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Phytotoxicity of ionic liquids with different structures on wheat seedlings and evaluation of their toxicity attenuation at the presence of modified biochar by adsorption effect

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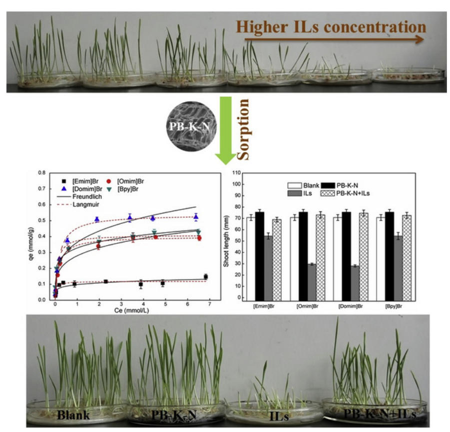
HIGHLIGHTS

- The toxic effect of eight ionic liquids (ILs) on wheat seedlings was evaluated.
- Modified biochar (PB-K-N) all efficiently removed the ILs from aqueous solutions.
- Explore removal regularities and the possible mechanisms involved in ILs sorption.
- PB-K-N could strongly decrease or alleviate toxicity of most of ILs toward wheat.

GRAPHICAL ABSTRACT



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ABSTRACT

The toxic effects of eight common ionic liquids (ILs) on wheat seedlings was evaluated with specific emphasis on the influence of concentration range, anion species and cation chain length of ILs. The growth of wheat seeds was significantly inhibited by ILs, especially under higher concentration, presence of the fluoride anion and the longer alkyl chain length of the cation. The modified biochar (PB-K-N) efficiently removed the ILs from aqueous solutions, the order of the adsorption capacities was as follows: [Bmim]OAc [Bmim]$C_7H_5O_2$ [Bmim]BF_4 [Bmim]Br, [Domim]Br [BPy]Br [Omim]Br [Bmim]Br [Emim]Br. Furthermore, the wheat growth of all ILs groups except [Bmim]BF_4 group in the presence of PB-K-N was also similar to that of the control groups, which clearly demonstrated that PB-K-N could decrease or alleviate toxicity of ILs toward wheat by adsorption effect. Therefore, the biochar application was

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effective in improving plant resistance to ILs stress by adsorption, to reduce the phytotoxicity of ILs and provide an alternative approach for the utilization of PB-K-N in ILs contaminated water and soils.

1. Introduction

Ionic liquids (ILs) are completely composed of cations and anions which are considered as green replacements for traditional organic solvents (Dai et al., 2017). ILs have attracted tremendous attention due to their unique properties including low melting points, high thermal and electrochemical stability, negligible vapor pressure, non-flammability and good catalytic performance (Zhang et al., 2006). Therefore, ILs have been extensively used in gas capture (Zhang et al., 2012), electrochemistry (Kar et al., 2016), catalysis (Kar et al., 2016), separation and synthesis (Morandeira et al., 2017), as well as in the pharmaceutical field (Adawiyah et al., 2016), biotechnology and biodegradation (Quijano et al., 2011; Salar-Garcia et al., 2017). Given the above application, ILs may be released into the environment through transport, storage and discharge of industrial wastewater. With low volatility of ILs, their influences to atmospheric pollution are negligible. Accordingly, a large number of researchers have paid attention to their potential impacts on the aquatic and terrestrial environments (Bubalo et al., 2014b; Amde et al., 2015). Currently, the toxicity of ILs for enzyme, bacterium, microorganisms, algae, higher plants, animals and fish has been repeatedly reported (Pham et al., 2010, 2016; Biczak et al., 2016; Thamke and Kodam, 2016). Biological toxicity of partial ILs toward aquatic organisms is even higher than that of traditional organic solvents, which cannot be ignored or underestimated (Cho et al., 2008). Moreover, the potential toxicity of ILs may endanger human health because of the cytotoxic effects of ILs on mammalian cell lines such as human carcinoma cell lines (Frade et al., 2009). The toxicity of ILs is mainly associated with the cation kind and the alkyl-chain length, while various type of ILs anions is shown to be less significant for their acute toxicity (Ruokonen et al., 2016). Even though the toxicity studies linked to the properties of ILs have been discussed, the systematic studies for the toxic effects of ILs with different alkyl-chain lengths and anions on plants especially on crops have been rarely explored (Wang et al., 2009; Bubalo et al., 2014a; Liu et al., 2015).

ILs are difficult to degrade by natural processes owing to their high stability.Therefore, effective technologies need to be developed for the removal and recovery of ILs from ecosystem prior to their environmental impact. Adsorption is considered as a sustainable and green technique for contaminants removal from wastewater and remediation of contaminated soil media because of its easy operation, high efficiency and good economies (Mai et al., 2014; Yu et al., 2016c), especially for low concentrations of pollutants. Biochar, a kind of biomass-derived carbon material, is pervasively used to eliminate chemical contaminants such as heavy metals, organic compounds, and other emerging pollution (Tan et al., 2015; Liu et al., 2016a; Tang et al., 2017; Xu et al., 2017), among which ILs removal using the biochar may be the most promising control strategy with plenty of advantages over traditional adsorbents. Besides their abundant raw material and environmentally friendly properties, another main advantage of biochars is that their porous structure and functional groups play extremely important roles in ILs removal (Palomar et al., 2009; Lemus et al., 2012; Qi et al., 2014; Shi et al., 2016; Yu et al., 2016b). The corresponding relationships between physicochemical properties of ILs and their adsorptive performance on biochar are seldom studied in the relevant papers (Lemus et al., 2012; Shi et al., 2016; Wang et al., 2016). To the authors' best knowledge, the adsorption regularities of partial ILs in this work have not been investigated. Despite many studies regarding the alleviation or reduction toxic effects of heavy metal on plants by biochars (Mosa et al., 2016; Seneviratne et al., 2017), there is lack of adequate data concerning biochar (in particular modified biochar) effect toward plant under ILs stress.

In the present study, the effects of eight ILs with different length of alkyl chains and anions on the toxicology for wheat, and adsorptive behavior were studied. The four ILs containing the same cation and various anions were used for comparing different toxic and adsorptive influence from their chemical structure, and the four other elected ILs were comprised of the identical anions and different cations. The removal performance of modified biochar for ILs was comprehensively studied, and the seeds germination and early growth of the seedlings under the pressure of ILs with the modified biochar were also evaluated. The specific goals of this work were to:(1) evaluate the acute toxicity of the ILs with different chemical structures on wheat according to their growth patterns, (2) compare sorption capacities of the ILs on biochar and explore the possible mechanisms involved in ILs sorption, (3) determine the biological effects of ILs-loaded biochar on the seed germination and growth.

2. Materials and methods

2.1. Materials

In this work, peanut shell and wheat seeds (*Triticum aestivum* L.) were selected from a local farm in Henan, China. The wheat was selected to evaluate toxic effects of the ILs since it is one of the most widely planted crops in China and around the world. The eight different ILs were all purchased from Chengjie Chemical Co., Ltd. (Shanghai, China), whose detailed informations are depicted in Table 1. All other chemical reagents used in this study were of analytical grade. All other chemical reagents used in this study were of analytical grade and all solutions were prepared with deionized (DI) water.

2.2. Preparation and properties of biochars

Biochar was produced from peanut shell through slow pyrolysis and modification, which could be found in our previous study (Yu et al., 2016a). Briefly, the treated peanut shell was pyrolyzed in a tubular furnace at 700 °C for 2 h under N_2 atmosphere, and obtained biochar was mixed with KOH (mass ratio of 1: 2) for pyrolysis under identical conditions again. The activated product was dried after washing, and the sample was oxidized by $(NH_4)_2S_2O_8$ to prepare the modified biochar (i.e. PB-K-N).

The used instruments for characterization of modified biochar also have been detailedly illustrated in our previous reports (Yu et al., 2016a). The porous structures on PB-K-N were