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# Synthesis of highly-efficient functionalized biochars from fruit industry waste biomass for the removal of chromium and lead

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ABSTRACT

Plums and apricots are among the most popular fruits in Serbia and kernels of these are generally disposed of as waste. In common with other organic waste products there is potential to utilise these kernels in wastewater treatment. A new generation of highly-efficient biochars were therefore developed for low-cost wastewater treatment. The aim of this work was to prepare functionalized biochars from different fruit industry waste biomass and to evaluate their ability to for lead and chromium adsorption. Fruit kernel based biochars were synthesized by pyrolysis and functionalized with sulphuric acid. The biochars were characterized using: proximate-ultimate analysis, the Brunauer, Emmett and Teller technique, surface functional group analysis with Fourier-transform infrared spectroscopy, $pH_{pzc}$ and scanning electron microscopy with energy dispersive X-ray spectroscopy. Heavy metal adsorption by biochars was studied using different process parameters was shown to occur through different adsorption mechanisms. Three kinetic and two isotherm models were applied to the experimental data. Sulphur-containing functional groups on the biochar surface played an important role in binding. The high adsorption efficiency is attributed to surface complexation of biochar functional groups with heavy metal ions. Based on these results, biochars could be used as a highly efficient adsorbent for removal of heavy metals from aqueous solutions.



## 1. Introduction

Water is a critical resource; and clean, unpolluted water is required to help sustain living organisms and ecosystem function [1]. However, while heavy metals are natural components of the Earth's crust; mining, refining, use and global industrialization have all led to increased heavy metal pollution and concurrent damage to ecosystems [2].

Under favourable pH/Eh conditions, metals can be soluble in water and producing toxic effects and ecological impacts on aquatic biota [3, 4]. Heavy metal contamination remains a global environmental problem, and the Agency for Toxic Substances and Disease Registry (ATSDR) highlights lead and chromium as two of the most toxic heavy metals [1]. Trace amounts of Cr(III) are essential for human health, but long-term exposure to Cr(III) contaminated water can be harmful [5]. Cr(VI), on the other hand, is highly toxic and carcinogenic – but, is also an integral part of many industrial processes (i.e., within stainless steel production and electroplating) [6]. Lead also continues to be used in many industrial processes, i.e., during the production of dyes, paint coatings, glass, ammunition and batteries. A non-essential element, Pb(II) is highly toxic to humans and aquatic life and there is now no known "safe" level of exposure to this heavy metal [7]. Due to their toxicity, many techniques have been proposed to remove lead and chromium from industrial wastewaters, including membrane processes [8], flocculation [9], chemical precipitation [10], adsorption [11] among others. Among these, adsorption has several advantages, i.e., it can be simple, safe, low cost, and result in high recovery. Likewise, many potential adsorbents are cheaply/readily available [12]. One of the most frequently used adsorbents is biochar - a low-cost carbonaceous material, obtained from the thermo (−chemical) conversion of biomass in an "oxygen limited environment". High adsorption rates, high specific surface area (with microporosity), and high ion exchange capacity, mean that biochar has potentially widespread environmental applications [13]. In the last ten years, numerous types of biochar have been created from different feedstock's such as oak wood and oak bark [14], soft wood pellets [15], anaerobic digestion sludge [4, 16, 17], pineapple peel [18], herb residues [19], durian rind [20], mangosteen peels [21], and pig manure [22].

Here, we describe to production of a useful and low cost adsorbent from a common Serbian waste material to respond the growing demand in biochar market. The adsorption mechanisms of selected heavy metals

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onto two different biochars were determined and potential practical applications highlighted. The major novel piece of work described here is the process sulfurization of the biochar surface and demonstrating the formation of hydroxyl, carboxyl, sulphate and other functional groups which have a great affinity for binding metal ions. Plum and apricot kernel waste biomass was used to prepare biochar to capture heavy metal ions (in this case Pb(II) and Cr(III)) from aqueous solutions via a batch process. Kinetic and equilibrium experiments, scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX), Fourier-transform infrared spectroscopy (FTIR) and Brunauer, Emmett and Teller (BET) measurements were made to help elucidate the adsorption mechanisms at work.

## 2. Material and methods

### 2.1. Materials and chemicals

All chemicals and reagents used were of analytical grade. Lead nitrate (Pb $(NO_3)_2$), chromium nitrate nonahydrate ($Cr(NO_3)_3 9H_2O$), concentrated hydrochloric acid (HCl) and ammonium hydroxide ($NH_4OH$) were supplied by Fisher Scientific (Pittsburgh, USA). Stock solutions were prepared and diluted to the required concentrations using Milli-Q water (EASYpure® II, 18.2 MΩ). Residual metal concentrations in supernatants (following sorption experiments) were measured using flame atomic absorption spectrometry (FAAS, model Thermo Scientific S Series). Locally sourced plum and apricot kernels were collected from fruit plantations located in Novi Bečej (Serbia), and were washed with tap water prior to use.

### 2.2. Biochar preparation

The waste fruit biomass (plum and apricot kernels, separately) was dried at room temperature (22 ± 1 °C) and milled. To produce sulfurized biomass 100 g of each milled kernel was treated with 50% *w*/*v* $H_2SO_4$. Thereafter, the samples were introduced into a muffle furnace in ceramic cups and pyrolyzed at 500 °C. During the first phase of pyrolysis, the samples were heated at a rate of 10 °C $min^{-1}$ to 180 °C and held at this temperature for 30 min. In the second phase, the samples were heated at a rate of 10 °C $min^{-1}$ to 500 °C and held for the next 60 min. Following pyrolyzation, the samples were cooled, and then thoroughly washed with Milli-Q. The samples were then dried at 105 °C for 2 h, sieved to obtain a particle size of ≤200 μm and then stored in a sealed bottle for later use. The prepared biochar from plum and apricot kernel is hereafter abbreviated as PSuA and ASuA, respectively.

### 2.3. Characterization of the biochars

The yield of biochar is an indication of the pyrolysis process mass efficiency. The yield of biochar was calculated from the following equation:

$$\text{Yield}(\%) = \frac{w_b}{w_0} \cdot 100 \quad (1)$$

where $w_0$ and $w_b$ (g) are the weights of waste biomass and biochar, respectively.

A Vario EL III C, H, N, S/O Elemental Analyzer (Elementar, Germany) was used to determine the content of C, N, S and H in the two biochars via high temperature catalytic combustion. The moisture content, total ash content and suspension pH of the biochars in water ($pH_{sus}$) were determined using American Standard Test Method D2867-04, D2866-94 and D6851-02, respectively. $pH_{sus}$ relates with the overall acidity of the biochars. To determine the $pH_{sus}$, 0.2 g of each biochar was suspended in 30 mL of Milli-Q water and equilibrated for 72 h. The pH was measured using a WTW SenTix® 41 (WTW, Germany) pH meter. The moisture content of the adsorbent samples was determined by oven-drying the material at 110 °C until consistency of weight was obtained. The total ash content of the samples was determined by heating the dried biochars in crucibles in a muffle furnace at 650 °C until consistency of weight. After heating, the crucibles were allowed to cool in a desiccator and weighed. The weight of the residue was calculated and reported as percentage of ash. The pH "drift" method was used to deduce pH at the point of zero charge ($pH_{pzc}$) as reported by [23].

The release of Na(I), K(I), Mg(II) and Ca(II) from biochars to deionized water after mixing was determined using flame atomic absorption spectrometry to calculate the cation-exchange capacity (CEC) of the biochars. The procedure was carried out using 500 mg of PSuA and ASuA with 100 mL of deionized water and a 60 min contact period [24].

The surface properties and textural structure of the PSuA and ASuA were characterized using several techniques. The morphology and superficial structure were observed by SEM with a JSM 6460LV instrument (JEOL, USA). EDX was used to examine the surface elemental composition before and after adsorption. The specific surface area ($S_{BET}$), pore volume and pore size of each biochar was evaluated using BET experiments with nitrogen adsorption/desorption data at 77 K using an Autosorb iQ instrument (Quantachrome, USA). Surface functional groups of PSuA and ASuA were investigated using FTIR spectroscopy (Nexus 670; Thermo Nicolet, USA); the FTIR spectra were recorded in the range 400–4000 $cm^{-1}$.

### 2.4. Experimental design

The removal of Pb(II) and Cr(III) on PSuA and ASuA was studied using batch adsorption experiments. For all experiments, biochar was mixed with 50 mL of solution in an Erlenmeyer flask at room temperature (22 ± 1 °C). Flasks were placed on a mechanical shaker (Heidolph Unimax 1010; Heidolph, Germany) and agitated at 140 rpm. The pH was adjusted using 0.1 mol $L^{-1}$ HCl or 0.1 mol $L^{-1}$ $NH_4OH$. After the adsorption experiments, the samples were filtered with Macherey-Nagel filter paper (MN 640 m).

The effect of pH on heavy metal adsorption was first studied using: 200 mg (4.0 g $L^{-1}$) of biochar (added to a 50 mL solution) and initial metal concentrations of 50 mg $L^{-1}$ (for 30 min contact time). In order to study the effect of pH on Pb(II) and Cr(III) adsorption, initial pH varied from 2 to 6.

Biochar dose was also studied using PSuA and ASuA doses from 20, 50, 100, 200, 300, 350 and 500 mg in 50 mL solutions of 50 mg $L^{-1}$ (Pb(II) and Cr(III)) at pH 6, for a contact time of 30 min.

For kinetic studies, samples were taken at intervals (5, 10, 15, 20, 30, 40, 50 and 60 min) with initial metal concentrations of 50 mL $L^{-1}$, at pH 6.0, using 50 mL of solution and a biochar dose of 200 mg at two different temperatures (22 and 42 °C).

In order to assess the effect of initial heavy metal concentration on adsorption efficiency (isotherm study), initial adsorbate concentrations were varied to 5, 10, 20, 50, 100, 150, 200 and 300 mg $L^{-1}$ with a pH of 6.0, biochar dose of 200 mg and a contact time of 30 min. The percentage of adsorbate removal, *R*%, and equilibrium adsorption capacity, $q_e$, were calculated, respectively, from the equations given below:

$$R(\%) = \frac{C_0 - C_e}{C_0} \cdot 100 \quad (2)$$

$$q_e = \frac{(C_0 - C_e)}{m} \cdot V \quad (3)$$

where $c_0$ is the initial metal concentration and $c_e$ is the residual metal concentration (mg $L^{-1}$), *v* is the volume of solution (l) and *m* is the mass of the biochar (g). furthermore, the nonlinear chi-square test