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THE APPLICATION OF ENGINEERED PEACH STONE BIOCHAR IN REMOVING PHOSPHATES FROM AQUEOUS SOLUTION: KINETIC INSIGHTS

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Abstract (10 pt): New biochar-based material was synthesized via two-step process: pre-pyrolysis modification of waste biomass (derived from waste peach stones (PS)) and pyrolysis of chemically modified biomass. Obtained Mg-biochar composite (PS-M-B) was used for phosphates removal from aqueous solution in isothermal batch experiments under specified operational parameters. Sorption experiments were performed for the purpose of investigation of initial sorbate concentration (50-200 mg/l) and contact time (5 min to 24 h) on sorbent efficiency. It was observed that removal efficiency was higher than 90% after only 3 h of sorbet/sorbate contact and that equilibrium was achieved (in the whole concentration range) after 6 h of sorption. The overall rate of phosphate sorption from aqueous solution onto PS-M-B have been evaluated by non-linear form of two kinetic reaction models: pseudo-first and pseudo-second-order model. Obtained data followed better the pseudo-first order kinetics, indicating phisisorption as on of the most contributing mechanism in phosphate sorption process.
Key words: *waste biomass, chemical activation, biochar, phosphate removal, kinetics*

INTRODUCTION

Biochar (BC) is a solid, carbon rich multifunctional material produced by thermochemical conversion of mostly waste biomass in an oxygen-limited environment [1]. Huge amounts of feedstock are permanently available for BC production, among which agro-industrial residues are ones of the most importance due to the huge quantities generated all over the world and especially in developing countries [2]. As a low-cost material, BC has gained attention as an important material that can be applied in a diversity ways: as fertilizer that improves soil structure and promotes nutrient enrichment, as contaminated water/gas purifier, material for bioenergy production, additive to polymeric and concrete materials, super capacitor etc. [3,4]. Its valuable and sustainable role in variety materials production, promotes BC utilization in circular economy and suggest BC application as positive strategy for long-term decarbonisation [3,5].

The porous structure and active surface of biochar (full with functional groups) contribute to BC ability to bind variety pollutants from its environment [6]. However, unmodified, so-called "pristine" biochar has some limitations owing to its properties (e.g negatively charged surface, low specific surface area, and lack of specific functional groups, which may limit its utilization in sorption of specific pollutants (such as PO_4^{3-}) [7]. In order to improve that, the engineered biochars can be better alternatives instead of native biochars, because they have tailored sorbate binding capability and capability to slowly release bonded sorbates when applied into different matrix, for example into the soil. Physico-chemical modification might change the BCs morphology and surface area, change or induce new functional groups, metal contents, hydrophobicity etc. in such way to enhance the adsorption capacity and selectivity of BC towards specific pollutants [8]. Many studies have shown that these Metal-biochar-based composites can effectively enhance the adsorption capacity towards anions, especially phosphates. The modification method is usually carried out through impregnation and pre-pyrolysis or post-pyrolysis of the starting biomass [9].

A vast amount of waste biomass, which is generated in Serbia each year, can provide an excellent feedstock for BC production [2]. In order to examine potential of waste biomass (generated from fruit processing industries) to bind one of the most abundant eutrophication agent-phosphate ions, the authors of this paper have modified it my Mg salt; the modified biomass was further tailored via pyrolysis under specific operational parameters and applied it in order to bind phosphate ions from synthetic solutions. Studies of the sorption kinetics provide insights into the overall rate of the sorption process, which is a crucial factor in evaluating the efficiency of the adsorbent, as well as giving insights into the sorption mechanism [9]. For that purpose, we have further examined the kinetic of this sorption process in order to get insight on possible kinetic mechanism.

MATERIAL AND METHODS

Waste biomass, peach stones (PS) was taken from the local fruit processing company “Fruvita”, where they were characterized as a waste by-product. After receiving, stones samples were dried at room temperature and modified by Mg-salt according to the procedure adopted from Li et al. [10]. Modified PS samples were further pyrolysed into the biochar in pyrolytic reactor „APŽ-L-120-N; 03204“ (Elektron, Serbia), at heating rate of 10 °C/min, from room temperature until 500 °C, where they were kept for 90 min. At the end of cooling process, biochar sample (PS-M-B) was grinded at desired granulation (d_p < 0.1 mm) and stored for further experiments.
Sorption experiments were performed in isothermal batch system with stirring, under previously determined sorption parameters: solid/liquid ratio=4 g/L, pH_i=5.5, T=25 °C, 200 rpm, while the initial phosphate concentration varied from 50 to 200 mg/L. The concentrations of residual phosphates were determined using MD 610 (Lovibond, Germany) at desired time intervals, which ranged from 5 minutes up to 24 hours.
The effectiveness (R(%)) and the sorption capacity (q_e) of the PO_4^{3-} sorption by PS-M-B were calculated using following equations:

$$R(\%) = \frac{C_i - C_f}{C_i} * 100\% \quad (1)$$

$$q_f = \frac{(C_i - C_f) * V}{m} \quad (2)$$

Where C_i and C_f are initial and measured (at specific time) concentration of PO_4^{3-}, respectively, V is the volume of the phosphate solution and m is the mass of the sorbent.
Experimental data from kinetic experiments were fitted using non-linear forms of two most frequently used kinetic reaction models: pseudo-first [11] and pseudo-second [12] order model.

RESULTS AND DISCUSSION

To explore the kinetic of the phosphate sorption onto biochar, the effect of the contact time onto PO_4^{3-} sorption by PS-M-B at various initial concentrations was examined at 25 °C, at solid/liquid ratio of 4 g/L and at initial pH=5.5 (which wasn’t kept constant during the experiments) for different time intervals. It is interesting to notify that the final values of pH were higher than 10 for all concentrations investigated, indicating base nature of the sorbent and preferable medium for formation of the minerals (such as struvite) which is beneficial for phosphate removal. As can be seen in Figure 1, the rapid growth of the sorption capacity in the first 30 min was probably due to the high mass transfer and sufficient number of surface sorption sites, which suggested that there is a strong association between phosphate ions and PS-M-B surface. When these sites become saturated, the sorption tended to stabilize with a stable amount of phosphates bonded after only 3 h. The residual concentrations of phosphates were measured in regular intervals, up to 24 h, and remained constant in the whole time range (these data are not presented at the Figure 1) This indicate that the kinetic was fast in whole concentration range and that after saturation there are no desorption of bonded phosphates. The rapid initial sorption might be due to the electrostatic attraction between the positive

charged MgO deposited at the surface (during pretreatment (with $MgCl_2$) and pyrolysis) and the negative charged phosphate ions.
In the same time, lower initial concentrations were removed for shorter time: e.g. for initial phosphate concentration of 50 mg/L equilibrium was established after 120 min with removal efficiency (*R*) of 98%, while for the highest concentration of phosphates (200 g/L) the equilibrium was achieved after 4 h with the same removal efficiency. After 24 h of contact, 100% of removal efficiency was established for all concentrations. The experimental equilibrium capacities (under previously defined operational parameters) were found to be almost 12 mg/g ($Ci(PO_4^{3})$ = 50 mg/L) and 48 mg/g (($Ci(PO_4^{3-})$ = 200 mg/L).

Experimental data obtained through the batch sorption experiments were fitted by previously mentioned models and obtained curves are presented at Figure1.

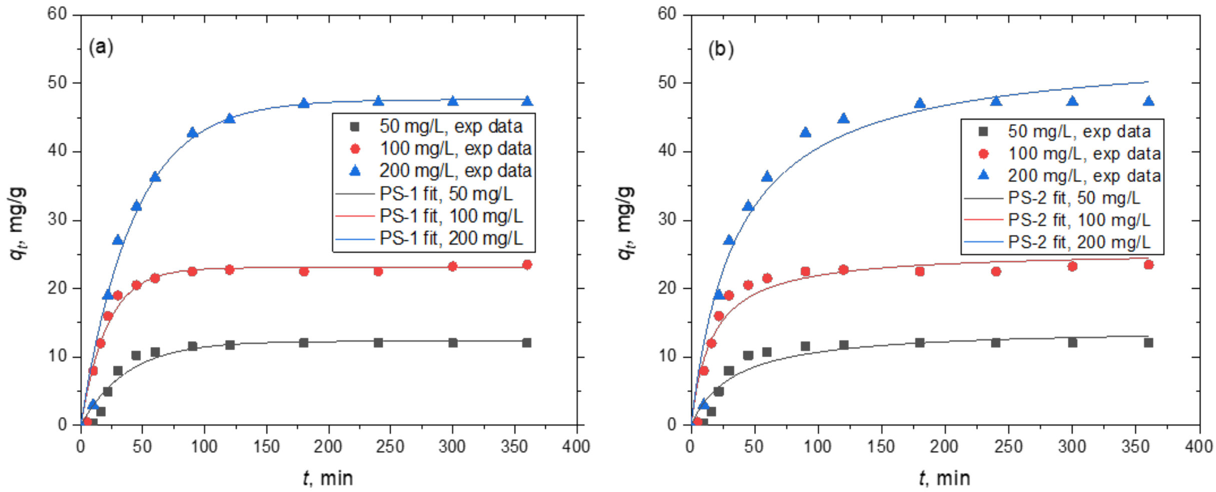

Fig. 1. *Fitting of experimental data by (a) pseudo-first model and (b) pseudo-second model*

Kinetic parameters for pseudo-first and pseudo-second order models are shown in Table 1. As it can be seen from Figure 1 and data presented in Table 1, the pseudo-second order model fit well the sorption kinetics with R^2 ranging from almost 0.9 at the PO_4^{3-} concentration of 50 mg/L and 0.96 at PO_4^{3-} concentration of 200 mg/L. In opposite, the sorption kinetics obeyed pseudo-first order model very well with R^2 higher than 0.93 in whole concentration range. In the same time, statistical parameter of model fitting, χ^2, was lower for pseudo-first than for pseudo-second order. The predicted values of the pseudo-first order were 12.3, 23.1 and 47.7 mg/g respectively for the sorption of 50, 100 and 200 mg/L of initial phosphate concentrations, and very close to the experimental values (q_{exp}) shown in Table 1.

Table 1. *Kinetic parameters for phosphate sorption by PS-M-B fitted by PS-1 and PS-2*

Model		**Initial phosphate concentration, mg/L**		
		50	**100**	**200**
	q_{exp}, mg/g	**12.0**	**23.5**	**48.0**
PS-1	**q_1, mg/g**	12.3	23.1	47.7
	k_1 (1/min)	0.027	0.045	0.024
	R^2	0.934	0.974	0.982
	χ^2	1.617	1.998	5.896
PS-2	**q_2, mg/g**	14.3	25.6	55.2
	k_2 (g/(mg min))	0.0021	0.0023	0.0005
	R^2	0.895	0.943	0.962
	χ^2	2.590	4.318	12.37

The results presented in Table 1 indicate that the pseudo-first-order model fits better removal of phosphates by biochar made from modified peach stone particles, suggesting that phosphate uptake may be driven more by physical adsorption (e.g., van der Waals forces or electrostatic interactions) than chemical bonding. This is interesting, since the most of the literately available data indicate that the pseudo-second order model better describes phosphate bonding by metal loaded biochars, suggesting the chemisorption as possible mechanism [10, 13]. The results of Karunanithi et al. [14] also indicate that sorption of phosphates by biochar derived from soybean stover was mainly a physisorption process, which was further substantiated through the absence of any additional chemical bond formation through FT-IR spectra and negligible phase change through XRD data. However, the pseudo-second-order model still shows a strong fit, so chemisorption can't be ruled out entirely. Thus, the phosphate sorption onto biochar is controlled by the synergistic interaction of many mechanisms, from physical to chemical capture mechanisms, where the physical sorption is associated with the structure and surface area of BC, while the chemical is associated with the biochar type and the number and type of present functional groups [15].

CONCLUSION

The kinetic of sorption performances of phosphate onto Mg modified biochar composite was investigated in this paper with the aim of elucidating necessary time for reaching equilibrium in wide concentration range. It was concluded that the mechanism of the removal process is combination of phisi and chemisorption process, and that further analyses are required, In the same time, synthetized sorbent have shown high removal efficiency in the whole concentration range, acting as promising material for phosphate removal from contaminated water streams. These results suggest that 20% PS-M-B composite has great potential to be used for removal of phosphate from this nutrient-rich surface waterbodies. It should be also underlined that the application of this sorbent is very attractive from both environmental and economic aspects, since the low-cost waste biomass readily available and could be obtained in large quantities from local producers. Unfortunately, current practice is to deposit this organic waste at open landfills, which represents significant resource losses and air quality concerns. Therefore, the thermochemical conversion of these biomass wastes into useful products support not only the reduction of greenhouse gasses emission but also improves the disposal strategy of agricultural solid waste disposal.

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