Geochemical and spectroscopic investigations of Cd and Pb sorption mechanisms on contrasting biochars: Engineering implications

Lukáš Trakal [a,*], Deniz Bingöl [b], Michael Pohořelý [c], Miroslav Hruška [a], Michael Komárek [a]

[a] Department of Environmental Geosciences, Faculty of Environmental Sciences, Czech University of Life Sciences Prague, Kamycka 129, Praha 6 Suchdol 16521, Czech Republic
[b] Department of Chemistry, Faculty of Sciences and Arts, Kocaeli University, Umuttepe Campus, 41380 Kocaeli, Turkey
[c] Environmental Process Engineering Laboratory, Institute of Chemical Process Fundamentals, Academy of Sciences of Czech Republic, v.v.i., Rozvojova 135, Praha 6 Suchdol 16502, Czech Republic

HIGHLIGHTS

- Metal removal efficiencies and mechanisms depended on the parent material.
- Ion exchange is the predominant mechanism during metal sorption on biochars.
- Metals were strongly bound to the biochars.
- Metal removal efficiency is strongly pH-dependent.

GRAPHICAL ABSTRACT
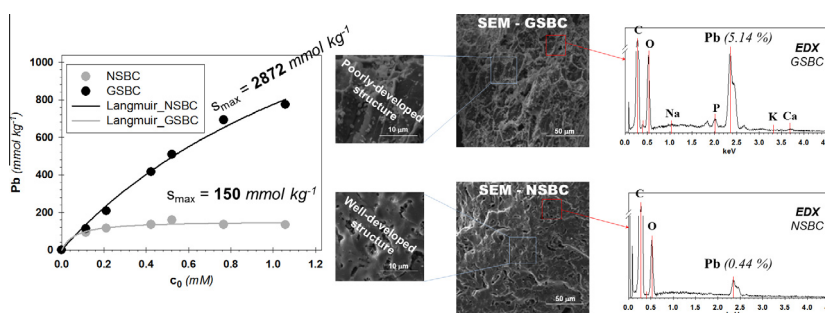
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ABSTRACT

Biochars prepared from nut shells, plum stones, wheat straws, grape stalks and grape husks were tested as potential sorbents for Cd and Pb. Mechanisms responsible for metal retention were investigated and optimal sorption conditions were evaluated using the RSM approach. Results indicated that all tested biochars can effectively remove Cd and Pb from aqueous solution (efficiency varied between 43.8% and 100%). The removal rate of both metals is the least affected by the biochar morphology and specific surface but this removal efficiency is strongly pH-dependent. Results of variable metal removal combined with different optimized conditions explain the different metal sorption mechanisms, where the predominant mechanism is ion exchange. In addition, this mechanism showed very strong binding of sorbed metals as confirmed by the post-desorption of the fully metal-loaded biochars. Finally, these biochars could thus also be applicable for metal contaminated soils to reduce mobility and bioavailability of Cd and Pb.

1. Introduction

Among other water treatment technologies, such as precipitation, coagulation or membrane filtration, biosorption should be taken into account as a potential "low-cost candidate" for removing toxic metals from wastewater. Biochar is an efficient biosorbent used for the removal of metals such as Cd and/or Pb (two common metal pollutants in Central Europe with contrasting geochemical behaviour) from waste waters (Inyang et al., 2011; Lu et al., 2012; Kim et al., 2013; Mohan et al., 2014a). This pyrogenic carbon-rich material is most commonly prepared from waste materials, such as woody biomass, animal waste, sludge or a variety of agricultural residues (Lehmann and Joseph, 2009). Many studies have described an effective removal of Cd and Pb using biochar originating from different agricultural wastes. For example, Kołodyńska et al. (2012), Xu et al. (2013a,b) reported

that biochars made from dairy and pig manure were able to sorb Cd and/or Pb in the range from 0.28 to 1.11 mmol g^{-1}. Inyang et al. (2011), Jiang et al. (2012), Han et al. (2013), Kim et al. (2013) and Xu et al. (2013a) described the high potential of sugarcane bagasse, rice straw, pinewood, rice husk and *Miscanthus sacchariflorus* to remove Cd and/or Pb from aqueous solution in the range of 0.004–0.66 mmol g^{-1}. These results thus present variable metal sorption efficiency of the tested biochars. This variability is caused by many factors, such as: (i) source and composition of the original waste material; (ii) pyrolysis process, mainly the temperature, (Kim et al., 2013); (iii) biochar post activation or modification (Xue et al., 2012; Mohan et al., 2014b); (iv) different content of various mineral components in the biochar (Xu et al., 2013a); (v) different sorption mechanisms (Lu et al., 2012); as well as (vi) the conditions used during metal sorption (such as pH value, contact time, temperature, initial metal concentration or the dose of used biochar; Kołodyńska et al., 2012; Bernardo et al., 2013).

The metal sorption process has been previously described as a result of three different mechanisms (Sohi et al., 2010; Lu et al., 2012): (i) ion exchange (Ca^{2+}, K$^+$, Mg^{2+}, Na$^+$); (ii) metal complexation onto free and complexed carbonyl, carboxyl, alcoholic, hydroxyl or phenolic hydroxyl functional groups; and (iii) physical adsorption or surface precipitation caused by sorptive interaction involving delocalization of π electrons of organic carbon (Inyang et al., 2011; Lu et al., 2012; Xu et al., 2013b; Bernardo et al., 2013). Nevertheless, there is a gap of knowledge in comparing different mechanisms that occur during metal sorption on contrasting biochars (originating from different waste materials).

Additionally, ideal conditions for metal sorption efficiency have also been tested for different biochar samples. However, these crucial experiments are time consuming and expensive. The multivariate chemometric technique was, therefore, used to identify the optimum combination of factors (conditions used during sorption) and interactions among the factors, which could not be identified using the univariate method (Bingöl et al., 2012). In general, these chemometric techniques have several important advantages over one-way optimization for analytical applications, including a relatively low cost, a reduced number of experiments, and possibilities to evaluate interactions among variables (Tarley et al., 2009). More precisely, the Response Surface Methodology (RSM; Myers et al., 2009) was employed to develop an approach for the evaluation of Cd and Pb optimal sorption on biochars originating from different waste materials.

The main objective of this novel study was to evaluate the feasibility of Cd and Pb removal by various biochars. For this purpose, the sorption of Cd(II) and Pb(II) was tested in a series of batch experiments. The effects of solution pH, contact time, metal concentration and dose of used biochar were accurately investigated using the efficient and time saving RSM approach. Furthermore, in order to deeply understand the different Cd and Pb sorption mechanisms in the interaction with all tested biochars, the geochemical and spectroscopic analyses of metal-loaded biochars were investigated.

2. Methods

2.1. Solutions preparation

Cadmium Cd(II) and lead Pb(II), as metals with different geochemical behaviour, were the sorbates studied in all experiments. Stock solutions (1000 mg L^{-1} of both metals) were prepared by dissolution of Cd(NO$_3$)$_2$·4H$_2$0 and Pb(NO$_3$)$_2$ (p.a.), (Lach-Ner, Czech Republic), respectively, in a previously prepared background electrolyte (0.01 M NaNO$_3$). Solution pH was adjusted using 0.1 M HNO$_3$ and NaOH, respectively.

2.2. Biochar preparation and analyses

Five different waste agro-materials (nut shells, plum stones, wheat straws, grape stalks and grape husks), which are commonly found in Central Europe, were used in this study. Although all the selected materials belong to the same group titled "herbaceous and agricultural biomass (HAB)", they differ in the content of structural components and also vary in their chemical composition (Vassilev et al., 2010, 2012). All materials were homogenised, air dried overnight and analysed (before biochar preparation) to determine the bulk density, moisture, ash content and material composition according to TAPPI T264 (1997) and TAPPI T211 (1993). Next, pH was measured using inoLab® pH-meter (7310 WTW, Germany); content of C, H, N, O and S was determined using the Flash EA 1112 apparatus in the CHNS/O configuration (Thermo Fisher Scientific, USA); and Fourier transform infrared spectroscopy (FTIR Nicolet 6700 analyser connected with a Continuum microscope, Thermo-Nicolet, USA) was performed to identify the chemical functional groups presence separately for each sample. These previously homogenised and analysed agro-wastes (Table A.1; see the Appendix section available as a Supplementary Material) were then pyrolysed at 600 °C in a muffle furnace under 16.7 mL min^{-1} nitrogen flow rate at atmospheric pressure and retention time of 30 min. Additionally, the yield of biochar (in %) was calculated as the quotient between the weight of biochar and weight of agro-waste. The resulting biochars were then cooled overnight under the same nitrogen flow rate as before. Pyrolysed products prepared in this way were then ground, homogenised, sieved (all used biochar particles were 0.25–0.50 mm in size), washed by ultra-clean water MilliQ Integral (Merck Millipore Corp., USA) and dried at 60 °C for 24 h until constant weight. Different biochars such as: nut shells biochar (NSBC); wheat straws biochar (WSBC); grape stalks biochar (GSBC); grape husks biochar (GHBC); and plum stones biochar (PSBC); were then used in all studies/experiments with a separate analysis for each. Selected initial characteristics of all five biochar samples were described before the sorption experiments started. All prepared biochar samples were analysed to determine the yield, bulk density, moisture and ash content. Surface areas were measured by N$_2$ adsorption isotherms at 77 K using ASAP 2050 (Micrometrics Instrument Corporation, USA) surface area analyser. Specific surface area and volume of micro-pores were detected by the layered adsorption isotherm BET model.22. For each biochar sample, a single estimate analysis of the element composition in triplicate was carried out using FlashEA 1112th (Thermo Scientific Company, USA). Additionally, ash mineralogical composition of each biochar was analysed, using the XRF method, by ARL 9400 XP spectrometer (Thermo Arl., Switzerland). Surface functional groups of all five biochar samples were then analysed using FTIR (Thermo-Nicolet, USA), cation exchange capacity was determined; pH value was measured and pH at point of zero charge (pH$_{zpc}$) was determined according to Fiol and Villaescusa (2009) using the immersion technique (IT). Finally, the surface structure and composition of the selected biochar samples was analysed by SEM-EDX using INDUSEM Scanning Electron Microscope (Tescan Inc., USA) equipped by the Electron Dispersive X-ray Spectroscopy (Bruker Quantax 125 eV).

2.3. Batch experiments

First, the batch sorption experiment was carried out with (i) initial metal concentration (0.1–1.5 mM); (ii) initial aqueous solution pH (2.00–8.00); (iii) specific dose of biochar (1.0–10.0 g L^{-1}); and (iv) contact time (1–48 h) to optimize the maximum Cd and Pb sorption efficiency of all biochar samples. Second, in order to test the sorption maximum of all biochar samples, two consecutive equilibrium sorption experiments (in triplicates) were implemented under