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Assessing arsenic redox state evolution in solution and solid phase during As(III) sorption onto chemically-treated sewage sludge digestate biochars

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Abstract

This work aimed to determine arsenic redox state distribution during As(III) sorption onto chemically-modified biochars. A solid-liquid extraction protocol using phosphoric (0.3 M) and ascorbic (0.5 M) acids at 80 °C for 20 min was established to ensure a quantitative recovery and stability of As(III) during the extraction. During sorption experiments, the redox conversions of As occurred and As(III) was either stable or partially oxidized in solution. The As distribution strongly varies depending on the biochar chemical treatment

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performed as well as the selected washing procedures (batch *versus* column washings).

As(III) oxidation was favored with the KOH-modified biochar washed in batch mode. This oxidation was mostly induced by the biochar solid compounds rather than by soluble compounds released in solution. The As redox state distribution of As sorbed onto the biochars was successfully assessed using the extraction procedure. Arsenic was predominantly sorbed as As(III) (76–92%) onto the biochars.

Keywords: Sewage sludge digestate biochar, As(III) removal, arsenic redox distribution, sorption

1. Introduction

Elevated concentrations of arsenic (As) in water bodies represent a global environmental and health issue because of its toxic features. The increasing threats of As contamination mainly originate from anthropogenic sources, particularly mining, industrial and agricultural activities (Vithanage et al., 2017). Arsenic toxicity in targeted organisms is strongly linked to its chemical speciation, especially its redox state. Indeed, organic forms of As such as monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA) present intermediate toxicity, whereas inorganic As species, *i.e.* arsenite (As(III)) and arsenate (As(V)), are known as the most toxic ones (Hughes et al., 2011).

Regarding the acute toxicity of As, efforts have been made to efficiently remove As from polluted water streams by using several treatment techniques such as oxidation,

coagulation-flocculation, ion exchange, phytoremediation, membrane separation and adsorption (Jadhav et al., 2015; Jain and Singh, 2012; Singh et al., 2015). Among these methods, sorption is well known as a cost effective approach to remediating metal(loid)s polluted water (Ahmad et al., 2014). Biochar is a charcoal obtained from pyrolysis of biowaste materials in an oxygen-limited environment (Novotny et al., 2015). Because of the low-cost and the great abundance of biowaste feedstocks (*e.g.* sewage sludge digestate obtained from wastewater treatment streams), biochars are considered as alternatively potential sorbents for metal(loid)s removal from water (Mohan et al., 2014). Most of the sewage sludge biochars were used to sorb cationic metals like lead (Pb(II)) and chromium (Cr(VI)) (Ifthikar et al., 2017; Lu et al., 2012; Zhang et al., 2013), and to a lesser extent to metalloids like arsenic (As) and antimony (Sb). Thus, the development of sewage sludge biochar with chemical modification to improve As sorption (Sizmur et al., 2017) as well as the investigation of As speciation is of great interest. To date, As redox species repartition during the adsorption process onto biochar, and the role of biochar on redox modifications of As are not known. Hence, it is worthwhile to investigate the redox transformation of As(III) during its sorption onto biochars, since As(III) is more toxic and weakly bound to solid material than As(V) (Manning et al., 2002). Therefore, the As(III) oxidation induced by biochars is an important reaction that can possibly decrease As toxicity in As polluted water bodies.

Arsenic speciation in solid-phase samples can be accessed via X-ray absorption near edge structure (XANES) spectroscopy (Niazi et al., 2018a, 2018b). However, the use of this technique is limited due to the very high operation cost and the accessibility to synchrotron

facilities. Solid-liquid extraction followed by separation techniques, for instance liquid chromatography (LC) coupled to spectrometric detection techniques such as atomic fluorescence spectroscopy (AFS) or inductively coupled plasma mass spectrometry (ICP-MS), could be an effective and more accessible technique to determine the As species sorbed onto the solid-phase samples.

The present study focused on the determination of the inorganic As redox distribution in raw sewage sludge digestate (SSD) biochar and the H_2O_2 and KOH modified biochars before and after As(III) sorption using an analytical approach based on a solid-liquid extraction. At present, no study has reported on the implementation of an extraction method to recover As(III) and As(V) from the solid-phase of biochar. An extraction method using phosphoric and ascorbic acids as extracting agents was thus investigated before studying the possibility of redox transformations of As(III) during sorption experiments onto the biochar. The main objectives of this work were to: (1) validate the extraction procedure for As(III) and As(V) speciation in the biochars; (2) investigate the sorption ability for As(III) by the raw and chemically-modified biochars; and (3) report on the redox conversions of arsenic during the sorption experiments.

2. Material and methods

2.1 Biochar production and chemical modification

Sewage sludge digestate (SSD) was collected from a wastewater treatment plant (WWTP) located in Limoges (France), after its dewatering and drying processes. Biochar was

produced from the SSD sample under slow pyrolysis conditions (at 350 °C for 15 min) (Wongrod et al., 2018a). The SSD biochar (100 g) was then modified with a 1 L of 10% H₂O₂ solution (modified from Xue et al., 2012) or with a 2.5 L of 2 M KOH solution (modified from Jin et al., 2014). For each biochar modification, the mixed biochar-solution was continuously stirred at room temperature for 2 h.

Raw and modified biochars were further washed with ultrapure water (18.2 MΩ, MilliQ Gradient A10, Millipore SAS 67120, Molsheim, France) in a batch system (triplicate in a row) followed by a continuous column washing (Wongrod et al., 2018a). These washing steps were performed to eliminate releasable organic compounds and inorganic ions (*i.e.* PO₄³⁻, HCO₃⁻, CO₃²⁻, Ca²⁺ and Mg²⁺) from the prepared biochars, particularly after chemical modification. The KOH modified biochar was also submitted to only a triple batch washing (Huang et al., 2017; Regmi et al., 2012; Wongrod et al., 2018a; Wu et al., 2017) to study the influence of washing steps onto As sorption and redox transformations.

The raw, H₂O₂ and KOH modified SSD biochars are labeled as BSS, BH₂O₂ and BKOH, respectively. The KOH modified SSD biochar with only batch washing is denoted as BKOH^{bat}.

2.2 Biochar characterization

The pH of the biochar was measured using a pH-meter (LPH 330T, Tacussel, France) after stirring 1 g biochar in 20 mL deionized water for 5 min and allowed it to settle for 15 min. The electrical conductivity (EC) of biochar was measured using a conductivity meter at 20 °C (CDM 210, Radiometer, Denmark).

The Brunauer-Emmett-Teller surface area (S_{BET}) of biochar was measured using N_2 sorption at 77 K (3Flex, Micromeritics, USA) after pretreatment of biochar by drying at 105 °C for 5 h. The pH of point of zero charge (pH_{PZC}) of the biochar was determined from the zeta potential at different pH ranges (Mahmood et al., 2011). The cation exchange capacity (CEC) of the biochar was determined by using a cobalt hexamine trichloride solution (99% w/w, Sigma-Aldrich) (Aran et al., 2008).

2.3 Sorption experiments

A 13.33 mM stock solution of arsenite (As(III)) was prepared from AsNaO_2 (98% w/w, Merck) and was diluted to 50 μM prior to As(III) sorption and arsenic speciation (*i.e.* As(III) and As(V)) experiments. Biochar (0.15 g) was separately added to 37.5 mL of As(III) solution in a polyethylene tube to obtain an initial 146 μg of As(III) in the solution. The initial pH was adjusted to 5.0 (± 0.5) by adding 0.01 M HNO_3 or NaOH. The sorption experiments were performed in triplicate at 20 (± 2) °C at 180 rpm for 24 h using an orbital shaker (KS 501 digital, IKATM, USA).

The significant presence in solution of releasable dissolved compounds (RDC) from BKO^{bat} (Wongrod et al., 2018a) could affect arsenic speciation. To determine whether the arsenic oxidation was mainly induced by the biochar itself or by these RDC, a control experiment was carried out. For this purpose, 1 g BKO^{bat} in 250 mL ultrapure water was stirred at 180 rpm for 24 h at room temperature (20 °C). The resulting solution was filtered with a 0.2 μm polyethersulfone (PES) membrane filter to remove the solid biochar. The

resulting solution thus only contains the RDC. A control experiment was then performed by replacing the BKOH^{bat} by this solution of RDC during sorption kinetics experiments.

In all these experiments, samples were collected at 1, 3, 7, 16 and 24 h. The total sampled volume was less than 5% of the initial volume to avoid any disturbance on the sorption equilibrium. Solutions were filtered through a 0.2 μm PES syringe filter and stored in a dark cold room at 4 °C until analysis.

2.4 Arsenic redox state distribution in biochars

Total As and its redox state distribution in raw and chemically-modified biochars before and after As(III) sorption experiments were determined through solution analysis, extraction and acid digestion as described in the following subsections.

2.4.1 Arsenic analysis in solution and deduction of sorbed arsenic.

Total arsenic analysis was performed using graphite furnace atomic absorption spectrometry (GF-AAS) (240Z, Agilent Technologies, USA) at λ 193.7 nm. The standard calibrations of As were prepared in the ranges of 10–50 $\mu\text{g L}^{-1}$. The detection limit was estimated from the mean of the blank and standard deviation, and the analyte solution was measured to produce a signal of at least 3 times higher signal than the noise level.

The arsenic redox distribution was assessed by liquid chromatography coupled to atomic fluorescence spectroscopy (LC-AFS) with hydride generation (HG) (PS Analytical Millennium Excalibur, PS Analytical, UK). The chromatographic separation was performed using a Hamilton PRP-X100 column with a phosphate buffer solution as the mobile phase

at pH 6.9 and at a flow rate of 1 mL min^{-1} . The details of the experimental conditions for speciation analysis can be found in a previous study reported by Wan et al. (2014). To avoid any transformation between As(III) and As(V), arsenic speciation on both liquid and extracted solutions was performed within 5 h after sample recovery.

The amount of As sorbed onto the biochar was calculated from differences between initial and final concentrations of arsenic during sorption experiments. The sorbed As onto biochar can be calculated following Equation (1):

$$Q_{sol.} = (C_i - C_f) \times V \quad (1),$$

where $Q_{sol.}$ is the amount of arsenic sorbed onto biochar (μg) (based on 0.15 g of biochar in this study), C_i and C_f are, respectively, initial and final equilibrium concentrations of arsenic in the solution, and V is the total volume of the solution (L).

2.4.2 Extraction of As(III) and As(V) from biochar

Due to the lack of a soft extraction procedure for arsenic from biochar in the literature, this study designed one extraction method based on the extraction procedures described by Thomas et al. (1997), Montperrus et al. (2002) and Zhang et al. (2015). The extractant was prepared from 0.3 M phosphoric acid (H_3PO_4 , 85% w/w, Carlo ERBA) with or without the addition of 0.5 M ascorbic acid (99.5% w/w, Fluka). Ascorbic acid was used to prevent the oxidation of As(III) in the solution during the extraction (Xu et al., 2015).

After the sorption experiments, 0.15 g of biochar was quickly rinsed 3 times with ultrapure water and transferred into a Teflon digestion tube with 25 mL of the extracting solution.

The extraction was operated using microwave assistance (Multiwave GO, Anton Paar, France) by heating at 80 °C for 20 min. The resulting solution was then centrifuged (Multifuge X3 FR, Thermo Fisher Scientific) at 3400 rpm for 20 min. The supernatant was collected and filtered through a 0.2 µm PES syringe filter and diluted to a constant volume of 50 mL. Samples were analyzed for As speciation using LC-AFS as mentioned in section 2.4.1.

2.4.3 Biochar acid digestion for total arsenic measurements

After the sorption experiments, the biochar (about 0.15 g) was rinsed with ultrapure water and transferred into a digestion tube (Teflon). Concentrated nitric acid (HNO₃, 69.5% w/w, Panreac ITW) (6 mL) was added to the digestion tube. Hydrogen peroxide (H₂O₂, 30% w/w, Carlo ERBA) (6 mL) was then slowly added into the digestion tube with a caution regarding its strong oxidizing property. The digestion tube was left overnight (12 h) to oxidize and digest organic matter in biochar prior to a microwave acid digestion (in order to avoid over-pressure due to the high initial release of CO₂). Finally, 3 mL of concentrated hydrochloric acid (HCl, 37% w/w, VWR) were added before starting the digestion that was operated at 180 °C for 4 h (4 cycles) using a microwave digestion (1 cycle per 1 h) to sufficiently digest all biochar particles. After digestion, the resulting solution was recovered and the dilution in a 50 mL volume was made with ultrapure water. It was filtered through a 0.2 µm PES syringe filter before analysis. Total arsenic content was analyzed by GF-AAS as previously mentioned in section 2.4.1. Regarding the analysis of total arsenic in the biochars, the As content that is already present in each biochar (before sorption) was

deduced from the sorbed As after the As(III) sorption experiments. This deduction was made to avoid errors in the experimental results.

2.5 Statistical analysis

The biochar characteristics and As(III) sorption experiments were carried out in triplicate. Results are reported as the mean value followed by standard deviation. Constants for sorption parameters were obtained by the non-linear regression using Statistica software (v6.1, StatSoft). Statistical analysis of the experimental data was performed by the t-test with two-tailed distribution at a statistical significance level of $p \leq 0.01$.

3. Results and discussion

3.1 Characterization of raw and chemically-modified biochars

The total As content in the raw and chemically-modified biochars is given in **Table 1**. Results show a significant ($p \leq 0.01$) decrease of the As content after treating the raw biochar with H_2O_2 or KOH from $47 (\pm 1) \mu\text{g g}^{-1}$ for BSS to $29 (\pm 1)$ and $13 (\pm 1) \mu\text{g g}^{-1}$, respectively, for BH_2O_2 and BKOH. These reductions can be due to the ability of KOH to dissolve ash contents (Lin et al., 2012; Liou and Wu, 2009; Liu et al., 2012) and H_2O_2 to oxidize organic matter present in the solid phase of the biochars (Xue et al., 2012). As a result, the As bound to the biochar matrix could be chemically altered and thus the As contents were lower in the chemically-modified biochars compared to the raw biochar (Table 1).

Considering BKOH and BKOH^{bat}, an almost 2 times decrease of As, from $23 (\pm 2) \mu\text{g g}^{-1}$ for BKOH^{bat} to $13 (\pm 1) \mu\text{g g}^{-1}$ for BKOH, was found after the subsequent continuous column washing.

The pH values of all biochar suspensions are also provided in Table 1. The pH of BSS (6.4 ± 0.1) increased to $8.4 (\pm 0.1)$ and $10.1 (\pm 0.1)$ for BKOH and BKOH^{bat}, respectively, whereas H₂O₂ induced no significant change ($p \leq 0.01$) on the pH suspension of biochar. The electrical conductivity (EC) of biochar suspensions remained in similar ranges from $4.0 (\pm 0.1)$ to $4.1 (\pm 0.3)$ and $6.2 (\pm 0.5) \mu\text{S cm}^{-1}$ for BSS, BH₂O₂ and BKOH, respectively. However, a significantly higher EC value ($324 \pm 2 \mu\text{S cm}^{-1}$) for BKOH^{bat} was found, compared to BKOH (Table 1). This highlights the ability of BKOH^{bat} to release a relatively high amount of dissolved ions as previously reported by Wongrod et al. (2018a).

The pH_{PZC} and zeta potential (at pH 5) values of the raw and chemically-modified biochars are given in Table 1. Results showed similar pH_{PZC} ranges (2.7–3.4) among the raw and modified biochars. Currently, there is still a lack of information regarding pH_{PZC} of biochars reported in the literature. Nevertheless, these findings are consistent with previous studies from Qiu et al. (2009) who reported a pH_{PZC} of 1.9 on straw biochar and Petrovic et al. (2016) with pH_{PZC} values of 4.5 and 6.0, respectively, on grape pomace biochar and its KOH modified biochar. Moreover, the negative zeta potential values of the biochars implied that all biochars carried net negative charges at pH 5, particularly for the BH₂O₂ (-16.5 mV) and BKOH^{bat} (-17.1 mV). These negatively charges may hinder the sorption ability for arsenic oxyanions at pH 5.

The BET surface area (S_{BET}) of all biochars is reported in Table 1. The S_{BET} was significantly improved by 7–20 times after H_2O_2 or KOH modification of the biochar compared to the non-treated biochar. In this case, the S_{BET} increased from $0.4 (\pm 0.1)$ (the raw biochar) to $5.7 (\pm 0.1)$ and $7.9 (\pm 0.1) \text{ m}^2 \text{ g}^{-1}$ for BH_2O_2 and BKOH , respectively. This implies that H_2O_2 and KOH induced higher porosity on the modified biochars, thus As sorption can be enhanced for these biochars (Mohan et al., 2014). These S_{BET} results are in agreement with those reported for sewage sludge biochars ($4.0\text{--}14.3 \text{ m}^2 \text{ g}^{-1}$) (Agrafioti et al., 2013; Yuan et al., 2015), but lower than biochar made from wood ($475 \text{ m}^2 \text{ g}^{-1}$) (Niazi et al., 2018b). Nevertheless, they remain very low compared to activated carbon which displays specific surface area beyond $1000 \text{ m}^2 \text{ g}^{-1}$ in most cases (Gonzalez-Garcia, 2018) (e.g. $1215.0\text{--}1316.0 \text{ m}^2 \text{ g}^{-1}$ for activated carbon prepared from coal) (Gong et al., 2015).

The CEC values for all biochars are also given in Table 1. Results demonstrate a similar CEC of the biochar after H_2O_2 modification, *i.e.* from $2.0 (\pm 0.1)$ to $3.0 (\pm 0.1) \text{ cmol}^+ \text{ kg}^{-1}$, whereas the CEC values were much higher (7–10 times) for BKOH ($13.4 \pm 0.1 \text{ cmol}^+ \text{ kg}^{-1}$) and BKOH^{bat} ($20.8 \pm 0.1 \text{ cmol}^+ \text{ kg}^{-1}$) (Table 1). Nevertheless, in the literature much higher CEC values are reported for wood and straw derived biochars, ranging from 45.7 to $483.4 \text{ cmol}^+ \text{ kg}^{-1}$ (Ding et al., 2016; Jiang et al., 2014).

The biochar properties reported in Table 1 highlight that the total As content, zeta potential and S_{BET} are the key indicators that were significantly affected by the biochar treatment.

Due to its lower negative charge and its higher S_{BET} , BKOH can potentially sorb more As compared to other biochars. Furthermore, the biochar washing procedure is an important

parameter to be considered after the chemical treatment, since the biochar properties significantly change between BKOH and BKOH^{bat}.

3.2 As redox state evolution during sorption kinetics by BKOH^{bat} and its dissolved solutions

Fig. 1a shows the As redox state distribution in the solution during adsorption experiments for As(III) onto BKOH^{bat}. The results demonstrate that while As was gradually sorbed onto BKOH^{bat} (corresponding to the decrease of total As over time), the oxidation of As(III) to As(V) occurred continuously. To elucidate whether this oxidation was promoted by compounds released from the biochar into the solution or by the biochar itself, a control experiment was performed by replacing the biochar by a solution of released dissolved compounds (RDC) from BKOH^{bat}. The experimental data and corresponding results is shown in **Fig. 1b**. From the results, a slight oxidation of As(III) with a final proportion of 9% As(V) in the RDC solution was found, compared to 43% oxidation with the presence of biochar. This demonstrates that the oxidation of As(III) to As(V) was mainly induced by the biochar material itself and to a lesser extent by the dissolved compounds being released from the BKOH^{bat}. At present, there is still a lack of information on the role of biochars and the released dissolved compounds towards the As(III) oxidation. Nevertheless, the findings are supported by Niazi et al. (2018a, 2018b) who found the oxidation of As(III) sorbed onto biochars prepared from Japanese oak wood and perilla leaf. However, Dong et al. (2014) showed the high potential oxidation of As(III) (up to 25%) induced by the dissolved organic matter from sugar beet tailing and Brazilian pepper derived biochars.

3.3 Extraction procedure for As redox state distribution in biochars

In order to assess the redox state distribution of As sorbed onto biochar by LC-AFS, it was first necessary to validate an extraction procedure that allows a quantitative As recovery without any conversion of As species, especially As(III) being oxidized to As(V).

The importance of adding ascorbic acid in the extraction solution to stabilize As(III) was assessed by applying the extraction procedure to a biochar sample with and without spiking with a known amount of As(III) just before performing the extraction step. In this study, the BKO^{bat} was selected due to its release of dissolved compounds and its ability to oxidize As(III) as previously reported by Wongrod et al. (2018a, 2018b).

Table 2 shows the recoveries of the arsenic species and total As after the extraction using H_3PO_4 with or without addition of ascorbic acid onto the BKO^{bat} sample, and with and without As(III) spiking just before the extraction. Results show that all spiked arsenic was recovered by the extraction procedure. The results also highlight that when using only 0.3 M H_3PO_4 , a significant amount of spiked As(III) was oxidized. Indeed, the addition of 12.5 μg of As(III) to the biochar before performing the extraction step resulted in an increase of 8.8 (± 0.7) μg and 3.5 (± 0.3) μg for As(III) and As(V), respectively. Thus, 29% of spiked As(III) was converted into As(V). In contrast, no oxidation of As(III) was observed during extraction with H_3PO_4 and ascorbic acid: the difference between the As(III) amount before and after spiking is 12.6 (± 0.7) μg , which is in agreement with the amount of As(III) added (12.5 μg). Therefore, the addition of ascorbic acid is essential to ensure As(III) stability during the extraction step. The findings are also in agreement with the study of Xu et al.

(2015) who reported the efficiency of using both phosphoric and ascorbic acids as extracting agents to quantitatively recover As(III) and As(V) from fly ash.

To estimate the extraction yield of As sorbed onto the biochar after the As(III) sorption experiments, the biochars were recovered and submitted to both acid digestion and extraction procedures (see section 2.4). The corresponding results are presented in **Table 3**.

For BSS and BH_2O_2 , the amount of total sorbed As was too low to allow an accurate determination after the acid digestion and/or extraction. As a result, no extraction yield was calculated. For BKO^{bat} , the total amount of sorbed As was quantitatively recovered by the extraction procedure. In the case of BKO, most of the sorbed As was recovered but about one fourth could not be extracted under the applied conditions. This difference in the extraction efficiency may result from different sorption mechanisms of As from one biochar type to the other. Nevertheless, the majority of As could be extracted from the biochars and thus the identification of the As species in the extracted solutions gives the main As species sorbed onto the biochars.

3.4 Determination of As(III) and As(V) sorbed onto biochars

Different types of biochars were exposed in the solution containing an initial As(III) amount of 146 μg . After 24 h of As(III) sorption, the biochars were recovered and the exposure solutions were analyzed to determine the remaining amount of As and to assess its distribution between As(III) and As(V). The biochars were separately submitted to acid digestion for the determination of the total quantity of sorbed As and to the extraction for the assessment of the redox distribution of sorbed As. The amounts of As(III), As(V) and

total As in the exposure solutions and sorbed onto the biochars (determined after acid digestion and extraction steps) are shown in **Table 4**.

Results showed that the total As (*i.e.* As(III) + As(V)) remaining in the final exposure solutions of BSS and BH₂O₂ were not significantly different from the initial As(III), indicating that no As was sorbed onto these biochars. In contrast, As was removed from the exposure solutions by both BKO_H and BKO_H^{bat}, corresponding to an As sorption efficiency of 67% and 50%, respectively. These results are in agreement with the sorption yield estimated with the amount of As quantified in the digestate-based biochars (Table 4).

The arsenic redox distribution in the final exposure solution shows almost no As(III) oxidation for both BSS and BH₂O₂ as the final amount of As(III) remained the same as the initial As(III) amount (Table 4). For the KO_H treated biochars, the assessment of the redox distribution only concerned the unsorbed As. In the case of BKO_H, no significant oxidation of As(III) was observed, whereas for BKO_H^{bat} about 28% of the remaining As was oxidized to As(V) (Table 4). These findings are in agreement with a previous study from Wongrod et al. (2018b) with a large oxidation of As(III) in BKO_H^{bat} and a partial oxidation in BKO_H during As(III) sorption. As previously discussed (Fig. 1a and 1b), the majority of As(III) oxidation was induced by the biochar solid compounds.

Considering As(III) and As(V) extracted from the biochars after the sorption experiment, a similar distribution of the As species was found for BKO_H and BKO_H^{bat} (Table 4). Arsenic was mainly sorbed as As(III) (90–92%) and only 8–10% was sorbed as As(V) onto the KO_H biochars. In the case of BKO_H, the redox distribution of As sorbed onto the biochar

is quite similar to the distribution observed in the final exposure solution. However, for BKOH^{bat} , the evolution of the As species in solution and on the biochar was different: As(V) represents only 8% of the sorbed arsenic whereas it corresponds to 28% of the dissolved As(V) (Table 4). This suggests that the As(III) sorption onto the KOH biochar was favored compared to As(V) sorption. This finding is consistent with results previously reported by Wongrod et al. (2018b) when comparing As(III) and As(V) sorption onto such biochars. Another possible explanation would be that As(V) could be reduced into As(III) during the sorption process, as observed by Niazi et al. (2018a, 2018b) who studied the speciation of As onto wood and leaf derived biochars using the solid-phase XANES technique. Depending on the nature and chemical treatment applied to the biochar, it could also contain chemical functions that act as electron donors to facilitate the As reduction (Choppala et al., 2016).

Comparison of the two KOH biochars showed that the adsorption capabilities for As(III) were quite similar for both the BKOH ($410 \mu\text{g g}^{-1}$) and BKOH^{bat} ($385 \mu\text{g g}^{-1}$) at As(III) concentration ranges of 0–4000 μM (or 0–54 $\mu\text{g L}^{-1}$) and the initial solution pH at 5.0. Nevertheless, a much higher As(III) sorption was observed onto the Japanese oak wood derived biochar ($3,890 \mu\text{g g}^{-1}$) (concentrations of 27–144 $\mu\text{g L}^{-1}$ and at pH 7.0 ± 0.1) (Niazi et al., 2018b). This is probably due to different biochar properties between the SSD-based biochars and the Japanese oak wood biochar. For instance, the specific surface area was substantially lower with the KOH modified biochars from SSD ($3.0\text{--}7.9 \text{ m}^2 \text{ g}^{-1}$) (Table 1) compared to the oak wood biochar ($475 \text{ m}^2 \text{ g}^{-1}$) (Niazi et al., 2018b).

In the case of BH_2O_2 , the amount of sorbed As being low, the results of the As redox distribution were less accurate and should thus be taken with caution. The percentage of As(V) sorbed onto the H_2O_2 -modified biochar appears to be higher than into solution, highlighting a potential oxidation of As(III) during sorption. This phenomenon was also observed by Niazi et al. (2018a, 2018b), who suggested that redox active species present at the biochar surface such as NO_3^- or $\text{FeO}(\text{OH})$ could induce As(III) oxidation. Therefore, the presence of iron (Fe) (65 g kg^{-1}) and manganese (Mn) (769 mg kg^{-1}) on the SSD biochar, that could be partially in metal oxide forms (Wongrod et al., 2018a), could promote the redox transformation of As(III) to As(V) on metal oxides associated onto the biochars (Vithanage et al., 2017). Such a phenomenon is also reported by several studies (Han et al., 2011; Manning et al., 2002; Wang et al., 2015).

4. Conclusions

The extraction using phosphoric and ascorbic acids allowed recovering sorbed arsenic, while preserving As(III) oxidation state. Arsenic redox distribution could thus be assessed in both solid and liquid phases. Arsenic was mainly sorbed onto biochar as As(III) but during sorption, As(III) oxidation may occur over time. This oxidation, mainly induced by biochar solid compounds rather than by soluble compounds released from biochar, can strongly vary depending on the chemical treatment and efficiency of washing procedures applied to biochar after chemical treatment. The KOH modification efficiently improves the biochar sorption capacity but also promotes As(III) oxidation, especially with an incomplete washing.

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Conflict of interest

The authors declare no conflict of interest.

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Table and figure legends

Table 1. pH, electrical conductivity and surface area of the raw and chemically-modified biochars.

Table 2. Arsenic speciation stability using H_3PO_4 with or without ascorbic acid (BKO^{bat} sample, with and without As(III) spiking just before extraction).

Table 3. Comparison of total amount of sorbed arsenic determined after acid digestion or extraction procedure.

Table 4. Comparison of As speciation and total As in exposure solutions and sorbed onto biochars (initial As(III) amount in exposure solution: $146 \mu\text{g}$).

Figure 1. Arsenic redox distribution in solution during adsorption kinetics for As(III) by BKO^{bat} (a) and for the control with only released dissolved compounds (RDC) from BKO^{bat} (b).

Tables

Table 1

Biochar	Total As ($\mu\text{g g}^{-1}$)	pH in water	pH _{pzc}	Zeta potential at pH 5 (mV)	Electrical conductivity (at 20 °C) ($\mu\text{S cm}^{-1}$)	S _{BET} ^a ($\text{m}^2 \text{g}^{-1}$)	CEC ^b ($\text{cmol}^+ \text{kg}^{-1}$)
BSS	47 ± 1	6.4 ± 0.1	2.7	-9.8	4.0 ± 0.1	0.4 ± 0.1	2.0 ± 0.1
BH ₂ O ₂	29 ± 1	6.5 ± 0.1	2.9	-16.5	4.1 ± 0.3	5.7 ± 0.1	2.9 ± 0.1
BKOH	13 ± 1	8.4 ± 0.1	3.4	-8.1	6.2 ± 0.5	7.9 ± 0.1	13.4 ± 0.1
BKOH ^{bat}	23 ± 2	10.0 ± 0.1	2.9	-17.1	324.0 ± 2.4	3.0 ± 0.1	20.8 ± 0.1

^a S_{BET} refers to Brunauer-Emmett-Teller surface area of biochar.

^b CEC refers to cation exchange capacity of biochar.

Note: all values reported are mean of triplicate followed by standard deviation, except pH_{pzc} and zeta potential.

Table 2

Extraction method		Extracted arsenic (μg)		Spiking recovery ^a (%)	
		As(III)	As(V)	As(III)	Total As
No ascorbic acid	Before As(III) spiking	$0.3^b \pm 0.1$	1.1 ± 0.1	-	-
	After As(III) spiking	9.1 ± 0.7	4.6 ± 0.3	71	99
	(12.5 μg)				
With ascorbic acid	Before As(III) spiking	$0.4^b \pm 0.1$	$0.8^b \pm 0.1$	-	-
	After As(III) spiking	13.0 ± 0.7	$0.8^b \pm 0.1$	101	101
	(12.5 μg)				

^a Recovery: amount of spiked As(III) recovered by extraction either as As(III) or total arsenic (*i.e.*

As(III)+As(V)).

^b Value close to limit of quantification.

Table 3

Biochar	Total arsenic (μg)		Recovery from extraction (%)
	Extraction	Acid digestion	
BSS	0.2 ± 1	1 ± 1	na ^a
BH ₂ O ₂	3 ± 1	6 ± 1	na
BKOH	70 ± 3	93 ± 3	75 ± 4
BKOH ^{bat}	63 ± 4	60 ± 3	105 ± 9

^a na refers to not available due to very low values detected by liquid chromatography coupled to atomic fluorescence spectroscopy (LC-AFS) and/or graphite furnace atomic absorption spectrometry (GF-AAS).

Table 4

Biochar	Exposure solution				Sorbed As onto biochar				
	Initial		Final		Acid digestion		Extraction		
	As(III)	As(III)+	As(III)	As(V)	Total	Sorption	As(III)+	As(III)	As(V)
	(μg)	As(V)	(%)	(%)	As	yield (%)	As(V)	(%)	(%)
		(μg)			(μg)		(μg)		
BSS	146	145 ± 2	99	1	1 ± 1	<1	0.2 ± 1	na ^a	na
BH ₂ O ₂	146	143 ± 3	96	4	6 ± 1	4	3 ± 1	76	24
BKOH	146	48 ± 3	98	2	93 ± 3	64	70 ± 3	90	10
BKOH ^{bat}	146	72 ± 5	72	28	60 ± 3	41	63 ± 4	92	8

^a na refers to not available due a value close to limit of quantification.

Figure

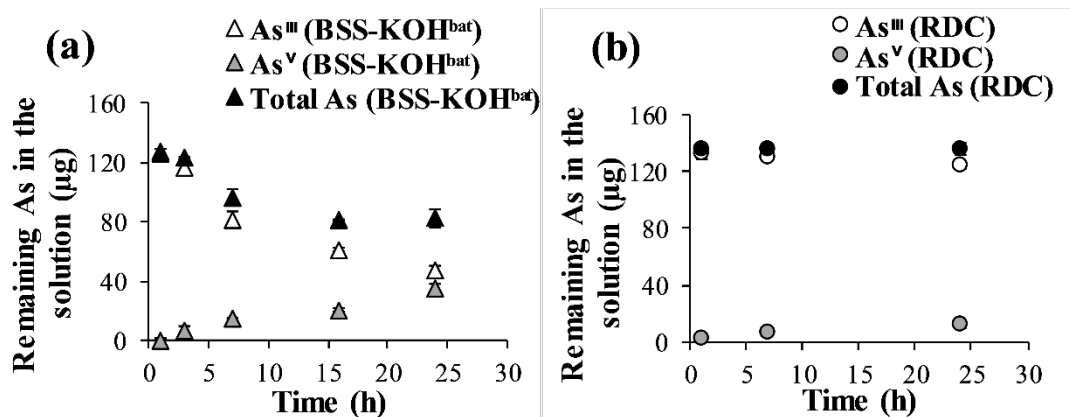


Fig. 1.