]^+$, which were separated according to the initially oxidized position *i.e.* middle of the long alkyl chain, end of the long alkyl chain, and end of the short alkyl chain. The degradation pathways showed that the long and short alkyl chains of $[OMIM]^+$ gradually degraded by repeating oxidation and carbon release. The results presented here shows that $[OMIM]^+$ can be easily biodegraded through three different degradation pathways in wastewater treatment plants.

1. Introduction

Ionic liquids (ILs) known as green solvent received a great deal of attention in the last two decades (Earle and Seddon, 2000; Plechkova and Seddon, 2008). Actually ILs have industrially applicable properties i.e. material dissolution, thermal stability, catalytic and electrolytic actions, and remarkably safe properties i.e. non-flammability and low volatility. These remarkable features offer a potential possibility for replacement of environmentally unfriendly organic solvents. In addition to these advantageous properties, ILs can be recycled, which is a preferable property for sustainable development (Welton, 1999; Abu-Eishah, 2011). By considering only advantages of ILs, numerous researchers have employed ILs for many applications in various fields, and this leads a dramatic raise in published papers. However the disadvantages of ILs were not completely studied or evaluated. For instance, even though ILs released into environment may not directly affect human beings and animals by inhalation, they may affect persistently the diverse organisms in aqueous environment due to their thermal and chemical stability. In this perspective many researchers have focused to evaluate environmental aspects of ILs in aqueous and soil systems.

During last two decades, several studies were carried to evaluate ILs' environmental aspects such as toxicity and biodegradability. The toxicological effects of ILs in groundwater were studied by using various organisms such as bacteria (Ranke et al., 2004), human cells (Stepnowski et al., 2004), rat cells (Ranke et al., 2007a; Stolte et al., 2007; Torrecilla et al., 2009), and various aquatic organisms including *Lemna minor* (Larson et al., 2008), algae (Cho et al., 2007, 2008a, 2008b, Latała et al., 2005, 2009a, 2009b, 2010, Matzke et al., 2007, Pham et al., 2008a, b, Wells and Coombe, 2006) the fresh water crustacean *Daphnia magna* (Bernot et al., 2005a, b), fresh water snail *Physa acuta* (Bernot et al., 2005a, b) and zebra fish *Danio rerio* (Pretti et al., 2006). In addition to these studies, for more convenient ways, some researchers were also focused to predict the toxicological effects of ILs and reported various methods for this purpose (Alvarez-guerra and Irabien, 2011; Cho et al., 2013; Fatemi and Izadiyan, 2011; Luis et al., 2007,

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2010; Torrecilla et al., 2009, 2010).

Along with the studies related to toxicity of ILs, biodegradation property of ILs is also a crucial issue to understand their whole environmental fate. _ENREF_22The biodegradability of ILs with different head groups, anions, alkyl chains, and functional groups was studied by Gathergood et al. (2004, 2006) and Garcia et al. (2005) by using CO2 headspace test. Harjani et al. (2008) also studied on biodegradable pyridinium based ILs using the same closed bottle method and reported that pyridinium bearing an ester positioned at 1 or 3 of alkyl chain has excellent biodegradability. And Wells and Coombe (2006) reported the biodegradability of imidazolium, ammonium, phosphonium, and pyridinium salts with different alkyl chain lengths by measuring the biochemical oxygen demand (BOD) for 28 days. Using the same method, Romero et al. (2008) also performed biodegradation tests of imidazolium-based ILs with the alkyl chain length (C1–C8) with different anions i.e. Cl^-, $[PF_6]^-$, $[CH_3SO_4]^-$ and $[C_2H_5SO_4]^-$ in the presence or absence of glucose. And they showed that the tested ILs were poorly degradable in presence and absence of other carbon source. Docherty et al. (2007, 2010) investigated the biodegradation of imidazolium and pyridinium with different alkyl chain lengths and suggested that imidazolium and pyridinium-based ILs with six or more alkyl chains are biodegradable. They also reported that the pyridinium ring was opened by bacterial metabolism, whereas the imidazolium ring was not open (Docherty et al., 2007). Unlike these studies performed in aqueous phase, Modelli et al. (2008) monitored the environmental fate of ILs in soil. Similarly, Markiewicz et al. (2015) examined biodegradability of an imidazolium based IL in soil and soil amended with activated sludge. Moreover, for the rapid degradation of ILs, Siedlecka et al. (2008) used a Fenton-like system that induces the catalytic decomposition of dilute hydrogen peroxide by iron (II), generating hydroxyl radicals. Furthermore, for the same purpose, Zhou et al. (2013a, 2013b), treated some ILs in an ultrasound assisted zero-valent iron activated carbon micro-electrolysis. For the treatment of non-biodegradable IL such as 1-butyl-3-methylimidazolium chloride, Stolte et al. (2008) performed an electrochemical degradation experiment in an electrolysis cell equipped with two electrodes made of iridium oxide (anode) and stainless steel (cathode). For further information about the environmental risk assessments of ILs e.g. toxicity and/or biodegradation, authors suggest review papers by Ranke et al. (2007b), Pham et al. (2010), Coleman and Gathergood (2010), Stolte et al. (2011), Petkovic et al. (2011), and Cvjetko Bubalo et al. (2014).

During biodegradation of ILs, identification of the degradation products is an important step because the original compound could be transformed into more toxic chemical structures by microbial activities as Deng et al. (2015) mentioned. And from that kind of study, we can have better understanding on the whole environmental aspects by providing chemical structures of intermediates which are required for detailed studies – e.g. toxicity, adsorption, and mobility etc. – of the intermediates. For the purpose, over the last decade, the studies on the degradation pathway of ILs have been investigated. Preliminary study on degradation pathway of IL was reported by Jastorff et al. (2003). They considered the degradation pathways of 1-butyl-3-methylimidazolium cation within their systematic algorithm. In a practical test, the degradation products of the same target compound were identified by Kumar et al. (2006) by gas chromatography mass spectrometry (GC–MS). Moreover, our research group (Pham et al., 2008) reported the degradation pathways of 1-butyl-3-methylpyridinium cation $[BMPy]^+$ by the oxidation on the butyl chain. In contrast, Docherty et al. (2010) indicated that the degradation pathways of pyridinium-based cations depend on the alkyl chain length, i.e., the biodegradation of $[BMPy]^+$ involved the unsaturation of butyl side chain and hydroxylation of aromatic ring, whereas the biodegradation of 1-octyl- and 1-hexyl-3-butylpyridinium cations involved the unsaturation and hydroxylation of the long side chain. Zhang et al. (2010, 2011) reported that 2-ethylpyridinium cation $[Py2]^+$ has different degradation pathways according to types of bacteria such as *Corynebacterium* sp(Zhang et al., 2010) and *Pseudomonas fluorescens* (Zhang et al., 2011), which are ubiquitous in soil. Stolte et al. (2008) identified the biodegradation pathway of 1-octyl-3-methylimidazolium cation $[OMIM]^+$ by LC-MS. The degradation pathway shows that the oxidation for the carbon fragment started from the end of long alkyl chain until forming 3-carboxymethyl-1-methylimidazolium cation. Very recently, Deng et al. (2015) reported biodegradability and the metabolites of pyridinium, pyrrolidinium, and ammonium based ILs with an isolated strain of *Rhodococcus rhodochrous* ATCC 29672 or activated sludge. Nevertheless the biodegradability and degradation pathways should be further studied especially with microbial communities from real activated sludge processes because they are dependent on spatial and temporal constraints. In the present study we therefore investigated if $[OMIM]^+$ is degradable and how $[OMIM]^+$ is degraded by microbial community taken from wastewater treatment factory located in Jeonju, South Korea. $[OMIM]^+$ was chosen because in general $[OMIM]^+$ based ILs have many possibilities to be used as catalysis (Maruyama et al., 2002, Maleki et al., 2007), metal extracting system (Chun et al., 2001) and lubricant additives (Yang et al. 2014) in industrial areas.

2. Experiments

2.1. Chemicals

$[OMIM]^+$ bromide was purchased from C-tri co. (99% purity, Su-Won, Korea). $[OMIM]^+$ bromide was used as received without any pretreatment. Acetonitrile and formic acid used as mobile phase in high-performance liquid chromatography system (HPLC) were purchased from J. T. Baker and Acros (USA), respectively.

2.2. Preparation of activated sludge

The activated sludge used to $[OMIM]^+$ biodegradation was obtained from aeration tank of a municipal wastewater treatment plant (WWTP) in Jeonju, Korea. According to the modified OECD screening test (OECD 301, 1997), the sludge was filtered using a fine sieve to remove any coarse particles and centrifuged at 3000 × g for 5 min. The settled sludge was washed with fresh medium comprised 85 mg KH_2PO_4, 217.5 mg K_2HPO_4, 334 mg $Na_2HPO_4 \cdot 2H_2O$, 5 mg NH_4Cl, 36.4 mg $CaCl_2 \cdot 2H_2O$, 22.5 mg $MgSO_4 \cdot 7H_2O$, 0.25 mg $FeCl_3 \cdot 6H_2O$, and 0.4 mg EDTA di-sodium salt in 1 L. This process was repeated three times to ensure there is no present any chemical in the sludge. The final supernatant was decanted, and the remaining washed activated sludge was re-suspended in mineral medium to yield a concentration of 5 g SS/L (dry weight) and subsequently aerated.

2.3. Biodegradation test

2.3.1. Biodegradation test in the OECD 301 conditions

This study was performed according to the guideline of OECD 301 (1997). After filling 50 mL of the medium (pH 7.5) in a 100-mL Erlenmeyer flask, the prepared organisms of 1 mL were inoculated, and a stock solution of $[OMIM]^+ Br^-$ dissolved in deionized water was injected into the flask as the sole organic carbon at an applied $[OMIM]^+$ concentration of 36 μM. For the abiotic test, 1% solution containing HCl and 0.25 M $HgCl_2$ was used as the poison. The flasks were capped with air-permeable cotton bungs, and