



Research article

Metal sorption by biochars: A trade-off between phosphate and carbonate concentration as governed by pyrolysis conditions



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ABSTRACT

Three feedstocks, pine wood, grass and cow manure, were pyrolyzed under various conditions and tested on their ability to sorb metals in aquatic systems. The feedstocks were pyrolyzed at 2 different temperatures (350 °C and 550 °C) and 2 different residence times (10 and 60 min) and resulting biochars were assessed on their capability to immobilize Pb, Cu, Cd and Zn.

Manure-based chars, and to a lesser extent grass-based chars, featured high concentrations of phosphates and carbonates. These anions play an important role in metal sorption because they form insoluble complexes with the metals. Washing reduced the concentration of these anions, leading to a reduced sorption of metals by the biochar.

The carbonate concentration on the biochars' surface increased at higher reactor temperature and longer residence times. The opposite trend was observed for the phosphate concentration and the cation exchange capacity. Accordingly, the optimal temperature-residence time combination for sorption was a trade-off between these properties. Biochar produced from cow manure and pyrolyzed at 550 °C for 10 min showed the best sorption for all metals considered.

1. Introduction

In 2011 the European Environment Agency (EEA) reported that approximately 284 000 sites in Europe require a clean-up due to soil contamination with an estimated cost of 6 billion Euros/year (<https://doi.org/10.1155/2013/158764>). National reports indicate that metals are the most frequent soil contaminants.

A common approach to deal with soils contaminated with metals is to excavate the soil and dispose the soil into landfills. Alternative options have been investigated because this method is often not considered as a cost-effective or environmentally sustainable remediation technique (Boisson et al., 1999). One technology that has gained attention is the in-situ immobilization of metals by the addition of various amendments. The actual aim of immobilization is not to remove the metal contaminant from the soil but to reduce its bio-availability and activity (Gray et al., 2006). An interesting amendment in this context is biochar. Biochars are known to have a highly porous structure, contain various functional groups and be effective in the adsorption of metals, in both aquatic and soil systems (Park et al., 2011; Uchimiya et al., 2010).

Biochar is characterized by a high surface area, high cation

exchange capacity, high pH and low degradation rate in soil. The main mechanisms behind the sorption of metals on the biochar's surface are ion exchange, physical adsorption and (co-)precipitation. The typical pH amelioration of the soil after biochar application can be considered as a fourth indirect mechanism because pH changes influence physical, biological and chemical soil characteristics that in turn influence metal retention or release (Beesley et al., 2015; Gomez-eyles et al., 2013; Eugene et al., 2018).

The most important process parameters influencing biochar properties are the pyrolysis temperature, the pyrolysis residence time and the feedstock type (Novak et al., 2009). Table 1 gives an overview of the best chars from previous studies on the adsorption capacity of the relevant metals. Manure seems to be a promising feedstock and either short residence times and high temperatures or long residence times and low temperatures resulted in the highest adsorption.

This study's main goal is to test several biochars produced in different process conditions on their ability to immobilize selected metals (lead (Pb), copper (Cu), cadmium (Cd) and zinc (Zn)) and to selectively sorb metals by adjusting the key parameters (i.e. the reactor temperature and residence time applied during the pyrolysis process and the feedstock selection), which affect the properties of the produced

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Table 1

Overview of adsorption capacity tests in literature with different feedstocks and pyrolysis temperatures (a. Kolodyńska et al. (2012) b. Cao et al. (2009) c. Uchimiya et al. (2011) d. Pelleria et al. (2012) e. Xu et al. (2013) f. Qian et al. (2016)).

Element	Immobilization process	Best temperature	Residence time	Feedstock	Ads. (mg/g)
Pb ²⁺	Phosphate and carbonate precipitation	600 °C	10min	Pig manure	230,7 ^a
	Precipitation (84–87%) and surface sorption (13–16%)	200 °C	4h	Dairy manure	132,8 ^b
	Ion exchange with cations bound to oxygen functional groups	350 °C	4h	Cottonseed hulls	n.a. ^c
Cu ²⁺	Ion exchange	300 °C	6h	Rice husks	4,57 ^d
				Orange waste	4,92 ^d
				Olive pomace	5,12 ^d
				Compost	7,94 ^d
	Precipitation (> 90% carbonate)	350 °C	4h	Dairy manure	54,4 ^e
Cd ²⁺	Surface complexation through –OH groups or delocalized π -e ⁻	600 °C	10min	Pig manure	88,5 ^a
				Cow manure	88,23 ^a
	Phosphate and carbonate precipitation, surface complexation with –OH groups and delocalized π -e ⁻	350 °C	4h	Dairy manure	51,4 ^e
Zn ²⁺	precipitation with PO ₄ ³⁻ or CO ₃ ²⁻ (ions present in the char)	600 °C	10min	Pig manure	117,01 ^a
				Cow manure	118,4 ^a
	Phosphate and carbonate precipitation, surface complexation with –OH groups and delocalized π -e ⁻	350 °C	4h	Dairy manure	32,8 ^e
	Precipitation with PO ₄ ³⁻ or CO ₃ ²⁻ (ions present in the char)	600 °C	10min	Pig manure	79,6 ^a
				Cow manure	79,6 ^a
	Precipitation with ash anions	550 °C	n.a.	Pine needle	25,9 ^f

biochar. How these parameters influence carbonates and phosphates and how these anions in turn influence sorption was also investigated. Feedstocks included grass, manure and pine.

2. Materials and methods

2.1. Char production

Shredded and sieved pine wood chips (Bemap Houtmeel B.V., Bommel, The Netherlands) (Yildiz et al., 2015) were used as the first feedstock, further denoted as “Pine” (P). The second feedstock, “Grass” (G) was collected from the full-scale IFBB plant in Baden-Baden (Germany), where roadside verges, garden waste, and other green cuttings from the region are treated with the IFBB method (Van Poucke et al., 2016). Press cakes were used for these experiments before they were pressed into briquettes. Cow manure (CM) was collected at a local farm in Kruishoutem, Belgium (50°53'41.1"N; 3°29'55.1"E) in early August 2016. During that time of the year, the cows are allowed to graze and no additional animal feed is provided.

All feedstocks were first dried in the oven for 24 h at 105 °C, subsequently ground in a Retsch Cutting Mill SM2000 to a uniform size (2 mm) and fed to the pyrolysis reactor. From each feedstock, 4 chars were produced; two temperatures, 350 and 550 °C, and two residence times, 10 and 60 min, were chosen for this investigation. Abbreviations for the biochars are composed of the symbol for the feedstock (PW for pine wood, CM for cow manure and G for grass), temperature and residence time, e.g., G350_10 represents char produced from grass at 350 °C during 10 min.

Slow pyrolysis experiments were carried out in a lab-scale pyrolysis setup reported previously for bio-oil production (Yildiz et al., 2014) with modifications in residence time to optimize to produce biochar. Approximately 300 g of feedstock was fed to the reactor after which the reactor was heated up at a rate of ca. 15 °C/min to the desired temperature (350 or 550 °C). Dinitrogen was used as sweeping gas (45 L/h) throughout the experiment to remove the produced pyrolysis vapors and tars. After reaching the highest treatment temperature, the reactor was kept at that temperature for the duration of desired residence times. The reactor was then cooled down below 100 °C under dinitrogen flow before discharging the produced biochar to the solid collection vessel located underneath the reactor. The recovered biochar and the bio-oil weights for each experiment were recorded. The biochar yield was calculated on a dry biomass basis. The biochars were kept in a closed container at room temperature until further analysis or

adsorption tests.

2.2. Analysis

A biochar/water suspension (1:10 m/v) was shaken for 24 h to reach an equilibrium and was allowed to settle for 0.5 h before the pH was measured with a pH electrode (Model 520, Orion, Boston, MA, USA). To determine the cation exchange capacities of the chars, the ammonium acetate pH 7 method was used (Van Ranst et al., 1999).

For the CHNS-analysis, approximately 1.5 mg of every char was weighted in duplicate and wrapped in a tin foil cup. All samples were placed in a FLASH 2000 organic elemental analyzer (Thermo Fisher Scientific, Waltham, USA) using a CHNS configuration and equipped with a thermal conductivity detector. The oxygen content was calculated by difference, i.e. 100% subtracted by the ash content and the sum of the CHNS-values.

To determine the metal content in the organic amendments, filter papers or feedstocks, 1 g dry material was calcinated at 450 °C and dissolved in HNO₃ (Sigurnjak et al., 2017). The obtained solution was filtered and P, S, Fe, Mn, Zn, Cu, Co, Al, Pb, Ni, Cr and Cd concentrations were measured with ICP-OES (Varian Vista-MPX CCD Simultaneous, Varian Inc., Victoria, Australia). All tests were conducted in duplicate and included a blank. Detection limits, calculated as 3 × σ and expressed in mg/kg product were 0.63 for Cd; 1 for Cu; 0.63 for Mn; 5 for Ni; 25 for P; 13 for Pb; 1.3 for Zn; and 50 for S.

For the analysis of the surface area (m²/g) of the biochars and original feedstocks, all the samples were degassed at 300 °C for 6h before the analysis (Yang et al., 2018). Dinitrogen was employed as module gaseous adsorbate for surface probing based on the Brunauer-Emmett-Teller method. Standard analysis was conducted at 77K using a Micromeritics Gemini VI.

2.3. Single-element batch adsorption tests

For Pb, a solution of 1.876 g Pb/L was prepared by dissolving Pb (NO₃)₂ (ACS, 99.0% min, Alfa Aesar, Germany) in de-ionized water. To 50 mL of this Pb-solution, 0.5 g of each char was added. The mixture was shaken for 24 h, then filtered over a white ribbon Macherey-Nagel filter paper (640 m – diam. 90 mm) and collected in a plastic 50 mL conical centrifuge tube. All other filtrations in this study were performed with the same type of filtration paper. The pH was measured, after which a drop of concentrated HNO₃ was added to preserve the sample for analysis. The solutions were diluted and measured for Pb in

the ICP-OES (Varian Vista-MPX CCD Simultaneous, Varian Inc., Victoria, Australia). All adsorption tests were performed in duplicate and with the presence of a blank sample (i.e. metal solution without any biochar added). The other metals, Cu (1 g/L), Cd (0.364 g/L) and Zn (0.479 g/L), were prepared by dissolving $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ (Chem-Lab NV, 8210 Zedelgem, Belgium), $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Merck, 64293 Darmstadt, Germany), respectively, in de-ionized water. These metal concentrations were chosen to allow the biochars to reach their maximum sorption capacity based on a review compiled by Mohan et al. (2014).

2.4. Multi-element batch adsorption tests

A multi-element solution of all four metals (Pb, Cu, Cd and Zn) was prepared by dissolving the same salts as mentioned before to yield a final concentration of 5 mM of every metal. 10 mL of this solution was taken and 0.1 g of biochar was added. All samples were shaken, filtered and analysed as described in the previous section.

To remove single elements completely from the multi-element aqueous medium, the same procedure was also performed involving 0.3 and 0.5 g G350_10, G350_60, CM550_10 and CM550_60 in 10 mL of a 5 mM Pb–Zn–Cu–Cd mixed solution. Because some chars show a specific affinity towards Pb, the experiment was repeated using a 5 mM Zn–Cu–Cd-solution.

2.5. Phosphate and carbonate leaching in an aqueous medium

To test the leaching of the carbonates and phosphates released from the char in an aqueous medium, 0.5 g biochar was suspended in 50 mL Milli-Q, shaken for 24 h on an agitating table and filtered afterwards. For the second experiment 0–5 mM $\text{Pb}(\text{NO}_3)_2$ was added. The carbonates and phosphates were measured in a TOC-analyzer (TOC-Vcpn, Shimadzu, Kyoto, Japan) and in the IC (930 Compact IC Flex, Metrohm, Switzerland), respectively. All statistical analysis were performed using SPSS 22 software package.

3. Results

3.1. Biochar characteristics

More extreme process conditions (i.e. higher temperature and residence times) led to a lower char yield (Table 2). Due to the small particle size and the softwood structure, the lowest biochar production was observed for pine wood. The oxygen and hydrogen contents are generally lower when the process conditions become harsher (i.e. higher temperature and longer residence times). The process parameters also influence the final cation exchange capacity of the chars. For pine wood and grass, it appears that the reactor temperature has the greatest influence.

Almost all chars were richer in metals than their original feedstock (Table 2) and a higher reactor temperature led to higher metal concentrations. As expected, a high amount of phosphorus was measured in the cow manure feed and its char derivatives. The pine wood feedstock has a low ash content, which results in low mineral concentrations in the biochar.

3.2. Sorption tests

3.2.1. Single-element batch sorption

The char CM550_10 consistently sorbed the largest amount of any of the studied metals (Pb, Cd, Zn, and Cu) (Fig. 1). The grass-based biochars sorbed slightly less whereas the wood-based biochars exhibited a markedly lower sorption. The final pH measured after sorption (indicated as a line in Fig. 1) shows the capacity of the cow manure- and grass-based biochar to increase the pH. Nevertheless, this increase does not follow the same trend than the sorption.

3.2.2. Multi-element batch sorption

Fig. 2 reveals a strong and specific affinity towards Pb for all biochars in a four-element solution (Cd–Cu–Pb–Zn 5 mM). The sorption of Cd and Zn is initially below detection limit. With higher char to water ratio (30 g/L and 50 g/L), the char sorbs more Cu and especially Pb. In the 50 g/L set-up, the two cow manure chars (CM550_10 and CM550_60) removed almost all the Pb and Cu in solution. Remarkable is the increase in Cd and Zn sorption once the two preferred metals (Cu and Pb) are fully removed.

Because the selected biochars showed a specific affinity towards Pb and Cu, a three-component system was set-up with only Cd, Cu and Zn (each 5 mM). Fig. 3 shows the removal percentages for this three-component system with the addition of 10, 30 and 50 g biochar/L. These set-ups will be referred to as the 30 and 50 g/L experiments in this paper. In these experiments, Cu was fully removed by the char, causing the sorption of Cd and Zn to increase significantly.

3.3. Phosphate and carbonate experiments

After 24 h of shaking in Milli-Q water, the leached phosphate concentration decreased significantly for biochars with increasing reactor residence time and/or temperature ($p < 0.05$ for grass- and manure-based biochars) (Fig. 4). A char produced at a higher reactor temperature yields a higher concentration of carbonates ($p < 0.05$ for grass- and manure-based chars). The carbonates can possibly co-precipitate with metals and thus play an important role in the metal immobilization process. The concentration of these anions leached from pine-based biochars is significantly lower because of the lower initial P concentration (Table 2).

Fig. 5 shows a decreasing trend in carbonate and phosphate concentration in solution when the initial Pb concentration increases. A decreasing trend in pH is noticeable when the initial Pb concentration increases due to the hydrolysis of Pb. Even though the solubility of carbonates increases with decreasing pH the leached carbonates show the opposite trend. Phosphate release also decreased with decreasing pH whereas the optimal is normally around pH 8, indicating that other mechanisms such as precipitation are occurring.

Table 3 compares the difference in phosphates, carbonates and the sorbed Pb concentration of CM550_60 before and after washing the char. A significant amount of phosphates and carbonates ($p < 0.05$) were removed from the re-suspended char, which had a significant effect on its sorption of Pb.

4. Discussion

4.1. Linking sorption with production parameters

As observed in the current data (Table 2), pyrolysis at a higher reactor temperature leads to lower char yields and a higher carbon content of the char. This is caused by the increased removal of volatile matter at higher temperatures. A deoxygenation of the char at higher temperatures causes a decrease in oxygen-containing functional groups and accordingly in the metal adsorption capacity (Uchimiya et al., 2011). The deoxygenation effect is also reflected in a decrease in cation exchange capacity. For the grass- and manure-based chars, the highest CEC was measured when the least heating was applied (at 350 °C for 10 min).

Compared to literature, the BET surface areas of the investigated chars were within typical ranges for the applied process conditions. Rajkovich et al. (2012) reported a value of 4.7 m²/g for a pine wood derived biochar which was pyrolyzed at 500 °C for 20 min. Zimmerman (2010) measured BET surface areas equal to 4.1 m²/g; 12.9 m²/g; 31.5 m²/g and 425.9 m²/g for a grassy biochar produced at 250 °C, 400 °C, 525 °C and 650 °C respectively and a holding time of 3 h. The process conditions applied in this paper are shorter and colder in comparison with the conditions used by Zimmerman (2010), which can

Table 2
The elemental and mineral compositions (mean n = 2; ± standard deviation), pH, Cation Exchange Capacity and N₂ BET surface (mean n = 3; ± standard deviation) of all the produced chars.

	C (wt%)	H (wt%)	N (wt%)	O (wt%)	Mn (mg/kg)	Ni (mg/kg)	Pb (mg/kg)	Zn (mg/kg)	P (mg/kg)	S (mg/kg)	Ash (wt%)	Char yield (wt. %)	pH	CEC (cmol(+)/kg)	N ₂ BET (m ² /g)
PW _{feed}	46.46 ± 0.15	5.12 ± 0.04	0.14 ± 0.05	47.95 ± 0.06	161.12 ± 13.64	B.D.L.	B.D.L.	11.93 ± 0.45	35.80 ± 2.15	B.D.L.	0.33 ± 0.00	-	-	-	-
G _{feed}	41.16 ± 0.07	4.73 ± 0.04	0.68 ± 0.01	40.96 ± 0.13	168.09 ± 1.04	B.D.L.	9.16 ± 3.00	47.61 ± 0.63	727.60 ± 21.30	57.89 ± 2.61	12.47 ± 0.03	-	-	-	-
CM _{feed}	39.16 ± 0.25	4.62 ± 0.08	1.80 ± 0.01	30.48 ± 0.02	328.01 ± 3.17	B.D.L.	3.36 ± 0.59	112.99 ± 0.05	5914.50 ± 62.00	1781.13 ± 10.13	23.93 ± 0.31	-	-	-	-
PW350_10	66.07 ± 0.08	4.99 ± 0.06	0.12 ± 0.00	28.19 ± 0.03	179.39 ± 19.78	11.54 ± 0.55	3.42 ± 0.07	37.40 ± 0.76	90.95 ± 1.63	103.50 ± 3.13	0.63 ± 0.11	54	5.9	3.7	0.9461 ± 0.0244
PW350_60	66.73 ± 0.05	4.85 ± 0.00	0.11 ± 0.01	27.15 ± 0.69	180.42 ± 48.94	7.36 ± 1.25	1.28 ± 0.37	38.24 ± 1.81	92.62 ± 5.28	85.60 ± 4.08	1.16 ± 0.75	37	5.9	4.5	0.9360 ± 0.0225
PW550_10	70.13 ± 0.39	3.78 ± 0.21	0.11 ± 0.01	25.48 ± 3.94	128.84 ± 4.65	21.24 ± 0.68	2.93 ± 0.12	38.81 ± 0.62	94.69 ± 1.46	96.34 ± 3.72	0.49 ± 0.18	37	4.4	1.5	0.9454 ± 0.0357
PW550_60	77.03 ± 1.00	3.17 ± 0.13	0.14 ± 0.03	14.24 ± 1.16	435.56 ± 238.54	8.21 ± 0.67	2.13 ± 0.43	120.86 ± 31.52	145.73 ± 12.96	268.19 ± 48.65	5.42 ± 0.31	24	7.7	1.2	-
G350_10	51.75 ± 0.56	4.39 ± 0.02	1.01 ± 0.01	23.80 ± 1.64	284.82 ± 21.03	32.63 ± 3.87	8.27 ± 0.35	74.24 ± 6.38	1426.88 ± 28.25	603.93 ± 55.20	19.05 ± 2.23	54	7.7	9	1.8158 ± 0.0517
G350_60	57.39 ± 0.49	4.01 ± 0.06	1.05 ± 0.01	17.61 ± 0.10	366.47 ± 2.36	42.41 ± 1.25	11.62 ± 0.34	94.73 ± 0.88	1768.02 ± 107.49	693.14 ± 12.44	19.94 ± 0.65	46	8.2	6.7	1.7398 ± 0.0349
G550_10	51.10 ± 0.27	2.34 ± 0.01	0.92 ± 0.01	16.67 ± 0.49	407.40 ± 19.35	43.57 ± 1.54	11.24 ± 0.03	102.61 ± 3.76	2093.30 ± 17.69	652.53 ± 38.10	28.96 ± 0.24	35	9.1	4.1	1.8585 ± 0.0677
G550_60	55.98 ± 0.09	2.33 ± 0.01	0.91 ± 0.01	10.90 ± 0.18	431.09 ± 20.15	48.37 ± 1.48	14.57 ± 2.49	104.62 ± 6.35	2385.63 ± 99.81	700.44 ± 36.57	29.88 ± 0.27	37	10	3.8	2.1708 ± 0.0840
CM350_10	46.67 ± 0.04	3.78 ± 0.03	2.49 ± 0.03	22.18 ± 0.09	697.35 ± 8.43	7.97 ± 0.30	3.15 ± 0.11	423.15 ± 6.87	17372.00 ± 239.00	2706.90 ± 11.20	24.87 ± 0.06	55	9.8	9.2	1.3571 ± 0.0265
CM350_60	42.35 ± 0.29	3.42 ± 0.06	2.23 ± 0.01	14.61 ± 0.37	555.51 ± 8.91	10.53 ± 0.06	6.65 ± 0.47	188.48 ± 2.25	10388.50 ± 77.50	2066.18 ± 38.23	37.38 ± 0.73	59	9.7	6.3	2.1264 ± 0.0392
CM550_10	46.11 ± 0.22	2.27 ± 0.01	2.17 ± 0.05	17.03 ± 0.67	903.96 ± 29.31	15.37 ± 0.29	4.38 ± 0.18	551.81 ± 21.62	22391.00 ± 440.00	2578.70 ± 39.50	32.42 ± 0.40	40	11	8.7	1.5657 ± 0.0296
CM550_60	49.91 ± 1.13	1.82 ± 0.04	2.11 ± 0.02	13.16 ± 0.76	930.06 ± 24.12	21.73 ± 0.06	5.12 ± 1.29	543.39 ± 15.96	22739.50 ± 940.50	2629.35 ± 28.35	33.00 ± 1.94	38	12	5.7	-

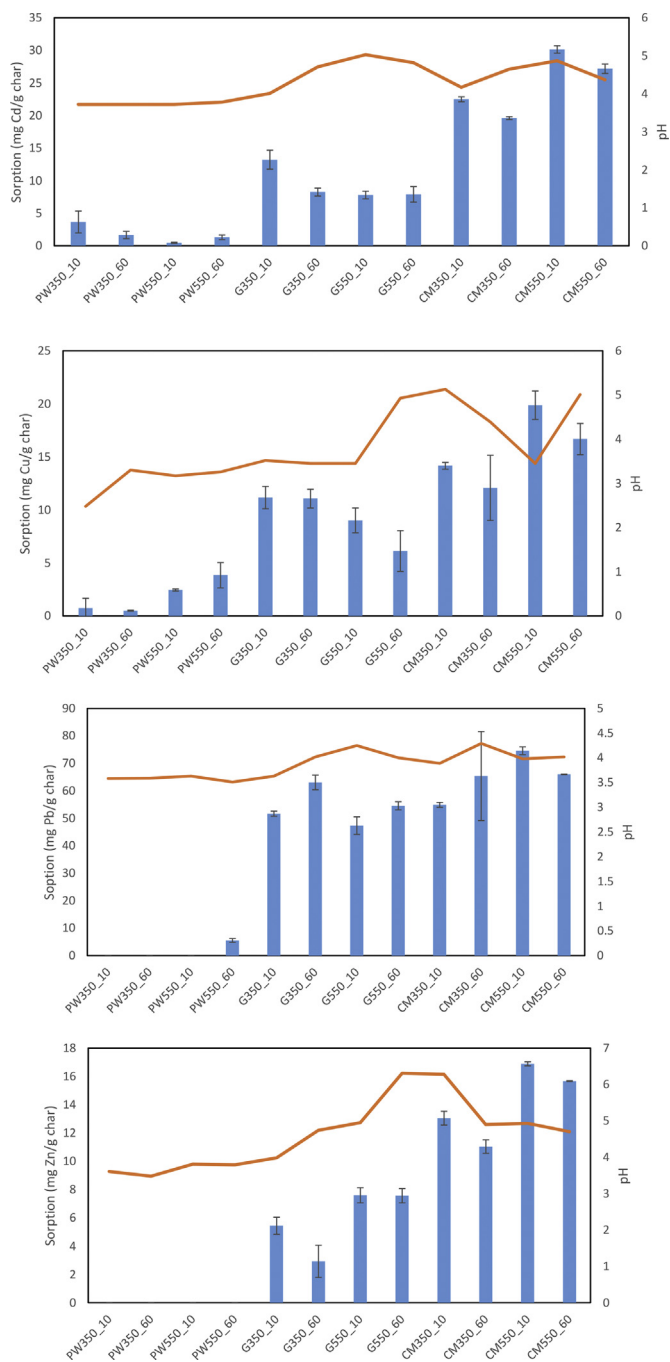


Fig. 1. Sorption of Cd, Cu, Pb and Zn on the chars. The error bars represent the minimum and maximum value (n = 2).

explain the lower BET surface areas for the grass-based chars observed in this study.

A higher ash content leads to a higher pH of the char because of the elevated presence of base cation oxides. The loss of acidic functional groups (e.g. carboxylic, lactone, phenol, and carbonyl) also contributes to a higher pH. Thus, there is an indirect link between the pyrolysis temperature and the char's pH (Table 2).

All the pine wood derived biochars show zero to low affinity for all metals concerned (Fig. 1). For Pb and Cu, PW550_60 was the best sorbing pine-based char showing a sorption of 5.54 ± 0.01 g/kg for Pb and 3.85 ± 0.01 g/kg for Cu. It is probably the combination of a low pH, low CEC (Table 2), low phosphate and carbonate levels that results in a generally low sorption for these type of chars. In previous studies, low adsorption capacities were noted for pine wood derived biochars.

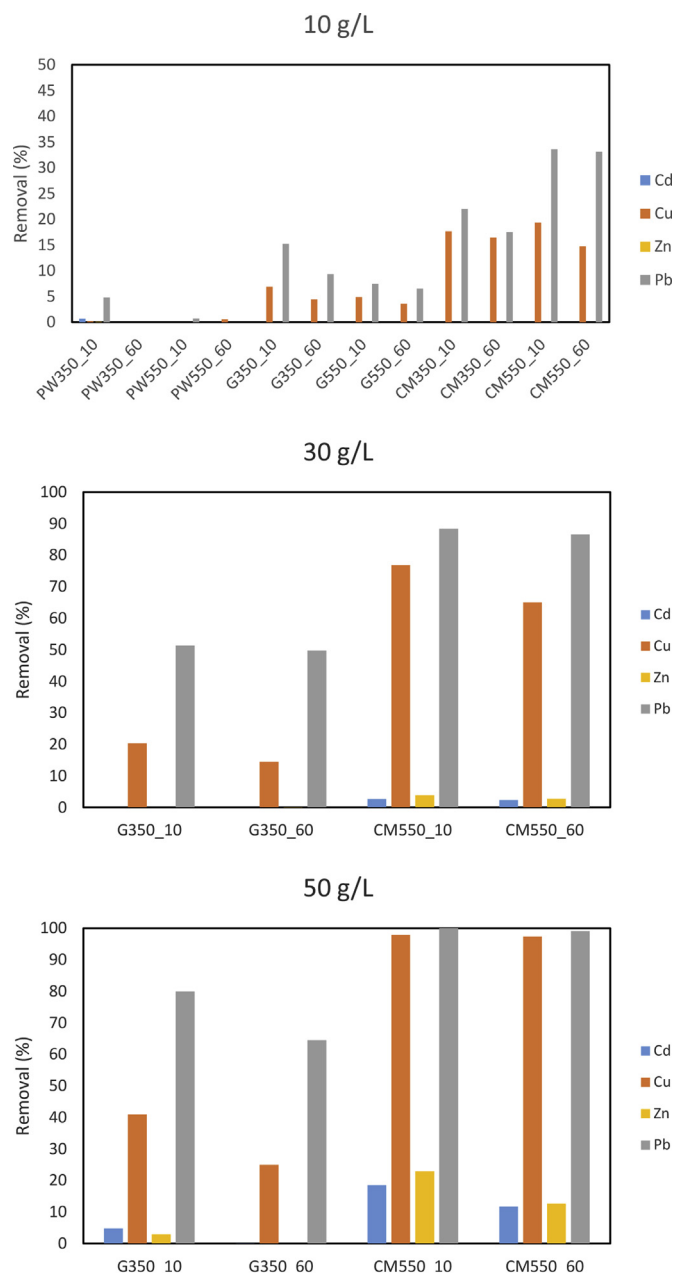


Fig. 2. The average removal percentages (n = 2) for selected chars (10, 30 and 50 g/L) in a quaternary component system with Cd, Cu, Pb and Zn (each 5 mM).

Jiang et al. (2016) reported adsorption capacities of 1.47 g/kg and 1.00 g/kg for Cu and Zn respectively and Mohan et al. (2007) published a value of 4.13 g/kg for the sorption of Pb. Liu et al. (2010) produced a pine wood derived biochar with a residence time of 2 h at 700 °C. The measured sorption for Cu was 2.73 g/kg which is in the same range as the pine wood derived biochars in this study.

With respect to the grass-based biochars, different chars were optimal for different metals. In literature, other grass-based feedstocks were used for metal immobilization. Roh et al. (2015) measured an adsorption capacity of 11.63 g/kg for Cd using a buffalo weed biochar produced at 700 °C for 4 h. For Cu and Zn, Han et al. (2013) reported values of 5.21 g/kg and 4.83 g/kg respectively for a char made from switchgrass at 500 °C with a holding time of 1 h. Except for Pb, all these reported values are lower than the ones reported in this study. This might indicate that the IFBB technology improves the characteristics of the char for metal sorption, which is possibly caused by the lower concentration of cations and the higher carbon content in the char (Van

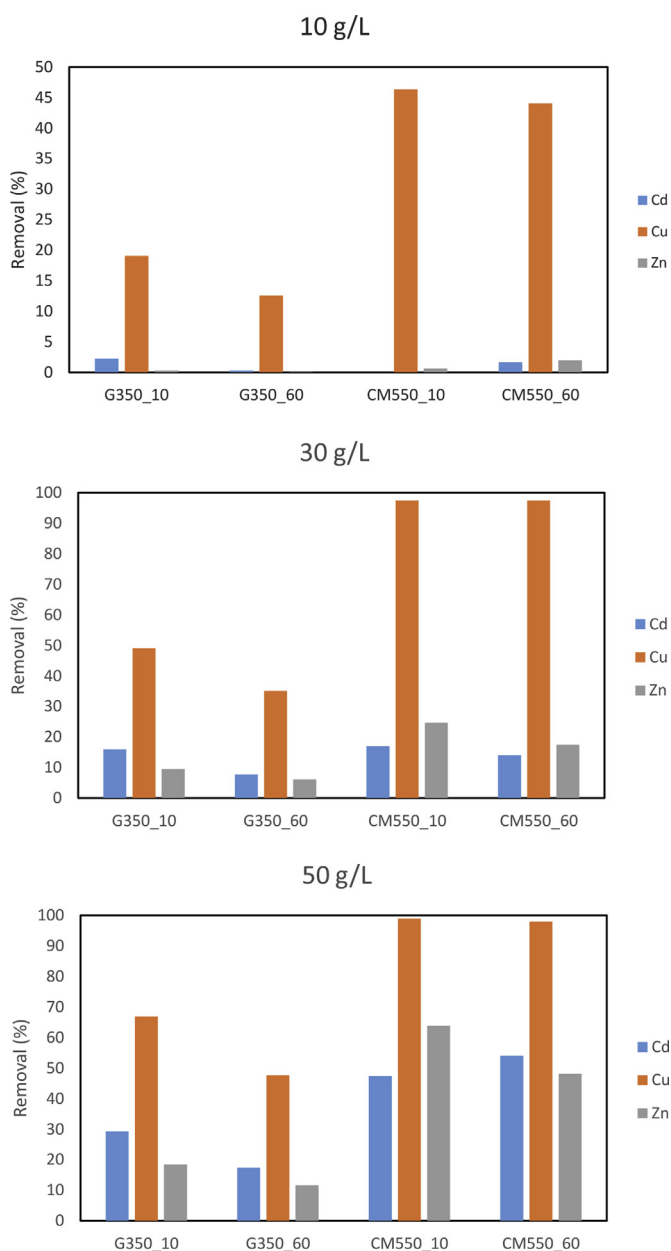


Fig. 3. The removal percentages for selected chars (10, 30 and 50 g/L) in a three component system with Cd, Cu and Zn (each 5 mM).

Poucke et al., 2016).

The chars produced from cow manure had the highest sorption capacity for all considered metals (Fig. 1). In accordance with the high ash content of the feedstock ($23.9 \pm 0.3\%$), all these chars have a high pH-H₂O (9.7–11.6). This can facilitate precipitation of the metals with the minerals present in the char (e.g. PO_4^{3-} , CO_3^{2-}). The amount of phosphorus in the ash minerals of the manure feedstock is remarkably higher than those of the other considered feedstocks (Table 2). This results in higher concentrations of phosphates in the char. The cow manure char produced at 550 °C and 10 min residence time had a high pH, a high CEC and a relatively higher phosphate and carbonate concentration, resulting in maximal sorption for all metals considered compared to the other biochars. As a comparison, Xu et al. (2013) used dairy manure feedstock and pyrolyzed it at 350 °C for 4 h. Adsorption capacities of the produced biochar of respectively 54.4 mg Cu/g; 32.8 mg Zn/g and 51.4 mg Cd/g were reported. A similar biochar was previously studied by Cao et al. (2009) for the adsorption of Pb. The adsorption capacity for Pb was equal to 93.65 g/kg. The sorption capacities of CM550_10 in this study are in the same range as the ones described in literature.

Carbonate and phosphate levels but also the amount of oxygen containing functional groups are temperature dependent. Production parameters may thus be chosen to optimize specific sorption properties. The choice of temperature is a trade-off between all the temperature-dependent properties of the char. A high pyrolysis temperature partly removes the oxygen containing functional groups and lowers the phosphate concentration, which is unfavorable for sorption. However, a higher pH and an increased carbonate concentration will favor sorption. The optimum conditions for manure-based biochars in this study were 550 °C and 10 min pyrolysis time. Both these results and the data in Table 1 imply the trade-off principle for chars with relevant amounts of phosphates and carbonates in its structure. In feedstocks with a lower amount of these anions present, it is recommended to apply milder process conditions to maximize the cation exchange capacity.

4.2. Multi element effect

All chars were tested on a multi-element component system with 5 mM of Cu, Pb, Cd and Zn to investigate possibilities to remove metals from contaminated streams. The overall sorption was lower than in a single-element system. For example, CM550_10 revealed a sorption of 74.58 ± 0.01 mg Pb/g in a single-element system compared to 34.09 ± 1.51 mg Pb/g in a quaternary component system. The added Pb concentration in the multi-element system is lower than in the single-element system but a comparison of these two adsorption capacities is still possible, because the adsorption isotherm suggests that the maximum adsorption capacity is reached in both experiments. The

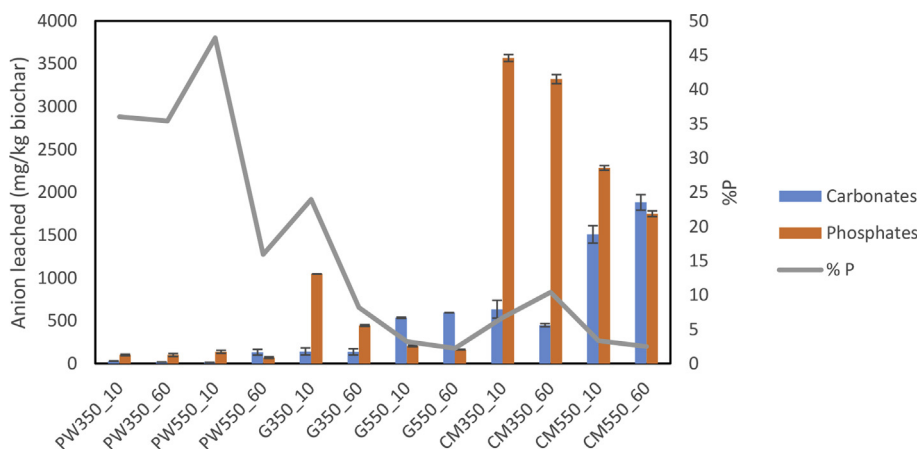


Fig. 4. Carbonate and phosphate leached from the biochars (mg/kg biochar). The error bars represent the minimum and maximum value (n = 2).

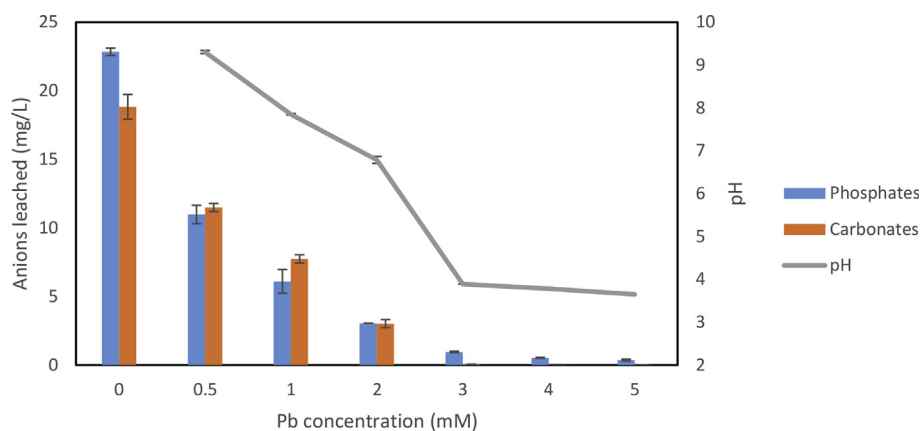


Fig. 5. Phosphate and carbonate concentrations leached (mg/L) as a function of a series of initial Pb concentrations (0,5-5 mM) for char CM550_60. The grey line indicates the pH values after sorption. The error bars represent the minimum and maximum value ($n = 2$).

Table 3

Comparison in phosphate (mg/L), carbonate (mg/L) and sorption of Pb (g/kg) before and after washing CM550_60 (mean $n = 2$, \pm standard deviation).

	Original	Re-suspended char
PO_4^{3-} (mg/L)	22.85 ± 0.27	8.21 ± 1.15
CO_3^{2-} (mg/L)	18.83 ± 0.90	5.20 ± 0.16
Sorption (g/kg)	65.99 ± 0.08	44.94 ± 0.99

quaternary system experiment also indicated that the sorption of Cu and especially Pb is preferred over Cd and Zn by the grass- and manure-based chars. In the 10 g/L-experiment (Fig. 2), it was observed that the affinity of the chars towards Cu and especially Pb is still present. Only very small amounts of Zn and Cd were removed. In the 30 g/L set-up (Fig. 2), it was observed that the preference for sorption of Cu and especially Pb is still evident. Only very small amounts of Zn and Cd were removed. In the 50 g/L set-up (Fig. 2), removal percentages close to 100% were obtained with the manure derived chars. Only when Pb and Cu were removed, the removal of Cd and Zn started to increase. This shows the selectivity and suggests that it is possible to specifically remove unwanted Cu and Pb from a contaminated water stream by optimizing the dosage of adsorbent or in a column set-up.

The chars were further tested on a tree component system with Cu, Cd and Zn (5 mM) (Fig. 3). Again, a high affinity towards Cu was observed. Sorption of Cd and Zn only started to increase once all the Cu was fully removed from the contaminated solution. This trend is clearer with the manure-based chars. The sorption preference of CM550_10 for the metals concerned in this study in a mixed system is as followed: $\text{Pb} > \text{Cu} \gg \text{Zn} > \text{Cd}$. For the other chars in this set-up (G350_10, G350_60 and CM550_60), the sorption order in a mixed system was $\text{Pb} > \text{Cu} \gg \text{Cd} > \text{Zn}$.

A similar experiment was performed by Uchimiya et al. (2010) where a broiler litter char was tested on a quaternary component system with Pb, Cu, Cd and Ni (each 1.5 mM). The sorption order in this case was equal to $\text{Pb} > \text{Cu} > \text{Zn} > \text{Ni}$.

Multiple explanations for the favored sorption of Pb are suggested in literature. Yakkala et al. (2013) also found a greater sorption of Pb on buffalo weed biochar in a mixed system with Cd and Pb. The higher sorption was explained by the difference in ionic radius. Pb has a larger ionic radius (0.119 nm) than Cd (0.095 nm, Shannon, 1976). This makes the Cd-ions easier to be hydrated and thereby a thicker layer of water can be formed on the ion's surface. This would make the Cd-ions more mobile and consequently decrease its tendency to adsorb and stay on the biochar compared to Pb (Huang and Fuerstenau, 2001). Unfortunately, because the ionic radius of Cu and Zn are respectively equal to 0.073 nm and 0.074 nm (Shannon, 1976) it seems unlikely that this hypothesis is compatible with the findings in this or the other multi-

element studies.

Another possibility is to look for the difference between the upper pH values where the metals tend to form insoluble hydroxide complexes. This possibility was rejected in the study of Uchimiya et al. (2010) because these values did not correlate with the order of sorption. Pb forms hydroxides upward of pH 7, Cu at pH 6, Zn at pH 8 and Cd at pH 8.3 ($\text{Cu} > \text{Pb} > \text{Zn} > \text{Cd}$). If this theory is applied to the sorption order ($\text{Pb} > \text{Cu} \gg \text{Cd} > \text{Zn}$) in our study however, there seems to be a slight correlation except for Cu and Pb.

A third possible explanation for the higher sorption of Pb is mentioned by Shi et al. (2009). In this report, the importance of the electronegativity of the metal is highlighted. A higher electronegativity leads to a higher tendency of the ion for specific sorption. The order of electronegativity of the metals in this study is: Pb (2.33) > Cu (1.90) > Cd (1.69) > Zn (1.60). This seems to correlate well with the sorption order found for CM550_10.

Uchimiya et al. (2010), at last, explained his results ($\text{Pb} > \text{Cu} > \text{Zn} > \text{Ni}$) by checking the stability constants for model phosphorus functional groups and the divalent metal ions. A clear trend was noticed between the stability constants and the degree of metal sorption. Lead can form a more stable complex with the char's phosphate than any of the other metals considered.

4.3. Contribution of precipitation

The three main mechanisms for metal immobilization are physical adsorption, ion exchange or (co-)precipitation with phosphates, carbonates and hydroxides (Bolan and Duraisamy, 2003; Bolan et al., 2003). PW550_60 has a very high carbon content ($77.03 \pm 1.00\%$) but a low sorption capacity for all metals. The surface areas of all chars are also low due to the overall mild process conditions applied. This may point towards a rather small contribution of physical adsorption in the metal immobilization.

The two other main mechanisms are ion exchange where the CEC-value acts as an indicator and (co-)precipitation which was investigated conducting several experiments on the phosphate and carbonate content of the chars. The concentration of these anions was clearly correlated with the performance of the chars (Figs. 1 and 4) but the relative contribution of these two mechanisms on the final adsorption can be estimated in two different ways.

A first possibility, as performed by Ding et al. (2014), is to look at the amount of phosphates and carbonates which disappear from solution after contact with increasing Pb concentrations. Fig. 5 reveals a decreasing trend in phosphates and carbonates recovered from CM550_10 as the initial metal concentration increases. This confirms the formation of insoluble phosphate and carbonate complexes with the metals. Ding et al. (2014) assumes a $\text{PO}_4^{3-}/\text{Pb}$ molar ratio of 3:5 for the

calculation of Pb-phosphate complexes. Cao et al. (2009), on the other hand, proved the presence of crystallized β - $\text{Pb}_9(\text{PO}_4)_6$ molecules in an experiment conducted with a biochar produced out of dairy manure. This crystal implies a $\text{PO}_4^{3-}/\text{Pb}$ molar ratio of 6:9. Due to the fact that Cao et al. (2009) specifically worked with a dairy manure and the small difference with the previously suggested 3:5 ratio, a molar ratio of 6:9 was chosen for further calculations. When the initial Pb concentration was equal to 5 mM, all the phosphate ions precipitated with the Pb ions (Fig. 5). Thus, 2.4×10^{-5} mol of phosphates are available in solution per gram of biochar. As these form complexes in a 6 to 9 ratio with Pb, 3.6×10^{-5} mol of Pb per gram of biochar can be precipitated. The total sorption capacity of CM550_10 towards Pb is equal to 0.360 mol/kg. Thus, it can be hypothesised that about 10% of the Pb is immobilized by phosphate precipitation. The same approach can be adopted for carbonates. Fig. 5 reveals a decrease in carbonate concentrations when the initial metal concentration increases. This indicates the formation of Pb-carbonate complexes. Cao et al. (2009) proved the precipitation of insoluble hydrocerussite $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ using a dairy manure char. The corresponding $\text{CO}_3^{2-}/\text{Pb}$ molar ratio of 2:3 is used in further calculations. The calculated contribution of carbonates for the Pb sorption on CM550_10 is equal to 10.5%. This means that with respect to Pb sorption onto CM550_10, at least 20.5% can be assumed to be sorbed by (co-)precipitation. The remainder may then be sorbed by electrostatic attraction, physical sorption, complexation with functional groups and/or by the formation of other precipitates. This percentage probably only represents a fraction of the Pb ions which precipitate because only soluble phosphates and carbonates were taken in consideration. Qian et al. (2013) reports that a certain fraction of phosphates is still bound to the biochar's surface in an aqueous suspension. These phosphates can probably still immobilize metals by forming precipitates on the biochar's surface. Accordingly, the calculated percentage of 20.5% precipitated Pb is probably an underestimation.

An experiment where the Pb content was measured on a paper filter after sorption and after manual biochar removal revealed that $11.8 \pm 0.3\%$ of the sorbed Pb could be found on the filter paper. These results imply that the main mechanism of immobilization are functional groups, physical adsorption or by complexation with the phosphates and carbonates which are still bound to the biochar's surface.

A second way to estimate the contribution of the precipitation mechanism to the Pb sorption was developed and tested. After washing, filtering and re-suspension in a Pb solution, the decrease in phosphates and carbonates was compared to the decrease in adsorption capacity. With all the values in Table 3 converted to moles, about 0.1016 mmol less Pb per gram of biochar is sorbed. The combined loss of CO_3^{2-} and PO_4^{3-} molecules is equal to 0.0381 mmol. Considering the molar ratio of the precipitates, the final contribution of carbonate and phosphate precipitation on the total sorption would be estimated at 56.3%. Compared to the earlier calculated 20.51% for CM550_10, this is a much higher value. Possibly other components, such as hydroxides, also were removed by the re-suspension. The pH drops from 9.18 to 7.50 after re-suspension may support this. A pH drop also lowers the CEC, adversely influencing metal immobilization (Silber et al., 2010). This suggests that this calculation method is probably not fully suitable to specifically estimate the contribution of phosphates and carbonates when it comes to metal immobilization. However, the two estimation methods applied in this study do indicate the importance of ash anions in the metal immobilization.

The latter experiment also revealed a potential issue regarding the use of biochar. The sorption drops with 32% by re-suspension of the char. This indicates a negative influence of washing the char before a sorption experiment. In multiple studies (Lima and Marshall, 2005; Liu et al., 2010; Yakkala et al., 2013; Zhou et al., 2013) the produced chars are washed with de-ionized water to remove the access of ashes on the char or to reduce the possible toxicity towards plants and animals (Beesley et al., 2011). Washing of biochars has a negative influence on the ash anions and thus on sorption. It is thus important to report how

the sample was treated when reporting data on sorption capacity of biochar. These findings also imply some issues for the applied use of biochar, for instance the limited re-use of biochar and the possible leaching of ash anions in a column experiment.

5. Conclusions

The results of this study suggest that biochars produced out of a grass or manure can sorb much more metals (Pb, Cd, Zn and Cu) from aqueous solution than wood-based biochars. Biochar from cow manure showed a greater sorption than the grass-based biochars due to a higher pH and a higher amount of phosphates and carbonates. These anions and sorption conditions allow the formation of metal precipitates, which contributes to the high sorption capacity. Because these anion concentrations are temperature-dependent, it is possible to design a biochar with a maximum adsorption capacity. However, a trade-off between the cation exchange capacity, phosphate and carbonate concentration has to be considered when selecting optimal pyrolysis process conditions. Furthermore, washing away these anions can result in a 30% reduction in sorbed Pb. For feedstocks with lower concentrations of these anions initially present, applying milder process conditions is recommended to maximize the cation exchange capacity. For cow manure, the optimal process conditions were found to be a reactor temperature of 550 °C and a residence time of 10 min.

The grass- and manure based biochars showed a specific affinity towards Pb and Cu in a multi-component system with Cd, Zn, Pb and Cu in it. After adjusting the dosage, removing all Pb and Cu from this solution was possible. Once these two metals were removed, Cd and Zn started to be sorbed. This points to a possibility to selectively remove Cu and Pb ions from a contaminated water stream by optimizing the dosage of adsorbent. Current results reveal several specific points that are of practical importance on optimizing the use of biochar as a metal adsorbent.

6. Future research

If biochar will be applied in industry, real wastewaters will contain mixtures of metals and other contaminants. It is important that more research is conducted to investigate how changing the concentration and type of biochar can lead to a selective removal of the contaminants. Engineering of the systems to accomplish this, needs better understanding before they can be applied.

There were many errors associated with the sorption mechanisms calculations therefore other analytical techniques should be considered to yield a better understanding of the behavior and interactions of the metals and the biochar. Voltammetry can quantify and differentiate metal-ligand bounds in the solution. What is happening on the surface of the biochar, is more difficult to assess. Synchrotron analysis gives a real time characterization of the metals in solution and on the biochar's surface using exafs and xanes. Ft-ir detects changes in the functional groups on the biochar's surface such as hydroxides or ketons. X-ray elemental dot mapping techniques combined with statistical analysis could indicate correlations between the elements on the surface of the biochar and the sorbed metal.

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