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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PAULOWNIA LEAVES AND THEIR HYDROCHAR FOR Pb^{2+} IONS REMOVAL FROM AQUEOUS SOLUTION

Marija Koprivica[1*], Jelena Petrović[1], Marija Petrović[1], Marija Mihajlović[1], Jelena Milojković[1], Marija Kojić[1], Zorica Lopičić[1]

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Abstract

Adsorbents prepared from agricultural and industrial biowaste are being investigated as efficient material for removal of various pollutants from wastewater. In this study, Paulownia leaves powder and its hydrochar prepared from hydrothermal carbonization at 200°C was investigated as potential adsorbents for Pb^{2+} ions from aqueous solution. Paulownia leaves and hydrochar at 200°C were characterized by FTIR spectroscopy before and after adsorption of Pb^{2+} ions. The experimental results showed that Paulownia leaves had better adsorption capacity (q=34.53 mg/g) than hydrochar produced at 200°C (q=11.26 mg/g) and could be considered as effective biosorbent for Pb^{2+} removal from wastewaters.

Keywords: Paulownia leaves, hydrothermal carbonization, biosorption, Pb^{2+}, FTIR

INTRODUCTION

Industrial wastewater is a type of environmental pollution and in the 21st century is one of major problem for humanity and nature. Containing various organic and inorganic pollutants, water represents source of toxically matters which negatively affect human health and environment [1,2]. Lead (Pb^{2+} ions) is one of the most toxic metals which often could be found in industrial effluents. It is well known that in humans lead may cause headaches, visual disturbance, anaemia, mental and liver damage, and also can be deadly for animals and plants [2–4].

Through the influence of industrial production and wastewaters, non-biodegradable, heavy metal ions are easily available and could be harmful for living organisms and their removal from aqueous media, before discharge into watercourses, are of the great importance [4]. Various methods have been reported for purifying wastewaters such as coagulation, ion exchange, membrane separation, oxidation, flocculation but most of them are costly or create undesirable byproducts [1,2]. The biosorption has represented powerful tool for the removal of pollutants from wastewaters. The adsorption of lead ions using waste biomass has been confirmed as a simple, inexpensive and efficient method for treatment of polluted waters [2,3,5]. During past years, there has been increasing in the use of plant waste and their products for heavy metals removal. Some alternative biosorbents have the advantage due low-cost, ease of operation, greater efficiency and profitability [5]. However, the most biosorbents

have limited biosorption capacities and new economical acceptable biomasses are always in demand.

The Hydrothermal Carbonization (HTC) is a promising process used to convert wet biomass into functional materials (called hydrochars) [6]. In HTC process added water reacts with fibrous component of biomass and cause reconstruction and degradation (hydrolysis, dehydration, decarboxylation, condensation, polymerization and aromatization) [6,7]. Hydrochar is a homogeneous and hydrophobic material which contains micro- to nano-sized carbon spheres with a porous structure and oxygen-containing functional groups. Due to its physicochemical features, hydrochars could be considered for numerous practical applications [6,8]. So far this material has been tested for use as solid fuel, soil supplement, as feedstock for pellets. By this technology, various types of biomass, municipal waste, wood and sewage sludge, can be quickly transformed into the solid carbonaceous products which characteristics strongly dependent on reaction conditions and feedstock type [8].

Paulownia is a genus of about 20 species of fast growing trees native to China. Good Paulownia wood characteristics, such as easily adaptable, fast growth, high biomass production, are reason that this plant is very popular and commonly used in industry [9–11]. Beside industry, Paulownia is grown like a decorative tree in parks thanks to the beautiful flowers and leaves. However, paulownia leaves represent biowaste during wood processing and in parks at the end of the season when it falls of trees [1].

In order to investigate the ability and efficiency of Paulownia leaves (PL) and Paulownia leaves hydrochar (200-PL) to remove lead ions from aqueous solution, preliminary adsorption test was performed. Additionally, for characterization of materials FTIR analysis was used.

MATERIALS AND METHODS

Materials preparation

The PL was collected from park in Belgrade, wash with distilled water, air-dried for two weeks and extensively grinded in order to obtain homogenous samples. Sieved fraction of 0.5 mm was used in HTC and biosorption experiments.

The HTC process was carried out in laboratory autoclave (Carl Roth, Model II). For production of hydrochar 10 g of PL powder was stirred with 150 ml of ultrapure water on reaction temperature at 200ºC constant for 1 h. After that period, the hydrochar was separated from liquid by filtration, rinsed three times with distilled water and dried at 105°C for 24 h.

Preliminary adsorption test

For preliminary adsorption test we used: adsorbent (PL and 200-PL) mass 0.08 g, lead solution with initial concentration 100 mg/L in volume 0.05 L, contact time 2 hours on pH = 5 value and at room temperature (25°C). Solution was separated from adsorbent by filtration and Pb^{2+} concentrations before and after adsorption were determined using atomic adsorption spectrophotometer (AAS, Perkin Elmer AAnalyst 300).

FTIR Analysis

Fourier transform infrared (FTIR) spectroscopic analysis was used to determine the presence of functional groups in surface of PL and 200-PL responsible for Pb^{2+} binding. The

FTIR of samples before and after metal sorption were recorded on Thermo Fisher Scientific Nicolet IS-50 spectrophotometer, in the spectral range of 400 - 4000 cm^{-1}. The FTIR spectra of the samples were converted into pellet form, using KBr as the reference material.

RESULTS AND DISCUSSION

Preliminary adsorption test

The amount of Pb^{2+} ion adsorbed on PL and 200-PL surface was calculated using equation:

$$q = ((C_0 - C_e) /m) \times V \quad (1)$$

Where, q - adsorbent capacity [mg/g]; C_0 - initial concentration of Pb^{2+} [mg/L]; C_e - metal concentration after adsorption [mg/L]; m - amount of adsorbent [g]; V - volume of the Pb^{2+} solution [L].

The percentage of lead ions removal (R) was calculated based on the difference in lead concentration in initial solution (C_0) and in solution after adsorption (C_e):

$$R[\%] = ((C_0 - C_e) / C_0) \times 100 \quad (2)$$

The preliminary adsorption test showed that leaves without structural changes had better adsorption capacity which was q=34.53 mg/g than hydrochar produced at 200°C, q=11.26 mg/g (Figure 1). Additionally, percentage of Pb^{2+} removal confirm that PL has higher efficiency as adsorbent (60.87%) in comparison with 200-PL (19.57%).

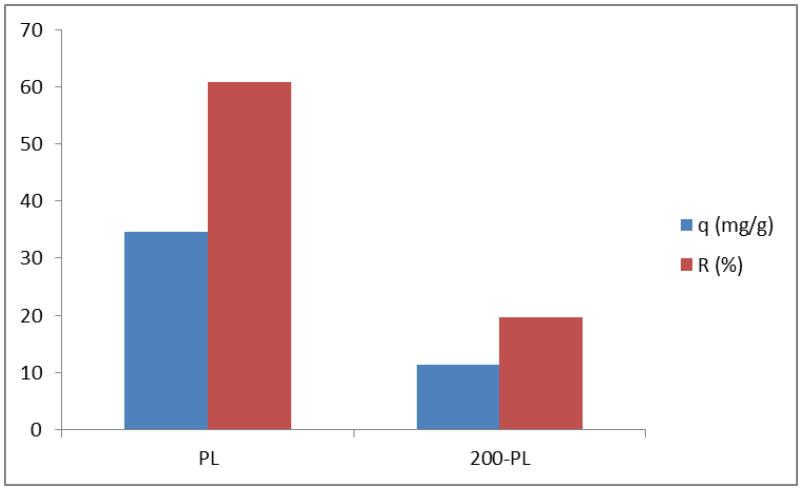

Figure 1 *Adsorption capacity (q) and Pb^{2+} removal (R) using PL and 200-PL*

FTIR Analysis

Selected FTIR spectrums of PL and 200-PL were shown in Figure 2 and the oxygen functional groups such as hydroxyl and carboxylic groups are crucial for adsorption of lead ions. Also, it can be seen that hydrothermal carbonization leads to a decrease in the intensity of the peaks in FTIR spectra. Unlike the PL and 200-PL, adsorbents with Pb^{2+} ions had a lower intensity of IR peaks between 1000 and 1400 cm^{-1}, peak at about 1700 cm^{-1} and peak at about 3300 cm^{-1}. The IR peaks between 1000 and 1400 cm^{-1} indicated C-O and O-H groups from alcohols, phenols, carboxylic acids [6,8], peak at about 1700 cm^{-1} can be attributed to the carbonyl group (C=O) from fibrous structure [6,7]. The wide and intense band at about

3300 cm^{-1} belongs to the vibration of the –O-H group [7,8]. Since the intensities of these peaks are reduced after the adsorption of Pb^{2+} ions, it could be concluded that those groups were involved in a metal adsorption on the surface of adsorbents.

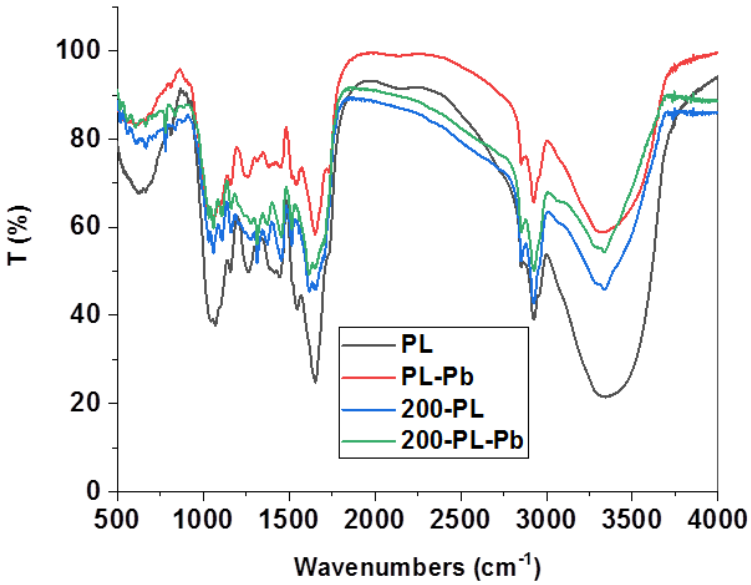

Figure 2 *FTIR spectra of* ***PL*** *and* ***200-PL*** *before and after* Pb^{2+} *adsorption*

CONCLUSION

The adsorption preliminary test showed that PL had better adsorption characteristic for lead ions removal. Adsorption capacity of PL was 34.53 mg/g and adsorption capacity of 200-PL was 11.26 mg/g. Also, adsorption efficiency was 60.87% for PL and 19.57% for 200-PL. With FTIR analysis it was observed that oxygen functional groups may have been the most important for adsorption of Pb^{2+} ions and hydrothermal carbonization process reduced their number on the surface of the sample. This study suggests that waste Paulownia leaves without any structural changes could be considered as more effective adsorbent for Pb^{2+} removal than their hydrochar at 200°C.

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