King Saud University

Arabian Journal of Chemistry

SPECIAL ISSUE: ENVIRONMENTAL CHEMISTRY

Copper removal from aqueous solution using biochar: Effect of chemical activation

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Abstract   The main aim of this study was to test the efficiency of biochar for Cu removal from synthetic and soil solutions, respectively.

The biochar was produced from brewers draff *via* pyrolysis. Additionally, the prepared biochar was also activated using 2 M KOH to enhance its sorption efficiency to remove Cu from both solutions. Two different aqueous solutions were prepared for these experiments: (i) a synthetic using Cu-nitrate salt with 0.01 M $NaNO_3$ and (ii) soil solution obtained from a Cu-contaminated soil using 0.01 M $CaCl_2$ leaching procedure. Batch sorption and column experiments were used to evaluate the efficiency of both biochar (BC) and activated biochar (BC_{act}) to remove Cu from the solutions.

Results showed that both biochar samples are pure amorphous carbon and the Cu sorption is thus mainly a result of physical sorption on the biochar surface. Next, chemical activation, using 2 M KOH, significantly increased the total volume of all pores in biochar (from 0.01 ± 0.002 to 8.74 ± 0.18 mL g^{-1}). On the other hand, the BET surface area was similar for both sorbents (BC = 9.80 ± 0.62 m^2 g^{-1} and BC_{act} = 11.6 ± 0.4 m^2 g^{-1}). Results also demonstrate enhanced sorption efficiency of the BC_{act} (10.3 mg g^{-1}) in comparison with the BC (8.77 mg g^{-1}). Additionally, enhanced Cu removal during column retention test was observed for the BC_{act} in both synthetic and soil solutions, respectively.

In summary, the results showed that biochar prepared from brewers draff was able to remove Cu from both aqueous solutions.

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1. Introduction

At higher concentrations, Cu is a potentially toxic metal in the environment, mainly as the soluble form Cu^{2+}. This metal is usually used in a number of industrial processes (e.g., metallurgy or foundries of brasses) as well as in agriculture (e.g., fungicides). It eventually leaves the aqueous (soil) solutions

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at a higher concentration that should be stabilized before discharge to the environment. Generally, the most frequently applied methods for immobilization/stabilization of metals are the many kinds of chemical precipitations (Tesoriero and Pankow, 1996; Basta and McGowen, 2004) or sorption methods using hydrated oxides of Mn, Al, Fe (Trivedi and Axe, 2001; Boukhalfa et al., 2007), nanoparticles (Feng et al., 2010; Fang et al., 2011; Ahmad et al., 2012) or biomaterials such as biochar (Uchimiya et al., 2011; Regmi et al., 2012). Biochar as a biosorbent was chosen mainly due to the high affinity of Cu to organic matter (Bradl, 2004; Komárek et al., 2009).

Biochar (pyrolysed organic carbon) is produced as a charred material by thermal decomposition of biomass under conditions of minimal oxygen presence (Beesley and Marmiroli, 2011). Usually, some waste material is chosen for the pyrolysis process. In the Czech Republic, there is a long historical tradition focused on beer preparation hence many breweries are situated in this country. In more detail, on an area of $79,000 \, km^2$ there are over 120 breweries. Due to this fact, 380 thousand tons of brewers draff are produced as a waste product in the Czech Republic (Czech Beer and Malt Association). This agricultural waste is usually used as pig food; nevertheless, there is another occasional way of utilizing it, such as the previously mentioned biochar preparation.

Biochar has been extensively studied in the past few years for its ability to enhance the nutrient level of soils (Schulz and Glaser, 2012) as well as its positive effect on the plant growth (Sohi et al., 2010). Next, biochar applied to the soil should also influence its chemical properties such as changes in pH, electrical conductivity, cation exchange capacity (Amonette and Joseph, 2009) and also metal sorption efficiency; (Uchimiya et al., 2011; Beesley and Marmiroli, 2011; Gupta et al., 2013). This metal sorption efficiency should then be enhanced using different kinds of biochar modifications such as: (i) composting (Borchard et al., 2012), (ii) iron-impregnation (Inyang et al., 2013), (iii) oxidation (Uchimiya et al., 2012), or (iv) chemical activation using hydroxides (Regmi et al., 2012). Additionally, inspired by the study of Regmi et al. (2012), pyrolysed brewers draff was chemically activated (using 2 M KOH) to enhance its ability to remove Cu from aqueous solutions.

The main aim of this study is therefore to test biochar obtained from the pyrolysis of brewers draff for Cu removal from aqueous (synthetically prepared and soil) solutions. Additional objective included: (i) usability – yield of tested biochar during the pyrolysis process; (ii) biochar chemical activation, which should improve porous structure and consequently should enhance its efficiency of Cu removal. Furthermore, biochar and activated biochar will also be compared for their potentially different physical and chemical characteristics (e.g., point of zero charge, BET surface area and total pore volume, pores distribution, Fourier transform infra-red spectroscopy and scanning electron microscope).

2. Materials and methods

2.1. Solution preparation and characterization

Copper(II) was the adsorbate studied in all experiments. In this case, two different types of aqueous solutions containing this metal were used. First, synthetic solution was prepared by

dissolving $CuNO_3 \cdot 3H_2O$ (p.a.), (Lach-Ner, CZE) into a previously prepared background electrolyte (0.01 M NaNO3). Second, soil solution was obtained from Cu-contaminated soil by 0.01 M $CaCl_2$ leaching procedure overnight. This soil originated from the vicinity of Le Palais copper refinery (Limoges, France) and all characteristics of this soil solution are listed in Table 1. Additionally, such prepared synthetic and soil solutions were analysed for: (i) pH value; (ii) all metal concentrations using ICP-OES (Agilent Technologies 700 series, USA), (iii) dissolved organic carbon (DOC) using TOC-L CPH Analyser (Shimadzu, Japan), (iv) available nutrients using ion chromatograph ICS 90 (Dionex, USA) and flame atomic absorption spectrometer F-AAS (Varian 280FS, Australia), respectively.

2.2. Biochar preparation and characterization

Local brewers draff obtained from the brewery at the Czech University of Life Sciences Prague was used due to its low cost and large amounts produced (Šillerová et al., 2013), was air dried overnight and consequently pyrolysed at 650 °C under $100 \, mL \, min^{-1}$ nitrogen flow rate. Such high temperature was chosen for the biochar preparation in order to get the brewers draff fully carbonized with low volatile amounts and high fixed carbon values (Agirre et al., 2013). Additionally, the yield of final char was measured at the temperature rate of $5 \, °C \, min^{-1}$ using thermogravimeter Stanton Redcroft TG 750. The resulting biochar (BC) was then cooled overnight under the same nitrogen flow rate (as before). Such prepared pyrolysed product was ground, sieved to less than 0.25 mm, washed by ultra-clean water MilliQ Integral (Merck Millipore Corp., USA) and dried at 105 °C. Biochar activation was implemented according to Regmi et al. (2012), when 4 g of BC was mixed with 1000 mL of 2 M KOH solution and stirred for 1 h. This solution was then filtered using 0.45 μm nylon filters (Whatman Ltd, USA). In the next step, filtered biochar was mixed with ultraclean water and the pH value of both biochars was adjusted using 0.1 M NaOH/HCl. Next, the biochar (BCact) was again filtered and dried overnight at 105 °C.

Surface area, total pore volume and pore distribution were determined using the BET surface and pore analyser SA 3100 (Beckman Coulter, USA). The BET surface area was measured by nitrogen adsorption isotherms at 77 K, total pore volume was determined from adsorbed volume of nitrogen at pressure $p = 1$ atm and pore distribution was then calculated from the desorption isotherm. Elemental composition was measured in triplicate by CHNS-O Analyser Flash 1112 (Thermo, USA). Moreover, surface functional groups of brewers draff, BC and BC_{act} were analysed using FTIR Nicolet 6700 analyser connected with a microscope Continuum (Thermo-Nicolet, USA). Point of zero charge (pH_{zpc}) was determined for both biochars according to Fiol and Villaescusa (2009) using potentiometric mass titration (PMT) and the immersion technique (IT). Additionally, SEM analyses of both biochar samples were also implemented using a scanning electron microscope JEOL JSM-7401F Fesem (USA).

2.3. Batch experiments

First, kinetic experiments were implemented in order to establish equilibrium for the subsequently prepared sorption/desorption experiment. More precisely, synthetic Cu-solution

Table 1 Initial soil solution description.

pH [-]	DOC [mg L^{-1}]	Metal concentration [mg L^{-1}]									
		Al	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
4.37 ± 0.1	30.9 ± 1.8	5.39 ± 0.04	0.01 ± 0.001	0.15 ± 0.001	0.03 ± 0.002	1.15 ± 0.01	0.10 ± 0.002	3.88 ± 0.03	0.08 ± 0.001	0.08 ± 0.004	0.93 ± 0.01

(In)organic anions/cations [mg L^{-1}]												
^{a}Ca^{2+}	K$^+$	Mg^{2+}	Na$^+$	NH$_4^+$	^{a}Cl$^-$	Br$^-$	F$^-$	NO$_3^-$	SO$_4^{2-}$	Oxalate	Malate	Tartrate
394 ± 1	10.5 ± 0.1	5.62 ± 0.05	1.59 ± 0.01	4.23 ± 0.02	465 ± 1	0.98 ± 0.03	0.21 ± 0.02	5.20 ± 0.03	1.90 ± 0.01	3.29 ± 0.05	0.02 ± 0.001	0.45 ± 0.02

^{a} 0.01 M CaCl$_2$-extracted solution from Cu-contaminated soil

at 0.1/0.25 mM was mixed with biochar samples at the ratio 1:500 (w/v). Suspensions prepared in this way were shaken (at 250 rpm), centrifuged, filtered (0.45 μm nylon filter) and the obtained supernatants were analysed at regular time steps (1, 2, 4, 8, 12, 24 and 48 h) in order to determine the Cu concentration. Next, 20 mL of synthetic solution (with Cu concentration steps of 0.02–2 mM) was added into 0.04 g of both prepared biochar samples (BC × BC$_{act}$) respectively, to establish their sorption maxima. Following the previously implemented kinetic experiments, the suspensions of the solution with the biochar samples were shaken for 24 h in order to reach equilibrium. Additionally, desorption experiment was also carried out. Background electrolyte (0.01 M NaNO$_3$) was used to obtain information about the desorbed volume of copper from the previously Cu-saturated biochar samples.

2.4. Column experiments

The retention column experiment used two identical glass columns (Bio-rad Laboratories, USA) of 13 cm length and 2 cm in internal diameter which were filled with 3 g of BC and BC$_{act}$, respectively. Such prepared columns were gravitationally leached from the top for 24 h under a constant flow rate (5 mL min^{-1}), which was maintained by a peristaltic pump EP-1 Econo Pump (Bio-rad Laboratories, USA). Two types of aqueous solutions were used for the retention test mentioned previously: (i) soil leachate; and (ii) synthetic Cu-solution, the concentration of which was adjusted to equal the Cu concentration in the soil leachate (approx. 0.02 mM). The pH value of the synthetic solution has also been adjusted to equal that of the soil leachate.

Both leachates were then automatically sampled over a 24 h period of time (at gradually increasing time steps) during the whole retention test, using the fraction collector FC 204 (Gilson, USA). Finally, obtained samples were analysed for Cu and DOC concentration in the leachate. Furthermore, other metals and all (in)organic anions/cations in the soil solution were also analysed.

2.5. Copper speciation model

The Minteq.v3.dat thermodynamic database (derived from the code MINTEQ+, version 3.0, released by the U.S. EPA in
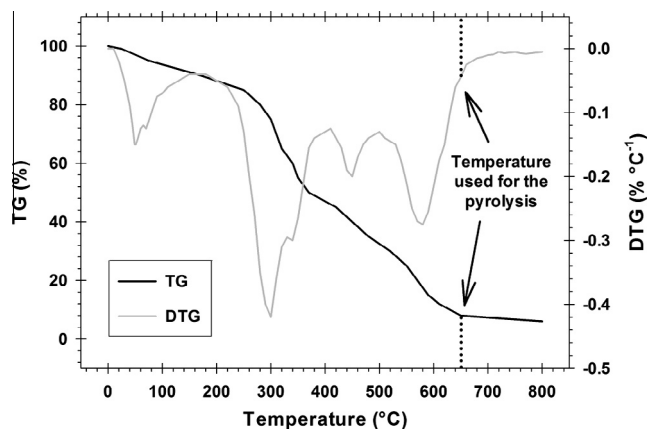
Figure 1 Thermogravimetric mass loss (TG) and derivative thermogravimetric mass loss (DTG) curves of used brewers draff.

1999) was used for all calculations. The initial soil solution (see Table 1; obtained by 0.01 M CaCl$_2$) with all characteristics (DOC; all (in)organic anions and cations as well as metal concentrations) was used for the calculation. Additionally, Cu speciation was also calculated at the final time step of the column retention test for both the BC and BC$_{act}$ variants, respectively.

3. Results and discussion

3.1. Thermogravimetric analysis of brewers draff

The thermogravimetric mass loss (TG) and its derivative curve (DTG) are shown in Fig. 1. Initial mass loss (approx. 10% reduction) ranging from 25 to 150 °C was mainly due to moisture evaporation. Next, devolatilization and biochar thermal decomposition were responsible for other mass losses (approximately 80% reduction) from 300 °C up (Gil et al., 2012; Yi et al., 2013). In more detail, there were two obvious peak values for the DTG curve of −0.42 and 0.28% °C^{-1} at 295 and 580 °C, respectively. In summary, total mass loss was approximately 90%, which demonstrated a very low yield of biochar during pyrolysis at 650 °C of brewers draff. Due to this fact a different char preparation would be more suitable, such as hydrothermal carbonization (HTC), hence the term hydrochar (Regmi et al., 2012; Titirici et al., 2007; Xue et al., 2012).

3.2. Chemical activation by 2M KOH

According to Regmi et al. (2012) cold alkali solution (2 M KOH) was chosen for the chemical activation of prepared biochar to enhance its porosity and clean up blocked pores mainly by tar particles. Additionally, surface area of activated biochar was expected to increase which might have enhanced copper removal from both aqueous solutions. All characteristics of activated biochar compared with biochar are shown in Table 2; Figs. 2–4 and the results are discussed in the next subsection in more detail.

3.3. Characterization of prepared biochar samples

3.3.1. Main physical characteristics, SEM images and elemental composition

These characterizations of BC and BC$_{act}$ are presented in Table 2. First, total pore volume showed significant increases (874-times higher) after 1 h of stirring in 2 M KOH, which could be due to the change in the pore distribution. In more detail, pores with the size of less than 6 nm were represented only in the case of BC$_{act}$ (18.7%), most likely as a result of the tar particles having been removed especially from these small pores by 2 M KOH which, in the end, caused a dramatic total pore volume increase. The neutralization reaction between 2 M KOH and the dust particles is here the specific mechanism, which affects the total pore volume. On the other hand, BET surface area showed quite identical values for both biochar samples, due to the subsequent precipitation of tar particles onto the surface of bigger-sized pores for the case of BC$_{act}$.

Next, scanning electron microscope (SEM) images of both biochars with and without chemical activation are shown in Fig. 2 to exemplify the potential physical changes caused by

Table 2 Biochar (BC and BC$_{act}$) characterization. Values are given as means ± standard deviation for triplicate measurements.

Sample	pH$_{zpc}$ [−]	BET surface [m² g⁻¹]	Pore distribution [%]				Total pore volume [mL g⁻¹]	Elemental composition [g kg⁻¹]			
			<6 nm	6–20 nm	20–80 nm	>80 nm		N	C	H	S
BC	6.80 ± 0.23	9.80 ± 0.62	n.d.	8.23	59.8	32.0	0.01 ± 0.002	47.7 ± 0.6	664 ± 0.4	24.9 ± 0.5	0.47 ± 0.03
BC$_{act}$	7.20 ± 0.15	11.6 ± 0.4	18.7	18.1	38.8	24.5	8.74 ± 0.18	50.3 ± 0.2	691 ± 2	24.7 ± 0.4	0.68 ± 0.15

n.d. not detected.

the previously mentioned activation. The SEM images of both biochar samples (Fig. 2) show similar surfaces which corresponded with partly identical BET surfaces for both variants of used biochar. Nevertheless, the SEM image of the BC$_{act}$ (Fig. 2b) is represented on average by more intensive waving of the particle surfaces as a result of tar particles having been removed mainly from the small-sized pores. Additionally, as we had expected, the elemental composition was similar for both biochar samples.

3.3.2. Point of zero charge determination

The experimental curves corresponding to the PMT technique were obtained for both biochar samples and are presented in Fig. 3a and b. In the presented curves, the pH$_{zpc}$ is identified as the pH at which the blank and all titration curves of differ-ent biochar amounts converge (Fiol and Villaescusa, 2009). In more detail, the point of zero charge for BC samples was determined at pH = 6.80, nevertheless, pH$_{zpc}$ determination in the case of BC$_{act}$ was ambiguous due to quite different shapes of all titration curves (for each amount of biochar in suspension).

Therefore, another technique for determination of the pH$_{zpc}$ was implemented. The chosen immersion technique (IT; see Fig. 3c and d) confirmed the pH$_{zpc}$ for BC at pH = 6.80 and in case of BC$_{act}$ there was a minimum normalized ΔpH at pH = 7.20, which presented a realistic as well as expected pH value.

3.3.3. FTIR analysis

Fig. 4 shows the FTIR spectra for both biochar and chemically activated BC in the near IR region (wave number
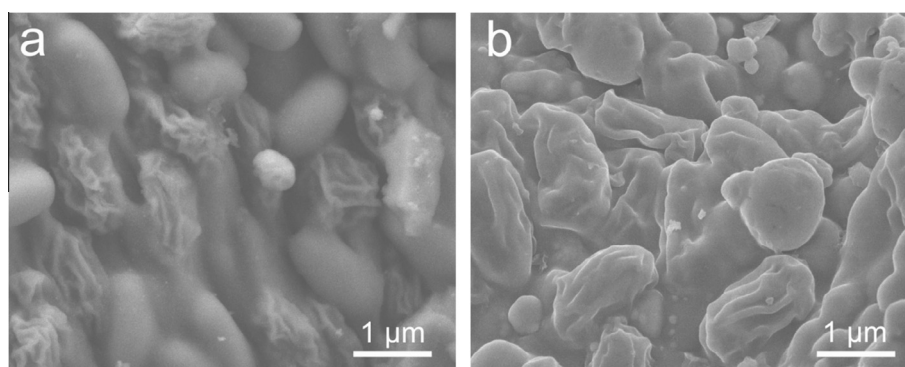

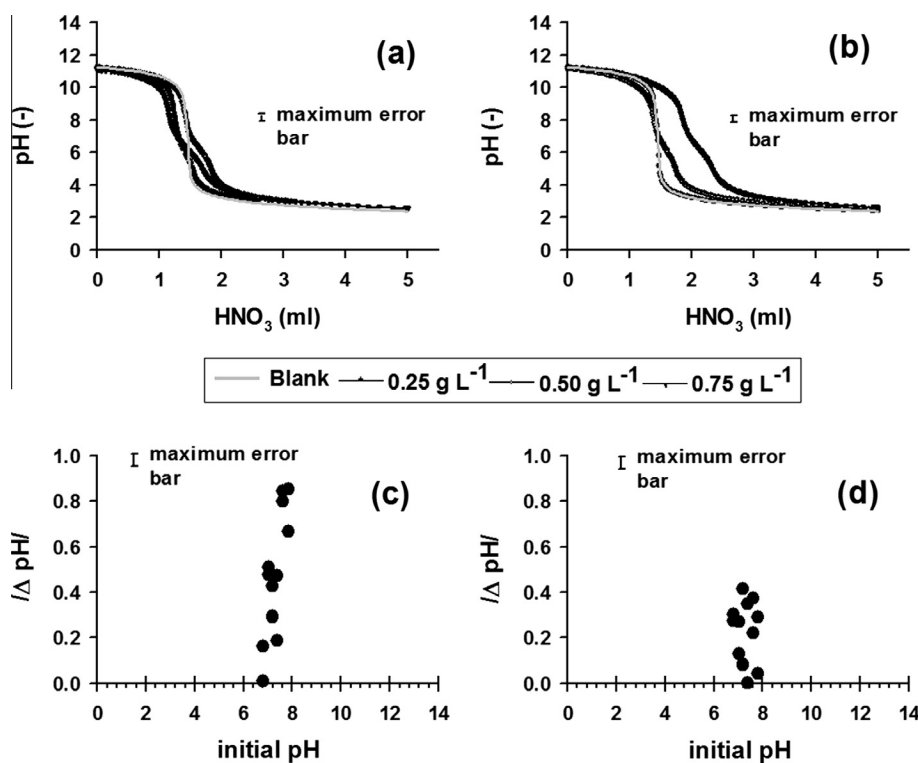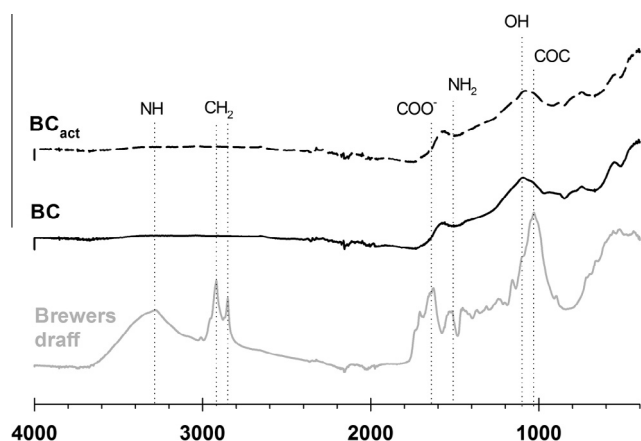**Figure 2** SEM images of biochar (a) and chemically activated biochar (b). 1 μm.

Figure 3 Point of zero charge (pH$_{zpc}$) using potentiometric mass titration (PMT) for biochar (BC) (a), activated biochar (BC$_{act}$) (b) and immersion technique (IT) for biochar (BC) (c) and activated biochar (BC$_{act}$) (d).

Figure 4 FTIR spectrum of (i) brewers draff before pyrolysis; (ii) biochar (BC), and (iii) activated biochar (BC_{act}).

4000–400 cm^{-1}). The presented spectra of BC and BC_{act} indicate the absence of functional oxygen groups responsible for chemisorption of metals such as Cu (Pellera et al., 2012; Regmi et al., 2012) in comparison with brewers draff before pyrolysis, where these groups are obvious (Fig. 4). These results of the functional group absence were caused by a high temperature of applied pyrolysis (650 °C), where the cleavage of these organic groups will contribute to a higher mass loss during thermal decomposition and gas (mainly the CO_2) product evolution (Tsai et al., 2012). The results suggest that both biochar samples are pure amorphous carbon; hence the Cu sorption is only due to physical sorption on the biochar surface. Additionally, the fact that both biochar samples had similar peaks has confirmed no significant impact of 2 M KOH on the functional groups. This is in agreement with the study of Regmi et al. (2012).

3.4. Batch experiments

First, the effect of contact time on Cu sorption onto both biochar samples was investigated. Fig. 5 provides information
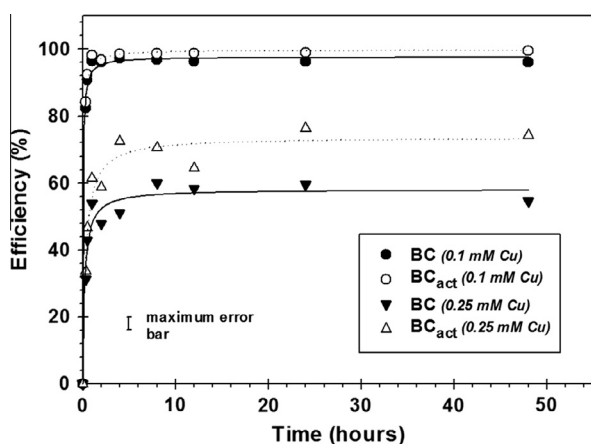
Figure 5 Influence of contact time of used biochar (biochar BC and activated biochar BC_{act}) with Cu synthetic solution at two different concentrations (0.10 and 0.25 mM).

about the reached plateau of Cu sorption (removal) from the synthetic solution on both biochar samples. The 24-h period was chosen for practical reasons as the equilibrium in this case. Furthermore, as stated by the paper of Chen et al. (2011) the equilibrium should be expected as early as 2 h (see also Fig. 5). Sorption efficiency (E) of both tested biochar samples at different time steps was calculated according to Eq. [1].

$$E = \frac{c}{c_{initial}} 100 \tag{1}$$

where E [%] is sorption efficiency, $c_{initial}$ [mg L^{-1}] is initial concentration and c [mg L^{-1}] is the final concentration of Cu in the solution. Additionally, using the paper by Limousin et al. (2007) the experimental kinetic data were fitted using pseudo-first-order [2] and pseudo-second-order [3] equations to describe the sorption mechanism over a period of time.

$$ln(s_{eq} - s_t) = ln s_{eq} - k_1 t \tag{2}$$

$$\frac{t}{s_t} = \frac{1}{k_2 s_{eq}^2} + \frac{1}{s_{eq}} t \tag{3}$$

where s_{eq} [mg g^{-1}] is the sorbed concentration at equilibrium time, s_t [mg g^{-1}] is the sorbed concentration at different time steps t [min], k_1 [min^{-1}] and k_2 [g mg^{-1} min^{-1}] are first-order-rate and second-order-rate constants, respectively. The results of kinetic modelling suggest that pseudo-second-order-rate equation fitted all modelled data excellently (Table 3). Additionally, results of pseudo-first-order-rate equation are not presented here due to ($R < 0$).

Next, following the kinetic results, sorption capacity of both biochar samples to remove Cu from synthetic solution was determined at equilibrium state ($t = 24$ h). The sorption efficiency of BC and BC_{act} was evaluated using Freundlich [4] and Langmuir [5] equations.

$$S = K_F C^n \tag{4}$$

$$S = \frac{K_L s_{max} C}{1 + K_L C} \tag{5}$$

where s [mg kg^{-1}] is sorbed concentration, s_{max} [mg kg^{-1}] is the maximum sorbed concentration, K_F [mg^{1-n} l^n kg^{-1}] and K_L [-] are the Freundlich and Langmuir sorption coefficients, respectively, c [mg l^{-1}] is concentration in the solution and n [-] is an empirical coefficient. Moreover, non-linear fitting models were chosen for isotherm parameter evaluation in order to avoid limitations associated with the linearization of sorption isotherms. In more detail, Microsoft Excel spreadsheet was used for the

Table 3 Pseudo second-order kinetic model parameters and model efficiencies (R) for both Biochars (BC and BC_{act}) in two different Cu-concentrated solutions during sorption experiment. All data are only for the synthetic Cu solution.

Sorbent/solution	Second-order kinetic model[a]		R [%]
	k_2 [g mg^{-1} min^{-1}]	s_{eq} [mg g^{-1}]	
BC/0.1 mM Cu	0.249	2.168	1.000
BC_{act}/0.1 mM Cu	0.530	2.232	1.000
BC/0.25 mM Cu	0.009	4.675	1.000
BC_{act}/0.25 mM Cu	0.007	5.831	0.999

[a] Parameters of used equation.

Table 4 Freundlich and Langmuir parameters (K_F, K_L, n and s_{max}) and model efficiencies (R) obtained for both Biochars (BC and BC$_{act}$) during Cu sorption experiment. All data are only for the synthetic Cu solution.

	Freundlich[b]		R [%]	Langmuir[b]		R [%]
	K_F [mg^{1-n} L^n kg^{-1}]	n [-]		K_L [L mg^{-1}]	s_{max} [mg kg^{-1}]	
BC	2309	0.315	0.829	0.271	8773	0.980
BC$_{act}$	3867	0.259	0.858	0.893	10257	0.967

[b] Parameters of both used equations.

Table 5 Initial (a) and final (b) Cu speciation for the soil solution after column retention experiment.

		Initial	Final	
			BC	BC$_{act}$
Species: [%]	pH [-]	4.37	4.65	4.76
	Cu^{2+}	54.5	49.7	48.3
	Cu-OM[a]	44.3	49.2	50.6
	Cu-LMWOA[b]	0.37	0.31	0.32
	Cu-others[c]	0.93	0.89	0.88
Total Cu content [mg L^{-1}]		1.15	1.06	1.07

[a] Cu species fixed on the organic matter.
[b] Cu species fixed on the low molecular weight organic acids (mainly oxalic for this case).
[c] Species such as CuOH$^+$; CuCl$^+$; CuSO$_4$(aq), and CuNO$_3$(aq).

evaluation of the fitting process (Bolster and Hornberger, 2007; Bolster, 2008). Obtained results suggest that in the case of synthetic solution both biochar samples (BC/BC$_{act}$) were able to sorb copper (8.77/10.3 mg g^{-1} respectively, Fig. 6) mainly due to affinity of Cu to organic matter (Bradl, 2004; Uchimyia et al., 2010), which is partly in agreement with the study of Regmi et al. (2012), where the Cu maximum sorption was 4.0 mg g^{-1} before and 31 mg g^{-1} after activation. Moreover, only physical sorption on the biochar surface was obvious as a result of the functional group absence (discussed previously in subsection 3.3.3). In comparison with biochar, its activation using 2 M KOH enhanced the Cu sorption capacity of BC$_{act}$ especially due to tar particles removed from micro-pores (<6 nm) which finally increased the total pore volume (see Table 2). A significant increase in the sorption capacity for BC$_{act}$ is also evident from the parameters of Freundlich and Langmuir isotherms (Table 4). Additionally, the Langmuir
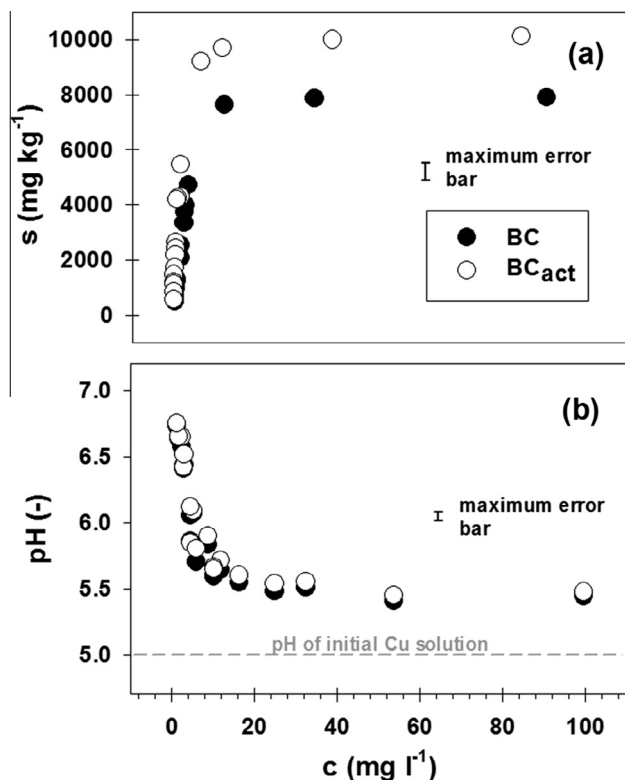
Figure 6 Sorption isotherms (a) and pH changes (b) during Cu sorption from synthetic solution for biochar (BC) and activated biochar (BC$_{act}$).
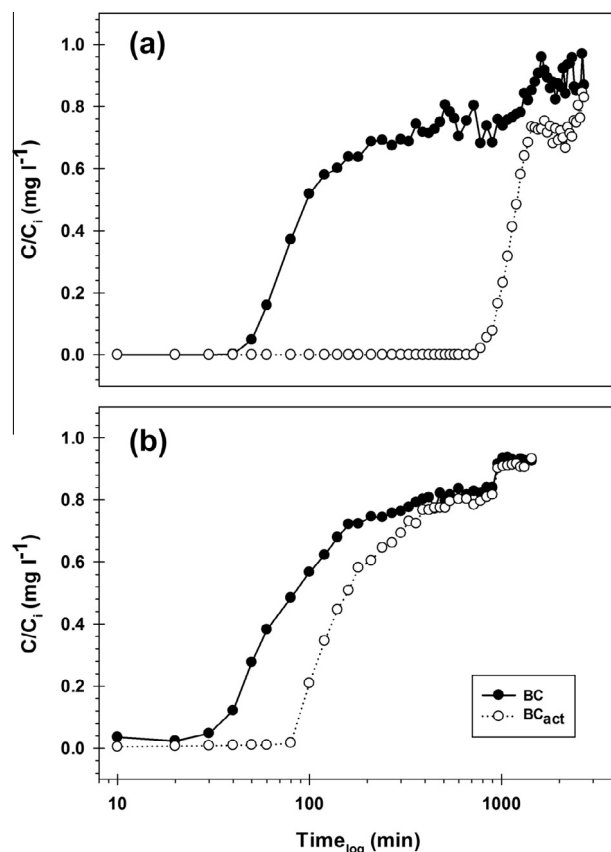
Figure 7 Breakthrough curves of copper retention for synthetic (a) and soil (b) solution over the period of time.

equation fitted the sorption data well ($R > 0.95$), better than Freundlich ($R < 0.90$), which confirmed the well-known fact about the better Langmuir isotherm fitting in the case of higher organic matter presence (Brown et al., 2000; Borchard et al., 2012; Xu et al., 2013).

Furthermore, decreases in the solution pH at a higher Cu concentration during the sorption experiment can be attributed to the hydrolysis effect (Ponizovsky et al., 2007; Mouta et al., 2008). The pH of both experimental solutions changed significantly due to the pH-buffering effect of both biochar samples (pH = 7.00).

3.5. Column experiments

In the final experimental step, Cu removal from aqueous solution was also measured over a period of time using the column retention test. As we had expected, the column studies showed that the Cu removal was more effective in the synthetic solution (Fig. 7a) solely due to Cu sorption over the period of time. In comparison with the synthetic solution, the effect of Cu removal from the soil solution was significantly reduced. For the synthetic solution, both BC and BC$_{act}$ were fully saturated by

Table 6 Comparison of maximal sorption capacity (s_{max}) of different biochars utilized for the Cu^{2+} removal.

Material	Biochar preparation[a]	Cu-s_{max} (mg g^{-1})	References
Peanut straw	P-400	89.0	Tong et al. (2011)
Soybean straw	P-400	52.8	Tong et al. (2011)
Peanut straw	P-400	38.4	Tong and Xu (2013)
Peanut straw	P-500	38.4	Tong and Xu (2013)
Canola straw	P-400	37.5	Tong et al. (2011)
Switch grass	H-300 + KOH$_{act}$	31.0	Regmi et al. (2012)
Soybean straw	P-400	30.9	Tong and Xu (2013)
Peanut straw	P-300	29.7	Tong and Xu (2013)
Hard wood	P-500 + N$_{2act}$	25.4	Han et al. (2013)
Canola straw	P-400	24.0	Tong and Xu (2013)
Rice straw	P-400	15.5	Tong and Xu (2013)
Corn straw	P-600	12.5	Chen et al. (2011)
Commercial activated carbon[b]		11.4	Tong et al. (2011)
Brewers draff	P-650 + KOH$_{act}$	10.3	This study
Brewers draff	P-650	8.77	This study
Compost	P-300	7.94	Pellera et al. (2012)
Compost	H-300	7.72	Pellera et al. (2012)
Hard wood	P-700	7.44	Han et al. (2013)
Switch grass	P-500 + N$_{2act}$	7.12	Han et al. (2013)
Hard wood	P-450	6.79	Chen et al. (2011)
Soft wood	P-500 + N$_{2act}$	6.36	Han et al. (2013)
Switch grass	P-700	6.23	Han et al. (2013)
Orange waste	H-300	5.81	Pellera et al. (2012)
Hard wood	P-500	5.53	Han et al. (2013)
Olive pomace	P-300	5.12	Pellera et al. (2012)
Orange waste	P-300	4.92	Pellera et al. (2012)
Switch grass	P-500	4.58	Han et al. (2013)
Rice husks	P-300	4.57	Pellera et al. (2012)
Soft wood	P-700	4.39	Han et al. (2013)
Switch grass	H-300	4.00	Regmi et al. (2012)
Hard wood	P-500	3.94	Han et al. (2013)
Rice husks	H-300	3.49	Pellera et al. (2012)
Compost	P-600	3.38	Pellera et al. (2012)
Soft wood	P-500	3.37	Han et al. (2013)
Commercial powdered activated carbon[b]		1.80	Regmi et al. (2012)
Soft wood	P-500	1.59	Han et al. (2013)
Switch grass	P-500	1.46	Han et al. (2013)
Olive pomace	H-300	1.43	Pellera et al. (2012)
Commercial activated carbon[b]		1.32	Tong and Xu (2013)
Composted commercial gasification coke[b]		0.98	Borchard et al. (2012)
Olive pomace	P-600	0.66	Pellera et al. (2012)
Commercial gasification coke[b]		0.63	Borchard et al. (2012)
Orange waste	P-600	0.42	Pellera et al. (2012)
Rice husks	P-600	0.27	Pellera et al. (2012)
Composted commercial charcoal[b]		0.21	Borchard et al. (2012)
Commercial flash-pyrolysis char[b]		0.16	Borchard et al. (2012)
Commercial charcoal[b]		0.06	Borchard et al. (2012)

[a] P-X00/H-X00 means pyrolysis and hydrothermal carbonization process respectively at the specific temperature (X00 °C), KOH$_{act}$ and N$_{2act}$ means the activation of the biochar.

[b] Material was not mentioned.

Cu (when the ratio $c/c_i \approx 1$) from $t = 2160$ min (Fig. 7a), whereas in the soil solution both biochars were fully saturated from $t = 960$ min.

Breakthrough curves with an early increase in the c/c_i ratio were observed for the biochar which had not been previously treated by 2 M KOH, for both synthetic and soil solutions, respectively, which is in agreement with the previously mentioned fact about better sorption of BC_{act}. In more detail, the activated biochar breakthrough curve point (BTCP; the final time step for the maximum sorption efficiency of biochar, when the ratio $c/c_i \approx 0$) was obvious at $t = 780$ min for the synthetic solution and at $t = 80$ min for the soil solution, respectively. On the other hand, BC started to saturate sooner hence BTCP was already at $t = 50$ and 10 min for the synthetic and soil solutions, respectively. Such dramatic differences of BTCP between BC and BC_{act} are most likely caused by free micro-pores (< 6 nm) in the BC_{act}. More precisely, these pores, which are created predominantly during high temperature pyrolysis (Tsai et al., 2012), were formed only in the case of BC_{act} due to the leaching out of the tar particles from these places using cold alkali solution stirring (discussed in subsections 3.2 and 3.3.1). Due to this fact, we assume that Cu was trapped inside these free micro-pores thus replacing the previously removed tar particles. Additionally, concentration of the dissolved organic carbon (DOC) was also measured over the period of time for both synthetic and soil solutions, respectively. All results show that DOC was unchanged over the period of time for both variants as well as for both solutions (data not shown).

Additionally, copper speciation of the initial soil solution was compared with the Cu-species in the soil solution, which was leached through both biochar samples (at the final time step). Table 5 shows Cu^{2+} species decreasing in the soil solution which was in contact with both BC and BC_{act}, respectively. On the other hand, Cu-species fixed on the organic matter significantly increased in this final soil solution. These Cu species in the final soil solution were thus changed mainly due to a slight continuous pH increase. Furthermore, minimum changes in Cu species have been registered for the BC_{act} in comparison with the BC.

Finally, desorption of Cu at the end of the column retention test was also implemented in the synthetic solution. More precisely, the Cu-fully saturated biochar samples (BC and BC_{act}) were shaken overnight using $0.01M$ NaNO₃. Obtained results showed minimum desorption of Cu from both biochar samples (0.48 ± 0.03 and 0.51 ± 0.05 mg L^{-1}). We can assume from these results that Cu is strongly bounded to the biochar surface. This is in agreement with other authors, i.e., Uchimyia et al. (2010), (2011), Trakal et al. (2011), Regmi et al. (2012).

4. Comparison with other studies

The data presented in Table 6 compare the maximum sorption capacity (s_{max}) of the different types of biochars used for the removal of Cu^{2+} from the aqueous solution. This value (presented in mg g^{-1}) is comparable with other chosen studies. The biochar prepared from the brewers draff is similarly efficient for removing Cu from aqueous solutions as compared to other waste materials (Table 6). The chemical activation using 2 M KOH improved only slightly its sorption efficiency, i.e., it is not cost efficient. Finally, the total mass loss during

the pyrolysis of brewers draff at 650 °C was approximately 90%, which demonstrates its very low yield. Therefore, a different char preparation such as hydrothermal carbonization (HTC) could be more suitable (Regmi et al., 2012).

5. Conclusions

The major conclusion of this study is that both prepared biochars (BC and BC_{act}) were able to remove Cu from synthetic and soil solutions, respectively. Both biochar samples are pure amorphous carbon hence the Cu sorption is mainly due to physical sorption on the biochar surface. Although the Cu removal efficiency did not surpass the best results from other studies, it was at least comparable. Furthermore, chemical activation using 2 M KOH significantly: (i) increased total pore volume; (ii) partly improved Cu sorption behaviour; and (iii) enhanced the Cu removal from aqueous solution during the retention test over a period of time.

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