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Assessment the ecotoxicity and inhibition of imidazolium ionic liquids by respiration inhibition assays

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ABSTRACT

The ecotoxicity and inhibition of 12 imidazolium ionic liquids (ILs) with alkyl chain from C4 to C10 and chloride (Cl^-), tetrafluoroborate (BF_4^-) and bis(trifluoromethanesulfonyl)imide (NTf_2^-) anions have been studied by means of respiration inhibition assays using activated sludge collected from a wastewater treatment plant. This test represents an alternative easy, economic and quick way to evaluate the true impact of ILs on activated sludge-based wastewater treatment. For comparison purposes, the EC_{50} values were also determined by the Microtox test (*Vibrio fischeri*). It was observed that this widely used microbial test overestimates the effect of the ILs on biological wastewater treatment facilities, especially in the case of ILs with lower ecotoxicity. The results of the biological tests showed that the alkyl chain length plays a crucial role in the ecotoxicity of ILs. A significant increase of the toxicity with the length of the n-alkyl chain was found. Regarding to the impact of the anion, the ecotoxicity measured by respiration inhibition assays follows the order $NTf_2^- > Cl^- > BF_4^-$, being the anion effect higher as decreasing the length of cation alkyl chain. According to the hazard substances ranking for aquatic organisms (Passino and Smith, 1987), imidazolium ILs with C4 alkyl chain can be classified as "practically harmless" compounds whereas those with alkyl chains C8 or C10 correspond to "highly toxic" species.

1. Introduction

In the past 20 years, ionic liquids (ILs) have attracted increasing attention as a new generation of green solvents with potential uses in various industrial fields (Petkovic et al., 2011). ILs are based on combined organic cations and organic or inorganic anions with a melting point below 100 °C. They are characterized by low vapor pressure and high thermal and chemical stabilities. Due to the large number of feasible combinations, it is possible to synthesize ILs with selected properties for numerous applications (Plechkova and Seddon, 2008). The increasing interest for these novel and versatile compounds is mainly focused on the following potential industrial applications: separation processes, catalysis, electrochemistry and materials science. However, the impact that ILs, especially those with high water solubility, can cause on aquatic organisms has been scarcely studied so far (Pham et al., 2010; Docherty et al., 2015).

ILs can be discharged into the aquatic environment due to accidental spills, containers washing operations, leaching from waste disposal sites, as well as waste streams inefficiently treated in current wastewater treatment plants (Tsarpali and Dailianis, 2015). Conventional biological processes are widely used as a cost-effective strategy for wastewater treatment. However, the potential application of such processes to a given effluent must consider some critical issues, as ecotoxicity and biodegradability. Preliminary results have revealed that there is insufficient evidence to confirm the degradation of imidazolium, thiazolium and pyridium ILs, whereas those derived from aliphatic amines and organic acids could be considered as potentially biodegradable (Peric et al., 2013; Neumann et al., 2014; Jordan and Gathergood, 2015; Diaz et al., 2016). In addition, the IL structure plays a key role on the inhibitory effect over the activated sludge performance. As example, alkyl methyl imidazolium ILs have been claimed as non-biodegradable compounds and they do not provoke any toxic effect on activated sludge (Gathergood et al., 2006; Romero et al., 2008; Quijano et al., 2011; Diaz et al., 2016; Rodriguez Castillo et al., 2016). The degradation of easily biodegradable substrates, like sodium n-dodecyl sulfate or glucose in presence of ILs, after long acclimation periods has been reported (Quijano et al., 2011; Rodriguez Castillo et al., 2016). However, the addition of ILs as Aliquat, 1-methyl-3–2-methoxyethyl-imidazolium or 1-methyl-3-butenyl-imidazolium provoked complete inhibition of the microbial community present in activated sludge (Quijano et al., 2011; Rodriguez Castillo et al., 2016).

Different standard toxicity tests have been proposed in the literature and regulations. Several organisms have been used as bioindicators, including invertebrate (*Daphnia magna*, ISO 6341) (Samorì et al., 2010;

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Pham et al., 2010; Stolte et al., 2012), algae (*Selenastrum capricornutum*, ISO 8692) (Cho et al., 2008; Peric et al., 2013; Costa et al., 2015), plant (*Lemna minor*, ISO/CD 20079) (Jastorff et al., 2005; Matzke et al., 2007; Stolte et al., 2007) or mammalian cells (*Rat leukemia cells*, IPC-81) (Ranke et al., 2007; Stolte et al., 2013), as a reproducible IL toxicity screening tool. These micro/organisms are exposed to different concentrations of ILs under controlled conditions and the evolution of a characteristic response of each organism is monitored. Among them, luminescent microbial test with the microorganism *Vibrio fischeri* (ISO 11348) is one of the most used for acute toxicity measurements because it is quick, simple, cost-effective and sensitive to evaluate IL ecotoxicity (Ranke et al., 2004; Johnson, 2005; Romero et al., 2008; Viboud et al., 2012; Ventura et al., 2014; Costa et al., 2015; Hernández-Fernández et al., 2015). However, the main drawback of the aforementioned methods is that the response of the microorganism used does not represent the behavior of the microbial community present in activated sludge from biological wastewater treatment systems. Consequently, the ecotoxicity data from those tests could over/underestimate the effect of ILs on wastewater treatment facilities. Meanwhile, the toxicity of ILs can be studied by a respiration inhibition test (OECD 209, ISO 8192) where the impact of ILs on activated sludge is inferred from specific dissolved oxygen uptake rate measurements, intimately related to the microbial activity. After data collection, the EC_{50} value (defined as the effective concentration of a sample that causes 50% inhibition) can be determined. Markiewicz et al. (2013) reported a pioneer work investigating the influence of ILs on activated sewage sludge communities. A respiration inhibition test was applied using activated sludge from different domestic and industrial sources. Results obtained generally match the IL ecotoxicity trends found for other organism and test systems. It was suggested that EC_{50} values obtained from *Vibrio fischeri* can be reliably used to assess the IL inhibition potential.

The alkyl methyl imidazolium ILs are non-volatile, non-flammable and present high thermal stability, being excellent wide-range solvents (Gordon, 2001; van Rantwijk et al., 2003). Thus, that family has a high potential of entering the water bodies through to industrial discharges. In the current work, the ecotoxicity of 12 imidazolium ILs in aqueous phase has been assessed by obtaining the EC_{50} values upon respiration inhibition assays with an activated sludge from a domestic sewage treatment plant. The effect of the IL structure in the ecotoxicity has been systematically analyzed by studying common cation/anion series, including imidazolium ring with different alkyl chain length (C_4-C_{10}) and three remarkably different anions (Cl^-, BF_4^-, NTf_2^-). For the sake of comparison, EC_{50} values were also obtained by the Microtox standard procedure. Structure-activity relationships were stablished to analyze simultaneously the cation and anion influence. Results obtained from two different tests were compare in order to check if the tests provide analogous information, which could be used to define a treatment strategy to deal with these compounds.

2. Materials and methods

2.1. Ionic liquids

Imidazolium ILs with different chain lengths (4, 6, 8 and 10 carbons) and anions (chloride (Cl^-), tetrafluoroborate (BF_4^-) and bis(trifluoromethilsulfonyl)imide (NTf_2^-)) were selected for this study (Table 1).

ILs are used without previous purification and named according to the number of carbons of the alkyl chain substituent as the butyl group “B”, hexyl group “H”, octyl group “O” and decyl group “D”, and the termination Cl, BF_4 or NTf_2 corresponds to the anion. The suffix “mim” corresponds with the imidazolium group (Table 2).

2.2. Inoculum and culture medium

Activated sludge for the respiration inhibition test (OECD 209, ISO 8192) was collected from a domestic sewage treatment plant (Madrid, Spain), and did not undergo to any acclimation process to the ILs studied. Waste sewage sludge was maintained in a sequencing batch reactor (SBR) at 25 °C and supplied with sodium acetate and glucose as carbon sources (50:50 w/w on chemical oxygen demand (COD) basis) at an organic load rate of 0.4 mg COD/mg VSS·day, referring VSS to volatile suspended solids. The medium was supplemented with ammonium sulfate, phosphoric acid and mineral salts as nitrogen, phosphorous and micronutrients sources ($FeCl_3$, $CaCl_2$, KCl and $MgCl_2$), respectively. A COD:N:P ratio of 100:5:1 (w/w) was fixed and mineral salts were also added as micronutrients supply in a COD: micronutrients (Fe, Ca, K and Mg) ratio of 1:0.05. Biomass concentration in the reactor was maintained at around 3500 mg VSS/L.

2.3. Inhibition assays

Respiration inhibition tests with activated sludge were carried out according to the method proposed by Polo et al. (2011). The procedure consists on short-term respirometric measurements using unacclimated sludge (350 mg VSS/L) where an easily biodegradable substrate (sodium acetate) is fed alone or together with different concentrations of ILs. Assays were carried out in a Liquid-Static-Static (LSS) respirometer (Chica et al., 2007), monitoring the dissolved oxygen concentration decay. Aeration and oxygen probes were controlled by an electronic interface. The respirometer operated with two independent reactors simultaneously to check the reproducibility. The reactors have very small headspace so that oxygen transfer from the gas to the liquid can be neglected. They were placed in a thermostatic bath and continuously stirred by magnetic bars. Nitrification was inhibited by using N-allyltiourea. Fresh activated sludge was used in each test to avoid partial acclimation of the microorganisms to the target chemicals, which could lead to possible underestimation of the toxic effects. The biomass activity was measured in terms of specific exogenous oxygen uptake rate (SOUR). The inhibition [1] is defined as function of the parameter γ [2] and the ratio the specific exogenous oxygen uptake rate for the reference substance (sodium acetate) in presence of a given concentration of the ILs ($SOUR_T$) and SOUR the obtained value for the reference substance ($SOUR_R$). Both measures are corrected by the value for the endogenous SOUR.

$$\text{Inhibition}(\%) = (\gamma)\cdot\frac{SOUR_T}{SOUR_R} \quad (1)$$

$$\gamma = \frac{SOUR_R - SOUR_T}{SOUR_T} \quad (2)$$

Inhibition caused by the ILs was assessed in terms of EC_{50}, defined as the effective concentration causing 50% reduction of SOUR ($\gamma = 1$). It is calculated using i) a logistic model that establish a relationship between the inhibition percentage and the logarithm compound concentration [3] and ii) a linear fit between the logarithm of parameter γ and the logarithm of IL concentration [4]:

$$\text{Inhibition}(\%) = \frac{100}{1+10^{-k(\log C - \log EC_{50})}} \quad (3)$$

$$\log\gamma = a + b\log C; EC_{50} = 10^{-a/b} \quad (4)$$

2.4. Ecotoxicity test

Ecotoxicity measurements were also carried out following the standard Microtox ® test procedure (ISO, 11348-3, 1998). This test is based on the decrease of light emission by the marine bacteria *Vibrio fischeri* (*Photobacterium phosphoreum*). A Microtox M500 Analyzer (Azur Environmental) was used to measure the inhibition of the light emitted by the bacteria after 15 min contact time with the sample. Previously, the pH was adjusted into the range 6–8. The results were expressed as EC_{50} defined as the effective concentration causing 50% reduction of

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