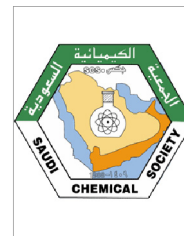




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Copper removal from aqueous solution using biochar: Effect of chemical activation

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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 NaNO₃ and (ii) soil solution obtained from a Cu-contaminated soil using 0.01 M CaCl₂ 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 m² g⁻¹ and BC_{act} = 11.6 ± 0.4 m² 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.

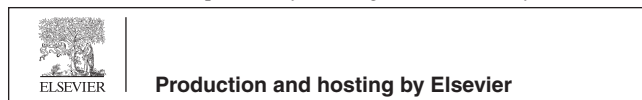
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1. Introduction

At higher concentrations, Cu is a potentially toxic metal in the environment, mainly as the soluble form Cu²⁺. 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 Pan-kow, 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 km² 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 CuNO₃·3H₂O (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 CaCl₂ 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

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