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Prof. Dr Snežana Šerbula

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REMOVAL EFFICIENCY OF HEAVY METAL IONS FROM AQUEOUS SOLUTION WITH WASTE TREE BIOMASS HYDROCHARS

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Abstract

In this study, Paulownia tree leaves hydrochars (PL-HTCs) were used as potential adsorbents for Zn(II), Cd(II) and Mn(II) ions from aqueous solution and their efficiency was investigated. The preliminary adsorption results showed that hydrochars had better affinity for Cd(II) than for Zn(II) and Mn(II) ions removal. In order to improve adsorption capacity, hydrochar obtained at 220°C were activated with NaOH and further investigated only for Cd(II) removal. Alkali activated hydrochar (AH-220) has significantly better efficiency (q=24.05 mg/g, E=52.57%) in removing Cd(II) ions than hydrochar before modification. Adsorption kinetic studies showed that Cd(II) ions sorption at AH-220 surface followed the pseudo-second-order model. This implies that the adsorption process was mostly controlled by the chemical binding.

Keywords: tree leaves hydrochars, adsorption, heavy metals, kinetic studies.

INTRODUCTION

The various, toxic metals can easily be found in the nature since they are extensively use in industry. The most heavy metals are nonessential and cause enormous health problems due their persistency and therefore accumulation in the food chain and environment [1,2]. Diverse conventional techniques are used to remove various organic and inorganic contaminants from wastewaters. Most of them have limited scope of application, due to various shortcomings such as expensive operation costs, production of second pollutants, poor regeneration [3,4]. These disadvantages could be avoided by choosing adsorption as purification strategy. Adsorption is a successful physicochemical method for contaminants removal, if a suitable material is chosen as adsorbents [3,5]. The usage of obtained hydrochar from biowaste as adsorbent have causes growing interests. It is extensively used due to renewable resources, eco-friendly quality, could have high efficiency and possibility to be chemically activated [3,6].

The hydrothermal carbonization (HTC) treatment of biomass is alternative, thermochemical process, which contributes to using of residual waste and convert them into valuable, low-cost materials (hydrochars) [7,8]. According to characteristics of the obtained hydrochars, the application of these materials was investigated in numerous fields [9,10]. Since the structure of hydrochars is porous with reactive, functionalized surface and increased aromatization, one of the fields for application include the adsorption of various contaminants

[4,11]. Additionally, in order to improve the reactivity and/or the selectivity, several methods are applied to further modify the hydrochar [9]. The alkali treatment activates the hydrochar through increasing the oxygen functional groups (OFG) as well as the surface basicity [11]. Also, cold alkaline activation is low-cost and easily treatment thus it is promising method for industrial application [12].

One of the biomasses available in large quantities is tree leaves. Our previous studies showed that *Paulownia* leaves (PL) biomass is very suitable for HTC treatment [11,13]. In this regard, the aim of this paper was to examine the possibility of PL hydrochars (PL-HTCs) as potential and efficient zinc(II), cadmium(II) and manganese(II) ions adsorbents. Thereafter, the selected PL-HTC was alkali modified and investigated for Cd(II) ions adsorption under kinetics study. For this purpose, the pseudo-first-order (PFO), pseudo-second-order (PSO) and Weber Morris intra-particle diffusion kinetic models were applied to experimentally obtained results.

MATERIALS AND METHODS

Materials preparation

The leaves of *Paulownia* tree were collected from park in Belgrade, Serbia, wash with ultrapure water, air-dried for two weeks and grinded, where sieved fraction of 0.5 mm was used in HTC experiments.

The HTC process was carried out in laboratory autoclave (Carl Roth, Model II), where 10 g of leaves powder was stirred with 120 ml of ultrapure water on reaction temperature at 180, 200, 220, 240 and 260ºC constant for 1 h. After that period, the hydrochar was separated from liquid by filtration, rinsed three times with ultrapure water and dried at 105°C for 24 h.

Alkali modification was performed by stirring 3 g of the hydrochar obtained at 220ºC with 300 mL of 2 M NaOH solution for 1 h at room temperature (about 25°C). Thereafter, the obtained modified hydrochar (AH-220) was filtered, rinsed with ultrapure water to the neutral pH value and dried at 105°C.

Preliminary adsorption test

For preliminary adsorption test we used: adsorbents (PL-HTCs) mass 0.020 g, heavy metals solution (Zn(II), Cd(II) and Mn(II)) with initial concentration 50 mg/L in volume 0.020 L, contact time 3 hours and at room temperature (25°C). Solution was separated from adsorbent by filtration and Zn(II), Cd(II) and Mn(II) concentrations before and after adsorption were determined using atomic adsorption spectrophotometer (AAS, PerkinElmer, PinAAcle 900T).

The amount of Zn(II), Cd(II) and Mn(II) ions adsorbed on PL-HTCs surface was calculated using equation:

$$q = (C_0\text{-}C_{eq})/m \times V \tag{1}$$

where q [mg/g] was adsorbent capacity, C_0 and C_{eq} [mg/L] were initial and after adsorption concentration of metal ions, m [g] was amount of adsorbent and V [L] was volume of the metal ions solutions.

The efficiency of Zn(II), Cd(II) and Mn(II) ions removal in percentages (E) was calculated based on the difference in metal concentration in initial solutions (C_0) and in solutions after adsorption (C_{eq}):

$$E = (C_0 - C_{eq})/C_0 \times 100\% \tag{2}$$

Effect of contact time, kinetics studies

The effect of contact time on Cd(II) removal from aqueous solution using alkali activated PL hydrochar (AH-220) was studied. For this experiment 0.020 g AH-220 was mixing with 20 mL Cd(II) solution, initial concentration 50 mg/L at different contact time from 10 to 1080 min. The used kinetic models included the non-linear Lagergren pseudo-first-order (PFO) rate equation [14]:

$$q_t = q_{eq} \times (1 - e^{-k_1 t}) \tag{3}$$

Additionally, the non-linear pseudo-second-order (PSO) rate equation [15]:

$$q_t = q^2_{eq} k_2 t /(1 + k_2 q_{eq} t) \tag{4}$$

where q_{eq} and q_t [mg/g] were the amount of Cd(II) adsorbed by AH-220 at equilibrium and time t [min] calculated from kinetic models. The k_1 [1/min] and k_2 [g/(mg×min)] were the pseudo-first-order and pseudo-second-order constant rate, respectively.

The Weber-Morris intra-particle diffusion model equation [16]:

$$q = k_{id} \times t^{0.5} + C \tag{5}$$

In which q [mg/g] represented the amount of adsorbed Cd(II) in time t [min], k_{id} [mg/(g× min$^{1/2}$)] represented the intra-particle diffusion rate constant and C was the intercept.

RESULTS AND DISCUSSION

Preliminary adsorption test

The preliminary adsorption test showed that hydrochars exhibited similar adsorption ability for Zn(II), Cd(II) and Mn(II) removal (Figure 1). The comparison of the examined ions revealed that Cd(II) ions were the most bound to the hydrochars surface (q ~10 mg/g), while the Mn(II) ions bound the least (q ~5 mg/g). Additionally, the hydrochar formed at 180°C

showed the best efficiency for Zn(II) ions (E = 23.86%), while the hydrochar at 220°C has the higher efficiency for Cd(II) and Mn(II) removal compared to other PL-HTCs (25.49% and 13.59%, respectively). Since the PL-HTC obtained at 220°C exhibited the best adsorption capacity and efficiency for Cd(II) ions, this sample was chosen for alkaline activation with NaOH and further kinetic studies for Cd(II) adsorption.
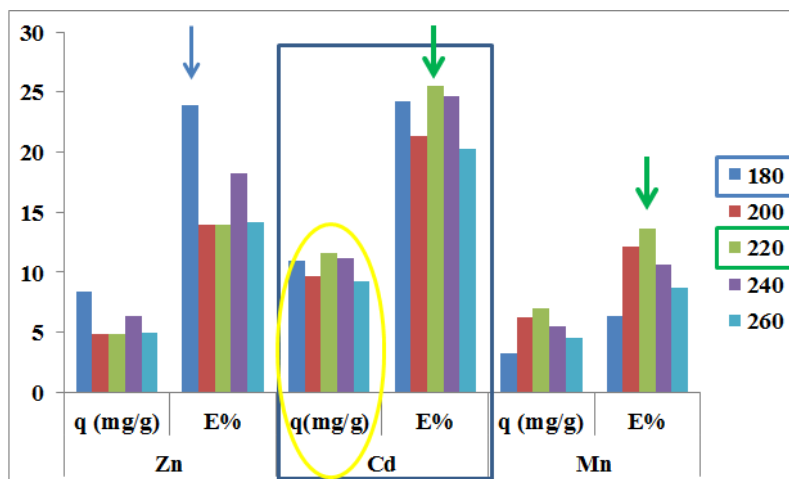

Figure 1 The preliminary results of the Zn(II), Cd(II) and Mn(II) adsorption onto the PL-HTCs

Effect of contact time, kinetics studies of Cd(II) sorption at modified hydrochar

In order to define the equilibrium time at the solid-liquid interface, the change in Cd(II) ion concentration during selected time period was monitored (Figure 2). The obtained results revealed that the AH-220 rapidly removed the Cd(II) ions from solution in the initial stage, probably due to plenty of availible active sites on the adsorbent surface [1,2]. After the two hours, a milder increase in capacity is observed and equilibrium was reached by approximately 360 min (Figure 2a).
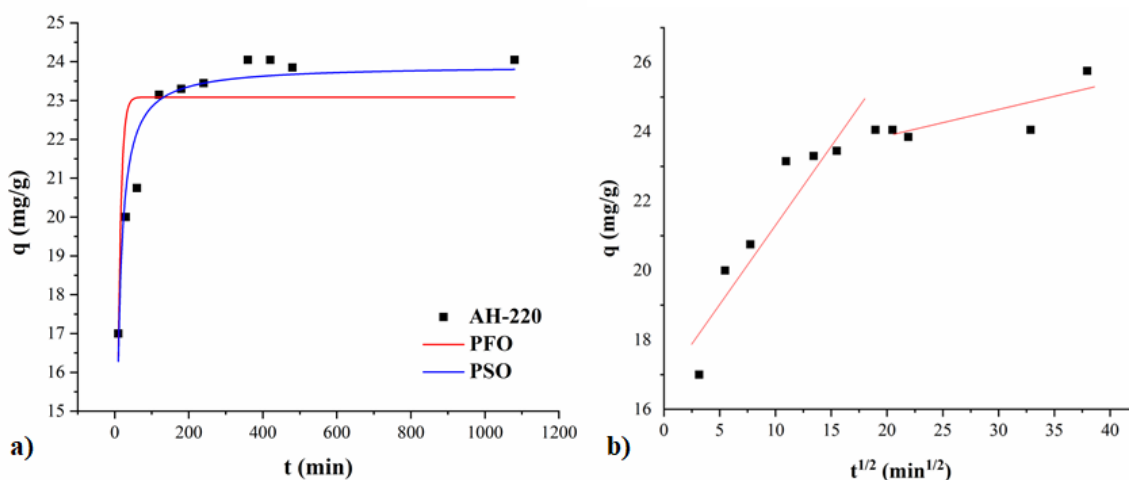

Figure 2 a) Effect of contact time and non-linear kinetic models; b) Intra-particle diffusion model of Cd(II) adsorption (50 mg/L) on the AH-220

To assume the adsorption mechanisms of Cd(II) ions binding, the pseudo-first-order (PFO) and pseudo-second-order (PSO) and Weber Morris intra-particle diffusion kinetic models were applied. The calculated kinetic parameters were shown in Table 1. According to these results, it can be concluded that PSO model the best fit with experimental data, $R^2 = 0.9307$. The calculated equilibrium adsorption value determined by the PSO model ($q_{eq,cal} = 23.90$ mg/g) was in agreement with the experimentally obtained result ($q_{eq,exp} = 24.05$ mg/g) (Figure 2a, Table 1). This implies that chemical interaction, such as covalent bonding, the complexation and/or the exchange of electron and ions, is controlling step during Cd(II) ions sorption onto the AH-220 surface [1,2,11]. Also, applied intra-particle model (Figure 2b, Table 1) revealed two different linear zones and indicated that intra-particle diffusion of ions was not the only rate-controlling step and that also some other mechanisms could be included [1,11].

Table 1 Kinetic parameters for Cd(II) adsorption onto the AH-220

Adsorbent AH-220	
$q_{eq, exp}$ [mg/g]	24.05
Pseudo-First-Order Model	
$q_{eq,cal}$ [mg/g]	23.09
k_1 [1/min]	0.12
χ^2	1.96
R^2	0.6887
Pseudo-Second-Order Model	
$q_{eq,cal}$ [mg/g]	23.90
κ_2 [g/(mg×min)]	0.009
χ^2	0.93
R^2	0.9307
Weber-Morris diffusion Model	
K_{id1} [mg/(g×min$^{1/2}$)]	0.50
C_1 [mg/g]	16.5
R^2	0.8864
K_{id2} [mg/(g×min$^{1/2}$)]	0.10
C_2 [mg/g]	21.39
R^2	0.6472

CONCLUSION

Based on the obtained results, it can be concluded that alkaline activation significantly improves the efficiency of hydrochar in order to adsorb metal ions. The kinetic studies revealed that the sorption of Cd(II) ions onto the alkali modified hydrochar surface followed pseudo-second-order model and that chemical adsorption was controlling step. Additionally, the intra-particle model revealed that adsorption occurred through two simultaneous stages. The results from this work presented that the waste tree leaves biomass had promising potential in further use as feedstock for metal ion adsorbents production.

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