# PROCEEDINGS

## 27th International Conference Ecological Truth and Environmental Research

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Prof. Dr Snežana Šerbula

18-21 June 2019, Hotel Jezero, Bor Lake, Serbia

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# REMOVAL OF Cd (II) USING HYDROCHARS PREPARED FROM SUBSTRATE FOR CULTIVATING MUSHROOMS

**Marija Kojić[1*], Jelena Petrović[1], Marija Petrović[1], Marija Mihajlović[1], Marija Koprivica[1], Jelena Milojković[1], Tatjana Šoštarić[1]**

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## Abstract

*In this study, the sorption capacity of Cd (II) removal from aqueous solution was investigated using hydrochar obtained from substrate for cultivating mushrooms. In order to increase the adsorption capacity, hydrochar was previously modified with 2M KOH. The obtained results showed that alkally modification increased the sorption capacity from 41.5 mg/g to 53.5 mg/g. Structural characterization of alkally modified and unmodified hydrochars were performed by Fourier transform infrared spectroscopy (FTIR). According to obtained results of FTIR analysis, the increased of the oxygen functional groups (OFG) in alkally modified hydrochars was observed, which is contributed to the increase in the adsorption capacity of this hydrochar. Results indicated that substrate for cultivating mushrooms can be converted into hydrochar as a sorbent for sorption of Cd (II), and the presence of OFGs play important role in the hydrochar's high adsorption capacity.*

**Keywords**: substrate for cultivating mushrooms hydrochars, Cd(II) removal, alkally modification

## INTRODUCTION

Excessive increased of population, industrialization and agricultural activities have caused contamination of water and soil with heavy metals [1]. The presence of these pollutants in the waters can have negative effects on the environment, because heavy metals are highly toxic and not degradable. Elements such as Cd, Hg, Ag, Se and Pb can be extremely toxic, while Cu, Zn, Mn, Fe, Ni and Co are considered essential for the functioning of living organisms and they are toxic in higher concentrations [2]. Cadmium is one of the most toxic heavy metal. Phosphoric fertilizers, wastewaters from industry, batteries, and dyes are often responsible for bringing Cd (II) into the aquatic environment [3]. Constant exposure to Cd (II) can cause various diseases in human such as lung cancer, prostate proliferative lesions, bone fractures, kidney dysfunction, and hypertension [2]. In order to avoid mentioning negative health effects, industrial wastewater should be purified and recycled using appropriate methods.

In recent years, various conventional wastewater treatments methods have been used, such as: precipitation, ion exchange, adsorption, electrochemical processes and membrane processes [3]. However, adsorption relative to other technology is the most commonly used method because it is efficient, environmentally friendly and economical [4]. A large number of different sorbents have been investigated for water purification, especially waste biomass. Biosorbents are by-products of agriculture that are easily accessible, high efficiency, and ability to remove organic and inorganic compounds from water [5]. Research on biosorbents was mainly focused on application of biochar from the pyrolysis process [2]. However, lately a greater emphasis is placed on the using of hydrochar, which is obtained during hydrothermal process. Kambo and Dutta [6] states that hydrochar has substantially greater adsorption capacity than biochar, considering that it is richer in functional groups on its surfaces and also it has lower surface area and porosity.

Hydrothermal carbonization (HTC) is thermochemical technology that can treat various types of organic waste materials into functional products with minimal environmental pollution [7]. HTC is operated in water as a reaction medium, moderate temperatures (180–260°C) and autogenous pressure [8]. The products obtained from HTC of feedstock are a carbon-rich solid product (hydrochar), process water and small amount of gas. The process parameters such as pressure, temperature, reaction time and biomass and water ratio has a significant impact on degree of carbonization of waste organic matter [9]. In contrast to feedstocks, the hydrochar is characterized by higher mass and energy density, better dewaterability, and improved combustion performance as a solid fuel [10]. HTC has been considered for various purposes, such as catalysis, adsorption, fuel, electrochemistry, template synthesis, nanostructured materials [11]. A number of studies have been performed on hydrothermal carbonization of a wide range of waste organic matter: food waste, animal manure, glucose etc. [9].

Petrovic *et al*. [12] examined the adsorption of $Pb^{2+}$ from aqueous solution with alkally modified hydrochar and found that the hydrochar showed the highest $Pb^{2+}$ sorption capacity of 137 mg/g. Elaigwu *et al*. [13] compared the adsorption capacities of the hydrochars and biochars, and found that hydrochars were able to adsorb the Pb (II) and Cd (II) more efficiently in contrast to biochars.

The aims of this study were to investigate the efficiency of substrate for cultivating mushrooms hydrochar as a sorbent for the removal of Cd (II) from wastewaters. Besides, the sorption capacity between alkali-modified and unmodified hydrochars will be compared, as well as their structural changes.

## MATERIALS AND METHODS

Substrate for mushroom cultivation (SM) is obtained from the local mushroom industry located in the vicinity of Belgrade. The compost used is from the following components: wheat straw, urea, gypsum and horse manure.

### HTC hydrochar preparation

The HTC experiments were carried out in 250 ml autoclave reactor (Carl Roth, Model II). The HTC reactor was equipped with a cooling system and controller for pressure and temperature. To analyse the effect of the HTC temperature on 200°C were adopted under the same reaction time of 1 h. For each test, 10 g of SM feedstock was mixed with 150 ml of deionized water into autoclave. The autoclave was held at final temperature at 60 min and the reactor was cooled down to the room temperature. The hydrochar was washed with deionized water and then dried at 105°C for 24 h.

*Alkaline modification*

Alkaline hydrochar modification was carried out according to the procedure shown in the paper Petrovic *et al*. [12].

*Adsorption studies and characterization of hydrochar*

A stock solution of 100 mg $L^{-1}$ $Cd^{2+}$ was prepared by dissolving Cd $(NO_3)_2{\cdot}4H_2O$. For adsorption experiment, 0.025 g of one of hydrochars (unmodified (SM-200) or alkali-modified (SM-KOH-200)) was mixed with 25 ml of $Cd^{2+}$ solutions. The flasks were capped and shaken at room temperature for 120 min at 250 rpm. After that, the mixtures were filtered and the concentrations of $Cd^{2+}$ were determined by atomic absorption spectroscopy (Perkin Elmer, AAS Analyst 300). The solids remaining on the filter were collected and dried at 105°C for Fourier transform infrared spectroscopy (FTIR; Thermo Scientific Nicolet iS50 FT-IR spectrometer in transmission mode) analysis. Materials were recorded in the spectral range 4000–400 $cm^{-1}$.

Adsorption capacities qe (mg/g) were calculated as follows:

$$qe = (C_0 - C_e) \times V/m$$

where *V*, is the volume of the $Cd^{2+}$ solution (L), *m* is the amount of adsorbent (SM-200 or SM-KOH-200) (g); $C_0$ and $C_e$ are the initial and equilibrium concentrations of the $Cd^{2+}$ ions (mg $L^{-1}$), respectively.

## RESULTS AND DISCUSSION

The FTIR analysis was carried out to explain the internal chemical structural changes of SM-200 and SM-KOH-200 after adsorption of Cd (II). The FTIR spectrums are presented in Fig. 1. The intensity of the peak 3280 $cm^{-1}$ was associated to -O-H stretching vibration from hydroxyl and carboxyl groups in the SM-200 and SM-KOH-200 [2,12]. The two bonds at around 2920 and 2850 $cm^{-1}$ probably originated from vibration of aliphatic C–H stretching in cellulose from wheat straw [14].

The bonds at 1620 $cm^{-1}$ could be attributed to C=O vibrations [15]. The band at 1521 $cm^{-1}$ are the results of the of N-O nitro groups, which can originated from protein and uric acid in horse manure [16]. The bonds at 1420 $cm^{-1}$ were associated with aromatic C=C stretching, indicating the presence of lignin in the hydrochars [17]. The stretching -COR aliphatic ethers and –COH primary alcohols were attributed to the bonds at 1030 $cm^{-1}$ [11]. The absorbance peaks at around 779 and 470 $cm^{-1}$, presented to the aromatic C-H bending vibration and aliphatic C-H stretching vibrations [11].

Based on research Han *et al*. [2], it can be noticed that there are a large number of active functional groups (-COOH, -CO, -OH) that can form complexes with Cd (II) on the surface of the hydrochars.

Similar observation was also noticed in this paper. The Figure 1 showed that SM-KOH-200 had a significantly higher intensity of peak at 3280, 1620 and 1030 $cm^{-1}$ compared to SM-200. This confirmed that SM-KOH-200 had more OFG in contrast to SM-200, which SM-

KOH-200 improved ability to adsorb Cd(II). Petrovic *et al*. [12] and Sun *et al*. [18], also found that alkaline modification of the hydrochars increased the number of OFGs, which had an impact on the improvement of the metal adsorption capacity to the hydrochars.

The results from FTIR analysis was confirmed by determining the preliminary adsorption capacity of the applied hydrochars. The adsorption capacity of the SM-KOH-200 was qe=53.5 mg/g, while the SM-KOH showed smaller capacity (qe=41.5 mg/g). It can be shown that alkally modified hydrochar had more OFGs on their surface, and thus more electron donating sites for adsorption of Cd (II) ions.

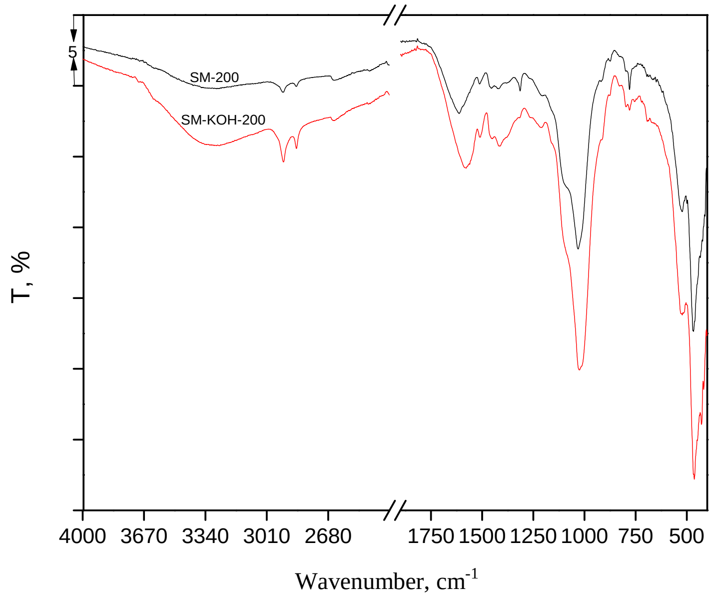


***Figure 1*** *FT-IR spectra of SM-200 and SM-KOH-200 after Cd (II) sorption*

## CONCLUSION

Based on this paper, we can conclude that alkaline modification contributed to the increase of OFG in hydrochars, which increased the adsorption capacity from 41.5 mg/g for SM-200 to 53.5 mg/g for SM-KOH-200. It showed that these materials could be used as low cost adsorbents in wastewater treatment and that HTC is sustainable method for conversion of this type of biomass.

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