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Effects of feedstock type and slow pyrolysis temperature in the production of biochars on the removal of cadmium and nickel from water

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ABSTRACT

Biochar is a universal sorbent suitable in strategies for removing contaminants from both soil and water. This study evaluated the potential of four biochars each produced from a different feedstock for removing Cd and Ni from water. Chicken manure mixed with sawdust (CM), sugarcane straw (SS), rice husk (RH) and sawdust (SW) were used to produce biochar through slow pyrolysis at two temperatures: 350 and 650 °C. The percentage removed and the removal capacity of Cd and Ni from water by biochars at both temperatures used in the pyrolysis followed the order: CM > SS > RH > SW. The removal percentage ranged from 31 to 98% for Cd and 24–72% for Ni, while removal capacity ranged from 0.3 to 12.5 mg g^{-1} for Cd and 0.2–10.9 mg g^{-1} for Ni. The type of feedstock had greater influence on the performance of biochars for removing metals than the pyrolysis temperature.

1. Introduction

Biochar is a soil conditioner and a potential carbon sink, also is a highly efficient low cost-benefit sorbent used in the removal of pollutants (Kong et al., 2011). It can be used as a low-cost substitute for activated carbon used in the purging of pollutants (Cernansky, 2015). Furthermore, biochars are materials which are highly resistant to biological degradation (Sohi, 2012) and are considered universal sorbents in the removal of organic and inorganic contaminants in both soil and water (Ahmad et al., 2014). Additionally, biochars with high sorption capacity are considered suitable materials for the purging of water contaminated with heavy metals (Doumer et al., 2016).

The physicochemical properties of biochars are not uniform, and the technologies used to produce this material have not yet been consolidated (Sohi, 2012). For this reason, the types of feedstock and pyrolysis conditions under which biochars are produced are the factors which most influence the sorption behavior of these materials (Ahmad et al., 2014), temperature being one of the main factors. Chen et al. (2014) evaluated pyrolysis temperatures in the range of 500–900 °C for biochars derived from urban sewage sludge and verified that as the temperature increased so did biochar microporosity and, consequently, cadmium adsorption. The micropores contribute significantly to increasing the surface area of biochars, and both properties influence the retention of chemical substances (Kookana et al., 2011; Qian et al., 2015).

Generally, biochars produced from animal manure have a higher metal adsorption capacity than those produced from vegetables (Ahmad et al., 2014; Mohan et al., 2014; Park et al., 2013). Xu et al. (2013) reported that the biochar produced from dairy manure was more efficient than the rice husk biochar in removing Cu, Cd, Zn and Pb from water regardless of the solution containing either a single metal or more than one metal. Probably the superior removal ability of biochars produced from manure is due to the higher levels of phosphate, carbonate and sulfate present in these materials which precipitate metals (Park et al., 2013; Xu et al., 2013).

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Despite low concentrations, heavy metals are not biodegradable and thus pose a public health risk as they are one of the most toxic groups of inorganic pollutants found in water (Han et al., 2013; Inyang et al., 2012). These elements are introduced into the environment in the form of waste dumped by battery, mining, electroplating, and paper industries (Inyang et al., 2012). Furthermore, contamination may spread to groundwater through the leaching of metals from landfills (Kabata-Pendias and Mukherjee, 2007). Cadmium (Cd) and nickel (Ni) are common carcinogenic pollutants of drinking water and wastewater (Lima et al., 2010).

There are few studies in the literature that feature evaluations by researchers of the potential of different biochars for purging water contaminated with Cd and Ni (Inyang et al., 2012; Lima et al., 2010; Uchimiya et al., 2010). Because of this dearth of research, our aim in this study was to evaluate biochars produced from different feedstocks by slow pyrolysis at two different temperatures for the purging of water contaminated by Cd and Ni. It is hoped that studies such as this one might contribute to the development of strategies for purging water contaminated with metals using low cost materials.

2. Materials and methods

2.1. Feedstocks collection

The biochars were produced using four types of feedstock: chicken manure (CM), sugarcane straw (SS), rice husk (RH) and sawdust (SW). These feedstocks were chosen because of the great availability of these materials in many regions of Brazil and also because they are common in other places in the world. The rice husk and chicken manure were collected from the laying hen production facility of the Department of Genetics of the Luiz de Queiroz College of Agriculture, part of the University of Sao Paulo (ESALQ-USP). These hens are part of a project for the production of sustainable agriculture being developed by the department whereby the laying hens are fed daily with gram. The dung is deposited on the floor of the installation and is mixed manually with sawdust weekly. The rice husks are used as a bed for broiler production. However, the rice husk samples used in this experiment were collected prior to being used as a bed, i.e., in pure pretreated form. The sugarcane straw samples were left intact and kept on the ground after harvesting before being removed manually for the production of biochar. The sawdust was provided by the Department of Forest Sciences, and was collected in the Laboratory of Technology and Wood Management (ESALQ-USP) being a residual from the process of log transformation into eucalyptus wood paneling.

2.2. Pyrolytic process

The pyrolysis process was conducted in a hermetically sealed 60 L-metallic cylindrical reactor. During the heating, the atmosphere inside the reactor was saturated with nitrogen gas (N_2). The biochars were produced by slow pyrolysis at temperatures of 350 and 650 °C, and the heating temperature was increased at a rate of 10 °C min^{-1}. Biochars were produced at these two contrasting temperatures based on the results from Shaaban et al. (2014) that showed intermediary properties of biochars produced between extremes temperatures. For this reason, we chose two contrasting temperatures to evaluate if the effect of temperature on the performance of biochars is pronounced. Pyrolysis temperature ranges typically used in the production of biochar are above 300 °C. Moreover, changes in the main components of biomass (cellulose, hemicellulose and lignin) and transformations of physical origin are found starting at this temperature and above (Brown, 2009).

The temperature (either 350 or 650 °C) was maintained for 15 min (residence time), and the biochar was removed only when the reactor inside temperature had cooled down to room temperature. The gases condensed in the condenser were directed into a reservoir, while gases not retained in the condenser were directed in an area outside the reactor to be purged in contact with water to prevent the release of these gases to the environment. The pyrolysis process performance was 30.6% of biochar, 39.8% of liquids (bio-oil) and 29.6% of gases that are within the range usually reported in the literature (Laird et al., 2009).

Biochars were labeled according to the specific pyrolysis temperatures applied as follows: CM350, CM650, SS350, SS650, RH350, RH650, SW350 and SW650.

2.3. Biochar characterization

The pH and electrical conductivity (EC) were determined according to the methodology proposed by Rajkovich et al. (2012), using a ratio of 1:20 (m:v) and stirring time of 1.5 h in an orbital shaker; after 12 h the EC was determined for the same samples. The determination of the cation exchange capacity (CEC) was based on Alcarde (2009) methodology; however, the method was adapted to a sample weight of 0.5 g. For this a hydrochloric acid solution (0.5 mol L^{-1} HCl) and calcium acetate solution (0.5 mol L^{-1}, $pH = 7$) with subsequent titration using sodium hydroxide (0.1 mol L^{-1} NaOH) were used. The determination of ash content followed the methodology of ASTM D1762-84 (ASTM, 2011) whereby 1 g of sample biochar was heated in a muffle furnace to a temperature of 105 °C for 2 h to determine humidity, and to 750 °C for a further 6 h to determine ash content.

The analysis of C, N, and H was carried out in an elemental analyzer (Perkin Elmer 2400 CNH), while the O content was calculated by difference (Angın, 2013). The nitro-perchloric digestion methodology of Enders and Lehmann (2012) was used to extract total nutrient and sodium contents. This method includes heating samples of 50 mg in a muffle furnace at 500 °C for 8 h, followed by nitro-perchloric digestion with the addition of nitric acid (1 mol L^{-1}) and hydrogen peroxide (30%). Next, the levels of ion content were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES), also referred to as inductively coupled plasma optical emission spectrometry (ICP-OES). The physico-chemical properties of biochars used in the experiment are presented in Table 1.

2.4. Metal sorption experiment

Biochar samples were used with a particle size < 2 mm having been previously dried for 24 h in a forced-air oven at 105 °C. Single metal solutions were prepared comprising 50 mg L^{-1} Cd and Ni separately from stock solutions of 1000 mg L^{-1} prepared after dissolving the corresponding nitrate salts of these metals in deionized water. In Falcon tubes of 50 ml, 100 mg of each biochar sample were weighed and agitated with 30 ml of Cd or Ni solutions at a concentration of 50 mg L^{-1} in a horizontal shaker for 24 h at 150 oscillations min^{-1} at room temperature. Three replicates were performed for all treatments and after being agitated, the extracts were filtered slowly through filter papers.

The pH of the Cd and Ni solutions were not adjusted and followed the procedure of Chen et al. (2014). After being agitated for 24 h, the pH and EC of the solutions of all the treatments were measured. The average pH and EC readings of the blank solutions (with no presence of biochar) were taken as the baseline because the readings registered by the blank solution were deemed to show no alteration after the agitation process. The concentrations of Cd and Ni in solution were identified in an atomic absorption