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The use of Biochar from Waste Wooden Biomass for Removal of Emerging Pollutants

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Abstract
The aim of presented research is to use biochar produced from waste biomass for removal of veterinary antibiotic tiamulin from model wastewater. Produced biochar was activated using different chemical methods (KOH treatment under various conditions). It was characterised using BET method for the determination of the pore size distribution and pore volume fraction as well as SEM microscopy. Results indicated importance of biochar activation to achieve applicable adsorption characteristics. In 180 minutes of batch experiment up to 78% of tiamulin was removed. Kinetic parameters were also determined by Lagergren model while for determination of adsorption isotherm Freundlich model fitted obtained data. It was concluded, that adsorption characteristics of produced and activated biochar are comparable to those of commercially available activated carbons and thus its feasibility for removal of tiamulin from model wastewater was confirmed.
Keywords: adsorption, antibiotics, biochar, kinetics, isotherm

1. Introduction

Biochar can be produced using variety of waste biomass to achieve goals of zero waste management and circular economy. It has been used as adsorbent in the past for water and wastewater treatment (Cetin, 2004). Recently, the application of natural porous materials for removal of emerging pollutants gained a lot of attention (Xiangyun, 2015). One of the important groups of emerging pollutants are also pharmaceuticals. Owing to recent concerns about their effects on naturally occurring bacterial communities resulting in development of antibiotic resistance different removal methods are studied and applied (Johnson, 2015). Many studies confirmed, that besides advanced oxidation processes adsorption could be used efficiently to remove or at least deactivate antibiotics and thus reduce their environmental impact (Johnson, 2015). Presented research work focuses on removal of veterinary antibiotic tiamulin from model wastewater by biochar, produced from waste wooden biomass.

2. Materials and Mehods

In the study, environmentally persistent, veterinary antibiotic tiamulin, in the form of fumarate was used (Figure 1). Tiamulin is entirely stable in the period of 180 days in the stored manure, while its half-life in surface waters is up to 100 days (Schluesener, 2006) so it belongs to the group of persistent pollutants.

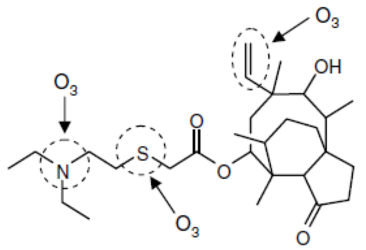

Figure 1. Chemical structures of tiamulin (Ben et al. 2012).

Adsorption experiments were performed using biochar produced from waste wooden biomass (apple tree branches, 1 cm x 2 cm), produced by pyrolysis in small pilot 1.5 L system at temperatures in the range of 400 – 600 °C. The efficiency of the process was evaluated by determination of the mass prior and after thermal process. To attain optimal adsorption capacity, treatment with KOH at 800 °C for biochar activation was accomplished.

Adsorption experiments with tiamulin (100 mg L^{-1}) were run out after SEM (Scanning Electron Microscopy) characterization of biochar in a batch mode (25 mL, up to 4 hours). The pore size and surface area was also determined by BET analyses (Marques, 2018). Kinetic mechanism for adsorption was well described by pseudo-second-order Lagergren model based on TOC (Total Organic Carbon) measurements (Xiangyun, 2015). For determination of adsorption isotherm Freundlich model was applied.

3. Results and Discussion

Waste wooden biomass contained 75% of solid matter content, after pyrolysis the production of biochar was 42.7%. Preliminary experiments indicated, that it had no adsorption capacity (less than 2% of tiamulin removal even at 1 g L^{-1} of biochar added). Next step was its activation which resulted in 54% loss of mass (Figure 2).

During batch adsorption experiments concentration of tiamulin (100 mg L^{-1}) decreased for 78%, 46%, 25% and 22% according to the amount of biochar added (Table 1) in 180 minutes of experiment.

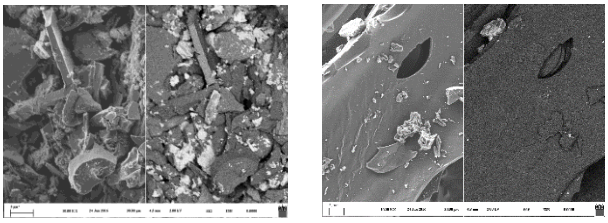

Figure 2. SEM characterization of biochar: Biochar afterpyrolysis (left) and KOH activated biochar (right).

To obtain its efficient removal, at least 1 g L^{-1} of activated biochar should be used while experiments with commercial biochar of the same particle size (100 µm) 92% removal was achieved in 5 minutes. Lagegren kinetic model fit the data well confirming good adsorption potential of KOH activated biochar:

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + K_2\, t \qquad (1)$$

For determinate pseudo-second-order rate constant and calculate concentration of tiamulin at the equilibrium, the linearization of the equation (Eq. 1) was performed (Eq. 2).

$$\frac{t}{q_t} = \frac{1}{K_2\, q_e^2} + \frac{1}{q_e}\, t \qquad (2)$$

K_2 stands for pseudo-second-order rate constant (g mg^{-1} min^{-1}), q_e is the amount of tismulin adsorbed at equilibrium (mg_{DOC} g^{-1}), q_t is the amount of tiamulin adsorbed at time t (mg_{DOC} g^{-1}) and t is time (min).

Applied Freundlich model adsorption isotherm confirmed significant adsorption potential of activated biochar.

Table 1. Kinetic parameters of obtained by Lagergren model and parameters of Freundlich isotherm.

	Activated Biochar	
Concentration of biochar [g L^{-1}]	K_2 [g mg^{-1} min^{-1}]	q_e [mg g^{-1}]
0.125	0.00005	423.9
0.25	0.00527	100.8
0.5	0.00010	127.5
1.0	0.00050	85.4
R^2 [/]	0.99	
K_F [mg g^{-1}]	44.3	
n [/]	5.26	

4. Conclusions

Biochar produced from waste apple tree branches was efficiently used for removal of veterinary antibiotic tiamulin from model wastewater. Experiments confirmed the need for chemical activation of produced biochar to increase its specific surface and remove possible impurities remained on surface after pyrolysis. 78% removal of tiamulin from model wastewater was comparable to treatment efficiency of commercial biochar confirming its possible use in actual treatment process.

Experiments confirmed that waste biomass is a viable source of natural adsorbents that can be used in treatment technologies for removal of emerging hazardous contaminants.

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