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Research article

Lead sorption by biochar produced from digestates: Consequences of chemical modification and washing

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ABSTRACT

The main objectives of this work are to investigate the consequences of different chemical treatments (*i.e.* potassium hydroxide (KOH) and hydrogen peroxide (H_2O_2)) and the effect of biochar washing on the Pb sorption capacity. Biochars derived from sewage sludge digestate and the organic fraction of municipal solid waste digestate were separately modified with 2 M KOH or 10% H_2O_2 followed by semi-continuous or continuous washing with ultrapure water using batch or a column reactor, respectively. The results showed that the Pb adsorption capacity could be enhanced by chemical treatment of sludge-based biochar. Indeed, for municipal solid waste biochar, the Pb maximum sorption capacity was improved from 73 mg g^{-1} for unmodified biochar to 90 mg g^{-1} and 106 mg g^{-1} after H_2O_2 and KOH treatment, respectively. In the case of sewage sludge biochar, it increased from 6.5 mg g^{-1} (unmodified biochar) to 25 mg g^{-1} for H_2O_2 treatment. The sorption capacity was not determined after KOH treatment, since the Langmuir model did not fit the experimental data. The study also highlights that insufficient washing after KOH treatment can strongly hinder Pb sorption due to the release of organic matter from the modified biochar. This organic matter may interact in solution with Pb, resulting in an inhibition of its sorption onto the biochar surface. Continuous column-washing of modified biochars was able to correct this issue, highlighting the importance of implementing a proper treated biochar washing procedure.

1. Introduction

Metal pollution is of very high concerns for human health due to their persistence and toxicity in the environment even in low concentrations. Lead (Pb) has been recognized as one of the most toxic metals in Europe (Tóth et al., 2016). Pb pollution often originates from smelters, mining, industrial discharges, car batteries and Pb-based piping for water supply. Discharge of untreated wastewater from the industry may cause an adverse effect to animals and humans. One study reported a case of severe Pb poisoning of children in Haina (Dominican Republic), attributed to a car battery recycling factory (Kaul et al., 1999). Many conventional treatment methods have been developed to decrease Pb levels in contaminated water, including chemical precipitation, coagulation, ion exchange and adsorption (Inyang et al., 2016).

Lead sorption by activated carbon (Cechinel et al., 2014), agricultural waste-derived biochars (*e.g.* pine wood or rice husk) (Liu and Zhang, 2009), natural zeolite and kaolinite clay (Andrejkovicova et al., 2016; Jiang et al., 2009) have been reported. Recent studies show the potential application of biochar in metal-polluted water treatment due to its high specific surface area and surface properties, *e.g.* surface charge and hydrophobicity (Liu and Zhang, 2009; Zielińska et al., 2015). Indeed, the solid organic by-product generated by anaerobic digestion of sludge from wastewater treatment plants has been considered as an alternative source of raw material to manufacture adsorbents (*i.e.* biochar) for metal removal (Zhang et al., 2013). Biochar is a black solid char derived from the pyrolysis of organic waste materials in a limiting oxygen environment (Inyang et al., 2016). Through the pyrolysis technology, it promotes the recycling of organic waste and supports

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the environmental sustainability for the community. Biochar has been widely used for many purposes in the environment, such as soil conditioner (Saifullah et al., 2018) or filtration medium in wastewater treatment (Mohan et al., 2014). However, there are only few studies on the use of organic by-product sludge biochar to remove metals from water. Biochar produced from organic digested sludge has been used for As(V), Cd(II), Cr(III), Cu(II) and Ni(II) removal from water (Inyang et al., 2012; Jin et al., 2014). A few studies have been dedicated to the Pb sorption by sludge biochars, which can be found in the literature (Table S1).

The main mechanisms involved in Pb sorption onto the biochar are cation exchange, surface complexation, surface precipitation and physical adsorption (Ho et al., 2017; Li et al., 2017). Among these mechanisms, cation exchange of Pb with Ca^{2+} and Mg^{2+} and is the main contributor to Pb sorption by sludge-based biochar, accounting for 40–52%. Exchanges can also occur to a lesser extend with K^+ and Na^+ and (<8.5%) (Li et al., 2017), which is in a good agreement with the study of Lu et al. (2012). The surface complexation between Pb and surface functional groups of biochar (*e.g.* carboxyl and hydroxyl groups) also plays a major role, contributing for about 40% of Pb removal (Li et al., 2017). Surface precipitation can also occur since sludge biochars generally contain high amounts of phosphate (PO_4^{3-}) and carbonate (CO_3^{2-}) on their surface. Finally, the high surface area of biochar may favor physical adsorption of Pb onto biochar active pore sites (Agrafioti et al., 2014). The relative importance of these sorption mechanisms depends on the biochar feedstock.

Compared to activated carbon, the sorption capacity for Pb by biochar is low and thus numerous modification methods have been applied to improve it. The common treatment methods of biochar are physical activation with steam and chemical treatment with acids, oxidizing agents and alkali solutions (Sizmur et al., 2017). The steam activation of biochar is usually performed at high temperature (>800 °C), thus increasing the adsorbent cost which it is not feasible for large scale operation (Wang and Liu, 2018). The chemical modification of biochar is considered as an inexpensive technique since no heat is required during the operation. Treatment of biochar with KOH increases the surface hydroxyl groups and the basicity on the biochar surface (Fan et al., 2016; Li et al., 2014), dissolves ash and condenses organic matter (*e.g.* lignin and celluloses) in the biochar (Lin et al., 2012; Liou and Wu, 2009; Liu et al., 2012). Modification of biochar with H_2O_2 was found to increase O–containing functional groups, particularly carboxyl groups, on the biochar surfaces (Rajapaksha et al., 2016). Such chemical modifications could induce a leaching of organic matter and mineral ash from biochar pore sites. Thus, after the treatment, several batch washing of the biochar with ultrapure water are required until the pH becomes stable or neutral (Huang et al., 2017; Regmi et al., 2012; Wu et al., 2017). Usually, batch washing of biochar is performed without any concerns on the release of organic or inorganic compounds (*e.g.* PO_4^{3-} and CO_3^{2-}) from biochar. Since this can influence the sorption of metals by biochar, the effective elimination of these released compounds should be considered. Unfortunately, there is currently a lack of information on the effect of biochar washing on the elimination of the released compounds from biochar after chemical treatment.

This work aims to study the consequences of chemical treatments of biochar and subsequent washing conditions on the Pb sorption capacity. Two chemical reagents (*i.e.* KOH and H_2O_2) and two washing modes (semi-continuous batch washing as usually performed in the literature and continuous column washing) were applied to raw biochars from sewage sludge and the organic fraction of municipal solid waste. The consequences onto the Pb sorption were evaluated through adsorption kinetic and isotherm studies.

2. Materials and methods

2.1. Feedstocks and biochar preparation

Raw sewage sludge digestate (RSS) and raw organic fraction of municipal solid waste digestate (RMSW) were obtained separately from a wastewater treatment plant and from a solid waste treatment plant located in France. Biochar from RSS was industrially pyrolyzed at 350 °C for 15 min using the Biogreen® technology, while biochar from RMSW was produced at lab scale. Based on the study of Pituello et al. (2014), the RMSW was dried overnight at 65 °C to reduce the initial moisture content to less than 10%. After that, it was crushed and sieved into a particle size of 2 mm to separate impurities such as plastic bags, needles and glasses. The RMSW-derived biochar was produced at 400 °C using porcelain crucibles with lid-cover (Haldenwanger 79 MF, Germany) in a muffle furnace (heating rate 15 °C min^{-1}) for 1 h. The obtained materials were left to cool down at room temperature with the lids cover.

As recommended by Jin et al. (2014), Wu et al. (2017) and Xue et al. (2012), biochars were washed by semi-continuous means with ultrapure water for 3–4 times (*i.e.* 2 g of biochar per 200 mL of ultrapure water per washing) until a stable pH was obtained. The RSS-derived biochar produced at 350 °C and the RMSW-derived biochar produced at 400 °C are named as SS^{sem} and MSW^{sem}, respectively.

2.2. Biochar chemical modification

In this study, KOH and H_2O_2 were selected for the chemical modification of biochar due to the great enhancement of metal sorption (Rajapaksha et al., 2016). To prepare the modified biochar with H_2O_2, 2 g of biochar was placed into 20 mL of a 10% H_2O_2 solution and shaken at 25 (±2) °C for 2 h (modified from Xue et al., 2012). Biochar treated with KOH was prepared by mixing 2 g biochar with 100 mL of 2 M KOH solution and was shaken at 25 (±2) °C for 2 h (modified from Jin et al., 2014). The total mass of biochar used was around 10 g per each chemical treatment. After chemical modification, biochars were all semi-continuously washed with ultrapure water. Some biochars were submitted to a subsequent continuously washing to study the influence of the washing conditions.

For the semi-continuous washing, the chemically modified biochar was washed in batch by stirring 2 g of biochar in 200 mL of ultrapure water at 20 (±2) °C. The batch washing was repeated for 3–4 times until the pH became stable (Jin et al., 2014; Wu et al., 2017; Xue et al., 2012). For the continuous washing, a part of the semi-continuous washed biochar was subsequently washed by continuous circulation of ultrapure water in a glass column (2.8 cm in diameter and 42.5 cm in height). A peristaltic pump (Ismatec Reglo Analog, Model No. ISM827, Ismatec SA Company, Switzerland) was used to maintain the up-flow velocity of 0.77 (±0.01) cm min^{-1}. Glass beads (2 mm size) were used at the bottom of the column to generate the flow distribution. The column was flushed continuously for at least 70 h at 20 (±2) °C with a hydraulic retention time of 6 h.

Once washed, the modified biochars were recovered using VWR filter papers, then dried in an oven at 50 °C overnight and further kept in a desiccator prior to use. The semi-continuously washed H_2O_2 and KOH-treated biochars are labeled as MSW-$H_2O_2^{sem}$, MSW-KOH^{sem}, SS-$H_2O_2^{sem}$ and SS-KOH^{sem} for RMSW and SS based biochar, respectively. The continuously washed H_2O_2 and KOH-treated sewage sludge biochars are labeled as SS-$H_2O_2^{con}$ and SS-KOH^{con}, respectively.