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ORIGINAL ARTICLE

Pine-wood derived nanobiochar for removal of carbamazepine from aqueous media: Adsorption behavior and influential parameters

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Abstract In recent years, application of biochar for removal of pollutants from aqueous solutions has been of interest due to favorable physicochemical properties and availability of feedstock. However, adsorption behavior has been reported only for raw and micro biochar particles and taking advantage of biochar nanoparticles, which offer superior specific surface area, did not receive any attention. The objective of this study was to investigate the adsorption efficiency of produced nanobiochar from pinewood. For this purpose, removal of carbamazepine (CBZ), a globally prescribed pharmaceutical, at very low concentrations (0.5–20 ppb) on as-produced nanobiochar with average particle size of 60 nm was studied. The results showed that nanobiochar can remove up to 95% of CBZ (74 μg CBZ/g nanobiochar) after 3 h contact time. Adsorption of CBZ on nanobiochar followed Freundlich isotherm model (R^2 = 0.9822) and pseudo-second order kinetic model (R^2 = 0.9994). It was found that increasing pH from 3 to 8 can enhance the adsorption efficiency by 2.3 folds. Also, due to the presence of surfactant in wastewater, the addition of Tween 80 as a model surfactant was studied in the range of 0 to 1 (Tween 80 to CBZ molar ratio) and the results showed that adsorption efficiency can be enhanced by 57%. Thus, the nanobiochar obtained from pinewood residues can be a promising sorbent for micropollutants.

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1. Introduction

Pharmaceutical compounds are widely used for curing or preventing human and animal diseases. The annual consumption of pharmaceuticals is estimated to be about 15 g and 50–150 g per capita in world and industrialized countries, respectively (Benotti et al., 2009). The occurrence of these compounds in the environment has attracted attention

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of regulatory organizations due to potential adverse effects, such as development of antibiotic resistance genes in pathogenic bacteria (Yu et al., 2008). Carbamazepine (CBZ) is one of widely used antiepileptic/anticonvulsant drugs around the world with more than 1000 tons annual consumption. The release rate of CBZ into water bodies is estimated to be around 30 tons per year and according to several reports, it is toxic for several aquatic organisms, such as cnidarians and crustaceans (Zhang et al., 2008; Vernouillet et al., 2010; Martin-Diaz et al., 2009). CBZ is electrically neutral at typical pH values of drinking water and its log K_{ow} (2.45) shows that CBZ is relatively hydrophilic (Mohapatra et al., 2012). CBZ has been among most frequently detected pharmaceutical compounds in wastewater treatment plant (WWTP) effluent and rivers in Europe and North America (Mohapatra et al., 2012; Chng and Pumera, 2011; Cai and Larese-Casanova, 2014). For example, the presence of CBZ in wastewaters (up to 6.3 $\mu g\,L^{-1}$), surface waters (up to 1.1 $\mu g\,L^{-1}$), and drinking water (up to 30 $ng\,L^{-1}$) was reported in Canada and Germany (Kosjek et al., 2009). However, the CBZ removal efficiency of WWTP did not exceed 7% (Nielsen et al., 2015). Therefore, developing new method for effective removal of this compound is necessary prior to effluent discharge or drinking water distribution (Westerhoff et al., 2005; Huerta-Fontela et al., 2011). Accordingly, novel treatment processes are being examined for treatment of micropollutants-containing water sources with a focus on adsorption processes considering hydrophobicity of targeted compounds, or on advanced oxidation methods considering susceptibility of compounds to oxidative processes (Cai and Larese-Casanova, 2014; Basile et al., 2011). In the case of CBZ, advanced oxidation methods do not necessarily lead to complete mineralization and sometimes the transformation products such as acridine are still harmful to the environment (Kosjek et al., 2009; Wiegman et al., 2003). Thus, they still need further development to offer complete mineralization of micropollutants.

Carbonaceous nanomaterials showed high chemical and thermal stability and found many applications in industrial and medical devices. Due to their high specific surface area, they can act as adsorbents with high capacity and affinity for micropollutants (Ahmed et al., 2015; Chen and Zhou, 2014; Zhao et al., 2016). For example, Cai et al. studied the adsorption of CBZ on graphene oxide powder and their isotherms fitted well with Freundlich model with 95% of removal efficiency (Cai and Larese-Casanova, 2014). In a similar study, Lerman et al. used single-walled carbon nanotubes (SWCNTs) as adsorbent for removal of CBZ and their calculations showed incomplete monolayer coverage of SWCNTs which suggested that CBZ might interact with preferably polar sites on SWCNTs (Lerman et al., 2013). Oleszczuk et al. investigated the adsorption of CBZ on multi-walled carbon nanotubes (MWCNTs) and their isotherm and kinetic data fitted well the Polanyi-Manes model (PMM) and pseudo-second-order kinetic model. According to their observations, up to 90.6% of CBZ was adsorbed after 24 h depending on the outer diameter of MWCNT (Oleszczuk et al., 2009).

Recently biochar, which is a waste biomass pyrolysis product, has attracted a great interest for purification of water sources due to their properties, such as porosity and capability of adsorbing and exchanging different organic and inorganic contaminants (Yargicoglu et al., 2015; Reddy et al., 2014; Krika et al., 2011; Aljeboree et al., 2014). The advantages of employing biochars for treatment of wastewater have already been reported (Inyang et al., 2012, 2014; Zhang et al., 2013). Nielsen et al. used biochar produced from sewage sludge, aquaculture waste and their mixtures for adsorption of CBZ from water. Their results showed that equilibrium was reached within 5 h and adsorption capacity of 90% sewage sludge and 10% aquaculture waste was 37.2 mg/g at an equilibrium concentration of 50 mg/L CBZ (Nielsen et al., 2015).

Meanwhile, depending on the pyrolysis conditions, the particle size of the biochars ranged from hundreds of micrometers to several centimeters (Lehmann and Joseph, 2015). In our previous works, we studied the physicochemical and adsorption properties of biochar in micro-sized range (10–600 μm) and reported that the reduction in biochar size led to increased adsorption capacity due to increasing available sites for adsorption (Lonappan et al., 2016; Taheran et al., 2016). However, reducing the particle size of biochar to nanosize range i.e. smaller than 100 nm can further improve its properties, especially surface to volume ratio which can enhance the adsorption potential and surface energy (Sulaiman et al., 2013; Song and Kim, 2009; Deguchi et al., 2006; Darroudi et al., 2011; Kumar et al., 2013; Kesavan and Venkatraman, 2014; Shameli et al., 2012). To the best of our knowledge, nanobiochar has not been applied for investigation of adsorption micropollutants. In this work, nanobiochar was produced for the first time from pinewood biochar through a simple physical method. Also, the adsorption behavior of pharmaceutically active compound, CBZ, at low concentration levels from aqueous phase on produced nanobiochar was investigated. In the first part of the work, different isotherms and kinetics models were fitted for the obtained data to find the appropriate models for adsorption behavior. In the second part, the effects of several important parameters including solution pH, adsorbent dosage, rotational speed and surfactant concentration were studied.

2. Material and methods

2.1. Materials

Pinewood Biochar (BC-PW) was obtained from Pyrovac Inc. (Quebec, Canada). BC-PW was derived from pine white wood (80% v/v, 3 mm) obtained from Belle-Ripe in Princeville and the rest included spruce and fir (20%). The production of BC-PW was carried out at 525 ± 1 °C by increasing the temperature of biomass at the rate of 25 °C/min in the presence of nitrogen under atmospheric pressure for 20 min and the produced BC-PW was used as obtained from the reactor outlet. Carbamazepine (CBZ ⩾ 99%) was purchased from Sigma–Aldrich (Oakville, Canada). Carbamazepine (D10) was purchased from CDN Isotopes (Pointe-Claire, Canada). Tween 80 and methanol were purchased from Fisher scientific (Ottawa, Canada). Ultrapure water was prepared in the laboratory using Milli-Q/Milli-Ro Milli pore system (Massachusetts, USA) and it was used for preparation of CBZ stock solutions and related samples for adsorption tests.

2.2. Nanobiochar production

Nanobiochar with the average size of 60 ± 20 nm was produced in laboratory using a planetary ball mill (PM100; Retsch Corporation) at ambient conditions. Briefly, 10 g of pinewood biochar was kept at -80 °C for 24 h prior to grinding. Ball milling was performed at 575 rpm for 100 min in a 500 mL stainless steel jar using stainless steel balls of 2.4 mm in diameter (800 balls with total weight of 45 g). The physicochemical properties of produced nanobiochar are listed in Table 1.

2.3. Equilibrium time

To determine equilibrium time for adsorption of CBZ onto nanobiochar, 5 mg nanobiochar was added to 20 ml of CBZ solution (C_0 = 5 ng/mL) in 50 mL flasks. All flasks were shaken at 150 rpm and 25 ± 1 °C for 15 days. The samples were taken at different intervals of 1 h, 2 h, … 6 h, 12 h, 1 day, 2 days,…15 days, centrifuged for 10 min at 11,000*g* (14,000 rpm) and then analyzed for residual CBZ. In all the experiments, one sample containing only nanobiochar and

Table 1 Physicochemical properties of produced nanobiochar.

Property	Nanobiochar
Specific gravity	0.40 ± 0.02
Moisture content (%)	2.11 ± 0.07
WHC[a] (g H_2O/g biochar)	9.75 ± 0.45
LOI[b] organic matter content (%)	96.9 ± 3.4
Volatile matter content (%)	96.9 ± 4.2
Ash content (%)	2.0 ± 0.1
Fixed C content (%)	1.06 ± 0.07
pH	6.61 ± 0.35
ORP[c] (mV)	132 ± 4
EC[d] (μs cm^{-1})	1737 ± 28
Zeta potential (mV)	−31.3 ± 2.6
∑ PAHs[e] (mg kg^{-1})	26.837 ± 3.291
CEC[f] meq/100	14.8 ± 1.2
Particle size (nm)	60 ± 5
Surface area (m^2/g)	47.25
Elemental analysis:	
C (%)	83.1 ± 2.5
H (%)	3.5 ± 0.11
N (%)	< 1
H:C (Molar ratio)	0.5
C:N (Molar ratio)	> 96.9

[a] Water holding capacity.
[b] Loss on ignition.
[c] Oxidation-reduction potential.
[d] Electrical conductivity.
[e] Polycyclic aromatic hydrocarbons.
[f] Cation exchange capacity.

one sample containing only CBZ were considered as negative and positive controls, respectively. The CBZ concentration in negative and positive controls was 0 (below detection limit) and 5 ppb, respectively. All experiments were done in duplicate and average was reported.

2.4. Isotherm test

About 20 mL of aqueous CBZ solutions with different concentrations (0.5, 1, 3, 5, 7, 10, 15 and 20 ng/mL) along with 5 mg nanobiochar was added to 50 mL flasks. The pH of all samples was adjusted to 6 and then all the flasks were tightly sealed and incubated at 150 rpm and 25 ± 1 °C for two days (the time was determined using equilibrium test). The samples were centrifuged for 10 min at 11,000*g* (14,000 rpm) to remove the nanobiochar and the supernatants were analyzed for residual CBZ. Subsequently, three models were used to fit the adsorption isotherms of CBZ into nanobiochar (Table 2). All experiments were performed in duplicate and average values were reported. The results of isotherm tests and kinetic tests were analyzed by SigmaPlot 12 (Systat Software, Inc.) to fit in the suggested models.

2.5. Kinetics study

To study the adsorption kinetics, 5 mg nanobiochar was added to 500 mL CBZ solution (5 ng/mL). The solution pH was adjusted to 6 and stirred at 150 rpm and room temperature. Samples were taken after 1, 2, 3, 6, 9, 12, 15, 18, 21, 24, 27 and 30 min of adsorption. Later, the samples were withdrawn at different interval times and centrifuged at 11,000*g* (14,000 rpm) for 2 min, filtered with Whatman paper (0.2 micron pore size) and analyzed for CBZ in supernatants. Different kinetic models were used to fit the adsorption kinetics of CBZ on nanobiochar (Table 3). All experiments were performed in duplicates and average values were reported.

2.6. Adsorption energy

The Dubinin-Radushkevich empirical model was used to determine the energy of adsorption. The nonlinear form of this model can be expressed as Equations (8) and (9):

$$q_e = q_s \exp(-K_{ad}\varepsilon^2) \tag{8}$$

$$Lnq_e = Lnq_s - K_{ad}\varepsilon^2 \tag{9}$$

where q_e is the equilibrium concentration of adsorbate in solid phase (mg/g); q_s is the theoretical isotherm saturation capacity (mg/g); K_{ad} (mol^2/kJ^2) is Dubinin-Radushkevich isotherm constant and ϵ is potential energy that can be related to the equilibrium concentration through following equation.

$$\varepsilon = RT\,Ln\left(1 + \frac{1}{C_e}\right) \tag{10}$$

Table 2 Models used for good fitting of isotherms.

Name	Equation	Term definition[a]
Freundlich model	$Non - Linear: q_e = K_F C_e^{1/n}$	K_f [(mg/g)/(mg/L)$^{1/n}$]: Freundlich affinity coefficient
	$Linear: logq_e = \log K_F + 1/n \log C_e$ (1)	$1/n$: Freundlich exponential coefficient
Langmuir model	$Non - Linear: q_e = Q^0 C_e/(K_L + C_e)$	K_L [mg/L]: affinity coefficient
	$Linear: \frac{1}{q_e} = \left(\frac{K_L}{Q^0}\right)\frac{1}{C_e} + \frac{1}{Q_0}$ (2)	
Partition-adsorption model	$q_e = K_p C_e + Q^0 C_e/(K_L + C_e)$ (3)	K_P [L/g]: partition coefficient K_L [mg/L]: affinity coefficient

Note: [a]*qe* [mg/g] is the equilibrium concentration of adsorbate in solid; *Ce* [mg/L] is the equilibrium aqueous concentration of adsorbate; Q^0 [mg/g] is the maximum sorption capacity for adsorbate.

where R, T and Ce represent the universal gas constant (8.314 J/mol K), absolute temperature (K) and equilibrium concentration of adsorbate in aqueous phase (mg/L), respectively. This approach can be applied to determine if the adsorption is physical or chemical by calculating the mean free energy E using the following equation:

$$E = \frac{1}{\sqrt{2 \times K_{ad}}} \quad (11)$$

This parameter represents the amount of energy (kJ) for removing one mole of adsorbate from its location in adsorbent to the infinity. If $E < 8$ kJ/mol, physical forces were dominant in adsorption. If E is in the range of 8–16 kJ/mol, ion exchange mechanism governed adsorption and in the case of $E > 16$ kJ/mol, particle diffusion dominated adsorption (Dada et al., 2012).

2.7. Effect of operational parameters

2.7.1. Surfactant concentration

The effect of four different concentrations of Tween 80 (0, 25, 50, 75 and 100 ng/mL) on adsorption of CBZ onto nanobiochar was studied. The required amount of Tween 80 along with 10 mg nanobiochar was added to 18 mL of ultrapure water (adjusted to pH 6 using 0.2 M solution of HCl) and mixed for 10 min on a vortex mixer. Subsequently, the required CBZ (10 ng/mL) was added from stock solution and the volume was increased to 20 mL using ultrapure water with pH 6. For all the samples, rotational speed (150 rpm) and time (1 h) were fixed during experiments.

2.7.2. pH

The effect of six different pHs (3, 4, 5, 6, 7 and 8) which are typical of different water sources (rivers, lakes, groundwater or wastewater) on adsorption of CBZ onto nanobiochar was investigated. About 10 mL ultrapure water containing 10 mg nanobiochar and 1 μg Tween 80 and 10 mL ultrapure water containing 0.2 μg CBZ were prepared separately and their pH was adjusted to the required level using 0.2 M solution of NaOH or HCl. Later, they were mixed to reach CBZ concentration of 10 ng/mL and surfactant concentration of 50 ng/mL. For all the samples, the rotational speed (150 rpm) and time (1 h) were fixed during experiments.

2.7.3. Rotational speed

The effect of different rotational speeds (90, 120, 150, 180, 210 and 240 rpm) on adsorption of CBZ onto nanobiochar was studied. About 10 mL ultrapure water containing 10 mg nanobiochar and 1 μg Tween 80 and 10 mL ultrapure water containing 0.2 μg CBZ were prepared separately and their pH was adjusted to 6 using 0.2 M solution of HCl. Later, they were mixed to reach CBZ concentration of 10 ng/mL and surfactant concentration of 50 ng/mL. Eventually, each sample was mixed at required rotational speed for 1 h.

2.7.4. Adsorbent dose

Effect of different concentrations of nanobiochar (4, 7, 10, 13, 17 and 20 mg in 20 mL of solution) on adsorption of CBZ was studied. About 10 mL ultrapure water containing 1 μg Tween 80 and desired amount of nanobiochar and 10 mL ultrapure water containing 0.2 μg CBZ were prepared separately and their pH was adjusted to 6 using 0.2 M solution of HCl. For all experiments, the rotational speed (150 rpm) and time (1 h) were fixed during experiments.

2.8. Quantification of CBZ

Quantification of CBZ was performed using Laser Diode Thermal Desorption (LDTD) (Phytronix technologies, Canada) coupled with a LCQ Duo ion trap tandem mass spectrometer (Thermo Finnigan, USA). The daughter ions identified for CBZ in LDTD were 194 and 192 Da. The method reporting limit was 10 ng/L. A calibration curve of CBZ concentration was developed with six standard solutions and with R^2 no less than 0.99. The details of quantification process were described elsewhere (Mohapatra et al., 2012). All the experiments were performed in triplicates and the average results were reported.

2.9. Fourier transform infrared (FT-IR) spectroscopy

FT-IR spectrum in the range of 400–4000 cm^{-1} was recorded using a Nicole IS50 FT-IR Spectrometer (Thermo Scientific, USA) through attenuated total reflectance (ATR) using 4 cm^{-1} resolution and 32 scans per spectrum. For taking the spectrum, enough sample was placed on the diamond crystal and to ensure that consistent contact, the gripper plate was

Table 3 Models used for fitting of kinetics data.

Name	Equation	Term definition
Pseudo first-order model	$Non-Linear: q_t = q_e(1-exp^{-k_1 t})$	k_1[min^{-1}]: adsorption rate constant
	$Linear: \log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t$ (4)	
Pseudo second-order model	$Non-Linear: q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t}$	V_0 [mg/g h]: initial adsorption rate
	$Linear: \frac{t}{q_t} = \frac{1}{k_2 q_e^2} \frac{1}{q_e} t$ (5)	k_2 [g/mg h]: pseudo second-order rate constant
	$V_0 = k_2 q_e^2$ (6)	
Intra-particle diffusion model	$Non-Linear: q_t = k_p t^{0.5}$ (7)	K_p [mg/g $h^{0.5}$]: rate constant for intra-particle diffusion

q_t represent the adsorption capacity (mg/g) at time t.

placed on the sample. The average of 16 times measurement was plotted.

3. Results and discussion

3.1. Equilibrium time of CBZ adsorption on nanobiochar

The evolution of CBZ residual concentration (C/C_0) in aqueous phase during first 4 days is plotted in Fig. 1. According to this plot, equilibrium was reached after 2 days ($C/C_0 = 0.00001$). Consequently, for isotherm experiments, 2 days was considered as required time to reach equilibrium since no changes in C/C_0 were observed after 2 days. In the literature, 12 days was identified as equilibrium time for adsorption of 94% of CBZ on coal-based and coconut-based granular activated carbons (Yu et al., 2005, 2008). It is noteworthy that more than 95% of CBZ (equivalent to 74 μg CBZ/g nanobiochar) was removed in less than 3 h which indicated rapid mass transfer of CBZ onto nanobiochar compared to other carbonaceous materials. For example, Oleszczuk et al. investigated the adsorption of CBZ on MWCNTs and observed that after 24 h, around 91% of CBZ was adsorbed onto MWCNT (Oleszczuk et al., 2009). Likewise, Cai et al. reported 95% of removal efficiency for CBZ using graphene oxide powder after 24 h (Cai and Larese-Casanova, 2014). Adsorption property of biochar is dominated by biochar surface chemical composition and physicochemical properties which in turn is affected by the pyrolysis conditions (Pintor et al., 2012; Tan et al., 2015). For mass transfer rate during adsorption, several properties including pore structure, pore size and surface affinity toward target compound play key role and therefore rapid equilibration of CBZ adsorption on nanobiochar compared to commercial adsorbents indicates its superior physicochemical properties to be a promising adsorbent.

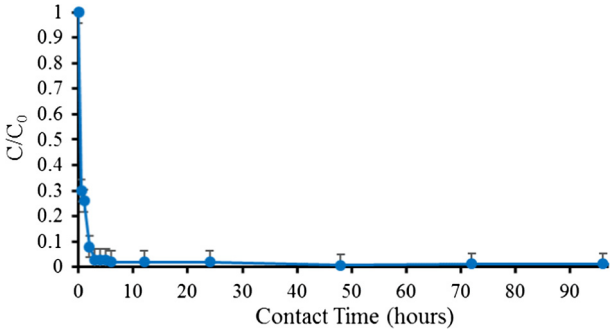

Figure 1 Aqueous concentration profile of carbamazepine with time (C_0 = 5 ng/mL, 0.25 mg/mL nanobiochar, 25 °C, pH 6 and 150 rpm).

3.2. Isotherm analysis

The isotherm tests were performed to obtain equilibrium concentrations of CBZ in aqueous media that were in contact with nanobiochar. The results showed that nanobiochar can remove 70–99% (56–79 μg CBZ/g nanobiochar) of CBZ from aqueous media. Three known isotherm models (Table 4), namely Freundlich, Langmuir and partition-adsorption were examined in their linear and nonlinear forms to fit the experimental data obtained in isotherms tests and their linearized forms are shown in Fig. 2. The calculated fitting parameters are listed in Table 4 and accordingly, Freundlich model in its linear and nonlinear forms showed the best correlation coefficients ($R^2 > 0.98$) with experimental data. In Freundlich model, K_f is an approximate indicator of adsorption capacity and $1/n$ is heterogeneity parameter. Since the value of the exponent n was greater than 1 for nanobiochar, it indicated favorable adsorption with little heterogeneity and major contribution of physical binding forces (Dada et al., 2012; Cheng et al., 2013). The results obtained for adsorption energy of CBZ on nanobiochar in Section 3.3 confirmed physical adsorption.

Dickenson et al. studied the adsorption of CBZ to powdered activated carbon and fitted the data with Freundlich isotherm model (Dickenson and Drewes, 2010). Also, Yu et al. used the Freundlich, Langmuir and three-parameter Langmuir–Freundlich (LF) models to evaluate the behavior of granulated activated carbon samples for the adsorption of CBZ from water and observed that Freundlich offered better fit for experimental data (Yu et al., 2008). Likewise, Cai et al. examined Freundlich, Langmuir, and PMM isotherm models for adsorption of CBZ onto graphene oxide powder, granular activated carbon, and carbon nanotubes and observed better fit with Freundlich isotherm (Cai and Larese-Casanova, 2014).

3.3. Kinetic studies

Kinetics of adsorption is important for understanding of contaminants removal, since it gives information on the transport mechanisms between two phases. In Fig. 3, the obtained data from kinetic tests were plotted in linearized forms of three common kinetics models, namely pseudo first-order, pseudo second-order and intra-particle diffusion models. CBZ molecules were adsorbed very rapidly during the early time interval (71% within 30 min) that can be attributed to the small size of particles and the presence of a large number of free adsorption

Table 4 Isotherm parameters estimated using three different models (p-value < 0.05).

Langmuir model			Freundlich model			Partition-adsorption model			
Q^0 (ng/mg)	K_L (ng/L)	R^2	K_f (ng/mg)(L/ng)$^{1/n}$	$1/n$	R^2	Q^0 (ng/mg)	K_L (ng/L)	K_P (L/mg)	R^2
Linear regression									
40	521	0.968	0.082	0.914	0.982	36	461	282	0.970
Nonlinear regression									
116	1440	0.889	0.068	0.963	0.985	1.06	10.2	0.049	0.976

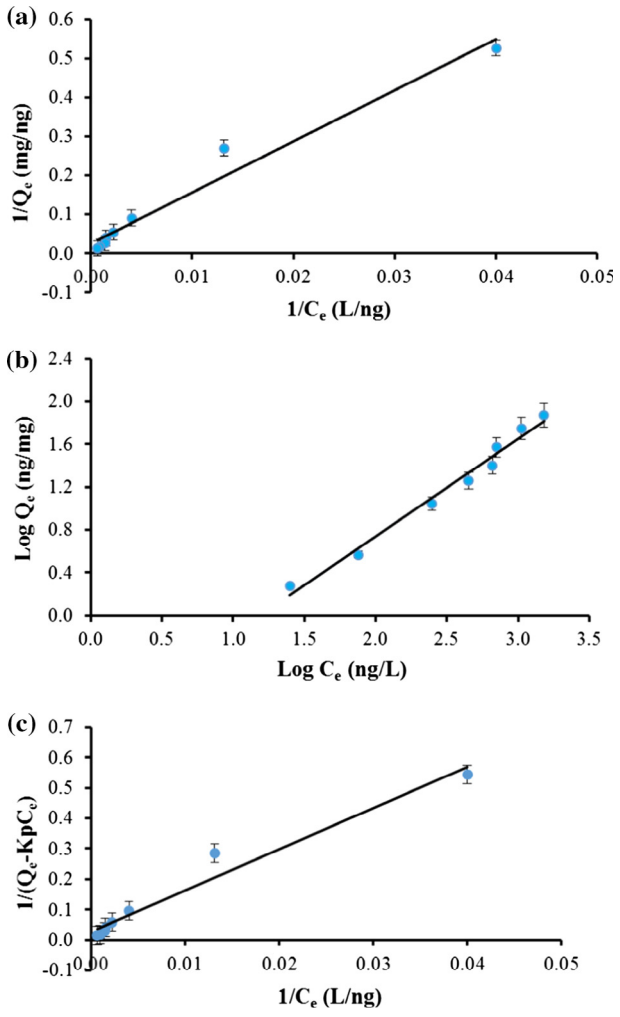

Figure 2 (a) Linearized Langmuir isotherm; (b) Linearized Freundlich isotherm and; (c) Partition-adsorption model for carbamazepine adsorption on nanobiochar (C_0 = 0.5–20 ng/mL, 0.25 mg/mL nanobiochar, 25 °C, pH 6 and 150 rpm).

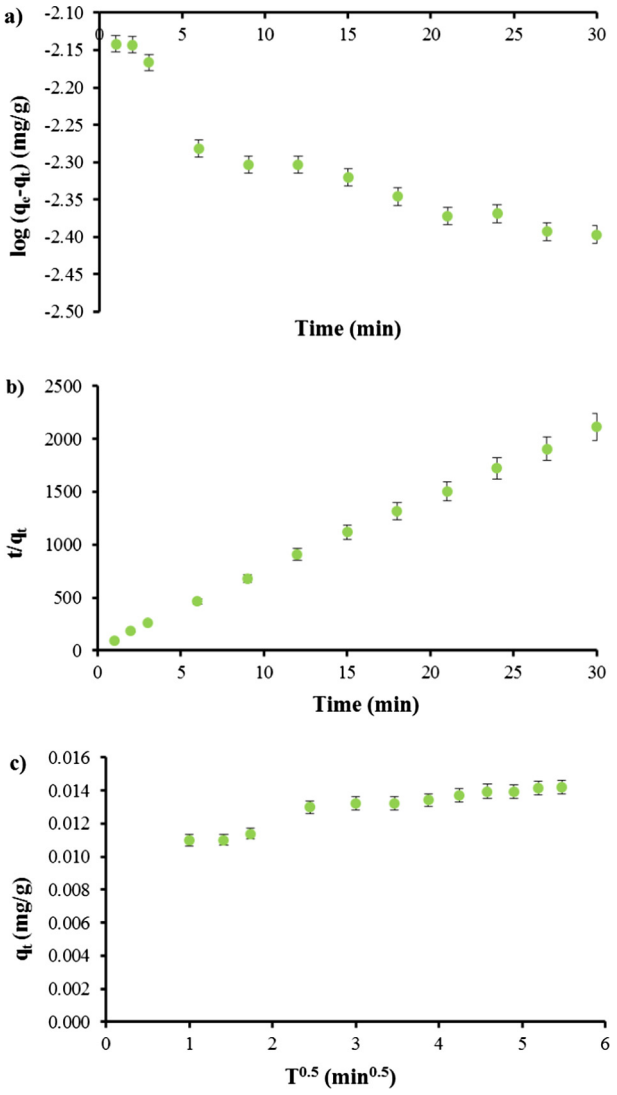

Figure 3 Fitting of three kinetic models: (a) pseudo-first order, (b) pseudo-second order, and (c) intra-particle diffusion model (C_0 = 5 ng/ml; 0.01 mg/mL nanobiochar; time = 30 min; pH = 6; T = 25 °C and 150 rpm).

sites. Zhao et al. reported similar rapid initial adsorption of CBZ on MWCNTs (74% within 30 min) and attributed to the fast mass transfer into the boundary layers near surface of carbon nanotubes (Zhao et al., 2016). In Table 5, the fitting parameters and related R^2 for different models in linear and nonlinear form are listed. Based on the fitting parameters, pseudo first-order kinetic model in its linear and nonlinear forms was the least probable model (R^2 < 0.85) which indicated that adsorption capacity could not be the major factor dominating the adsorption mechanisms of CBZ on nanobiochar (Jung, 2014). Similarly, the intra-particle kinetic models (Table 3, Equation 7) in which adsorption rate is proportional to square root of time did not fit well into the experimental data (R^2 < 0.910). Also, two other models including liquid film diffusion and second order were tested and the obtained R^2 were less than 0.8 (data not shown). On the other hand, pseudo second-order equation with R^2 = 0.999 in its linear form and R^2 = 0.946 in its nonlinear form fitted the experimental data very well. However, the experimental *qe* was 18.4 mg/g while the calculated *qe* for nonlinear pseudo-second order and linear pseudo-second order were 1.39 and 14.05 mg/g, respectively which confirmed better fitting of linear pseudo-second order kinetic model for CBZ adsorption. Although pseudo-second indicated that the adsorption kinetics may be dominated by chemisorption (Ho and McKay, 1999) employing equations 9, 10 and 11 rejected this possibility since the mean free energy (E) of CBZ adsorption on nanobiochar was calculated to be 5.5 kJ/mol which is consistent with physiosorption processes (Dada et al., 2012).

3.4. Effects of different parameters on CBZ adsorption on nanobiochar

3.4.1. pH

The effects of variation of pH on adsorption of CBZ on nanobiochar are presented in Fig. 5. The adsorption efficiency of CBZ was enhanced as pH increased from 3 to 6 and from 6 to 8 the effect of pH was insignificant. The solubility, ionization and hydrophilicity of many organic chemicals are

Table 5 Kinetic parameters for Lagergren and intra-particle diffusion models (p-value <0.05).

Pseudo first-order			Pseudo second-order			Intra-particle diffusion	
k_1 (h^{-1})	qe (μg/g)	R^2	k_2 (g/mg min)	qe (μg/g)	R^2	K (mg/g $h^{0.5}$)	R^2
Linear regression							
1.202	6.7	0.856	95.21	14.05	0.999	0.048	0.910
Nonlinear regression							
79.8	13.4	0.759	1.85	1.39	0.946	0.18	0.906

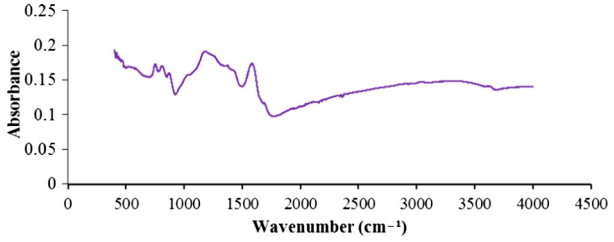

Figure 4 FTIR spectrum of produced nanobiochar.

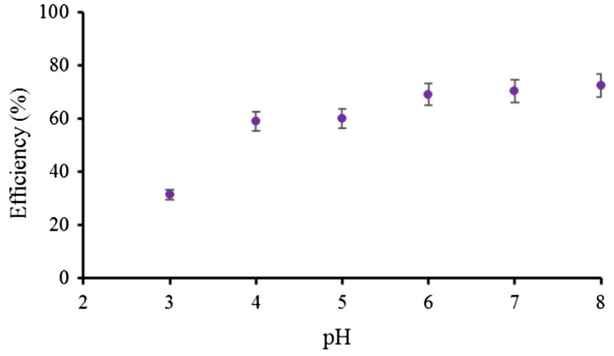

Figure 5 Effect of pH on adsorption efficiency of carbamazepine on nanobiochar (C_0 = 10 ng/mL, 0.5 mg/mL nanobiochar, 25 °C and 150 rpm).

increased by pH and therefore lowered adsorption on carbonaceous materials is expected. However, CBZ is a neutral compound in the whole pH range and its adsorption behavior is different from ionizable compounds which can be affected by electrostatic forces (Zhao et al., 2016). The NH_2 functional group in CBZ can interact with oxygen-containing functional groups of nanobiochar, such as OH and C═O through hydrogen bonding (Teixidó et al., 2011). In the FTIR spectrum of nanobiochar (Fig. 4), the significant bands at 3324 cm^{-1} (alcohol, O─H stretching) and 1185 cm^{-1} (phenolic, C─O stretching) confirmed the presence of oxygen-containing groups in nanobiochar.

Variation of solution pH may affect the properties of these functional groups on both adsorbate and adsorbent (Wu et al., 2012). At lower pH value, functional groups on nanobiochar and CBZ can interact with H^+ more easily due to the abundance of H^+ in the solution that decreases hydrogen bonding between nanobiochar and CBZ and consequently decreases adsorption efficiency. In contrast, as concentration of H^+ is reduced at higher pH levels, hydrogen bonding donor groups on CBZ can interact with hydrogen bonding acceptors or Π-donors in nanobiochar and therefore the adsorption efficiency is expected to be enhanced (Zhao et al., 2016; Yang et al., 2012; Lu and Su, 2007; Peng et al., 2012).

3.4.2. Rotational speed

Adsorption of CBZ at different rotational speeds (90–240 rpm) was studied and the results are presented in Fig. 6. CBZ adsorption was increased from 29% to 67% while increasing the rotational speed of the shaker from 90 rpm to 210 rpm and further increase in rotational speed did not show any considerable changes in adsorption efficiency. Walker et al. and Zarra suggested that increasing agitation rate can increase the magnitude of the external mass transfer coefficient (Walker et al., 2003; Zarraa, 1995). Per mass transfer principles, there is thin layer of fluid at the immediate vicinity of adsorbent surface where the viscous forces resist against fluid movement and play a key role in impeding mass transfer. Since the adsorbate molecules should pass through this layer to reach adsorbent surface, the thinner boundary layer results in higher rate of mass transfer. The thickness of boundary layer is inversely proportional to the square of water velocity (Srivastava et al., 2011) and therefore the enhancement of adsorption efficiency by rotational speed can be attributed to the increasing mass transfer rate as a result of reduction in resistance of surface film (Saruchi et al., 2016).

3.4.3. Adsorbent dose

The effect of adsorbent dose on removal of CBZ through adsorption on nanobiochar is illustrated in Fig. 7. Based on the results, removal efficiency of CBZ increased from 53% to 87% when the adsorbent dose of solution was increased from 200 mg/L to 1000 mg/L. Increasing adsorbent dose is equal to increasing surface and the number of adsorption sites, which enhances the collision frequency of target compounds with

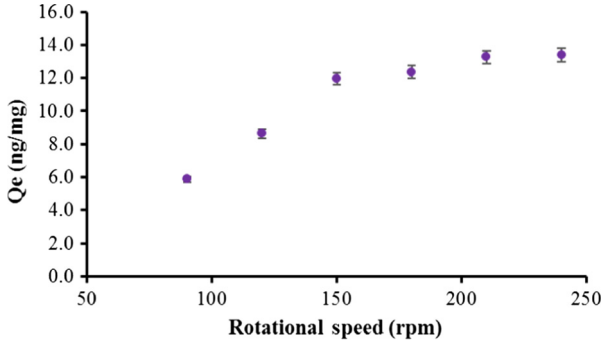

Figure 6 Effect of rotational speed on adsorption of carbamazepine on nanobiochar (C_0 = 10 ng/mL, 0.5 mg/mL nanobiochar, 25 °C and pH 6).

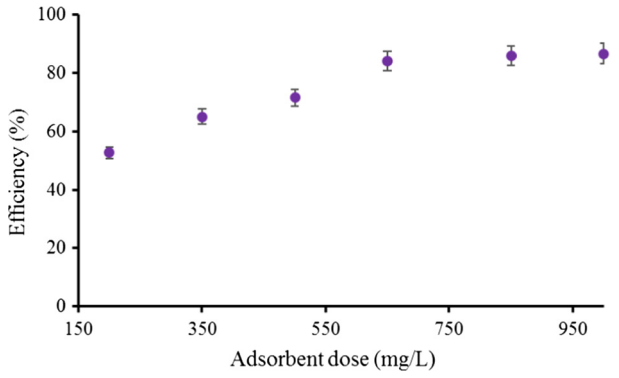

Figure 7 Effect of adsorbent dose on adsorption of carbamazepine (C_0 = 10 ng/mL, 25 °C, pH 6 and 150 rpm).

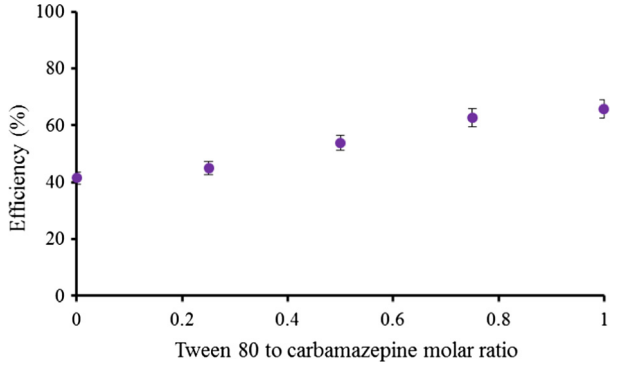

Figure 8 Effect of surfactant concentration on adsorption of carbamazepine (C_0 = 10 ng/mL, 0.5 mg/mL nanobiochar, 25 °C, pH 6 and 150 rpm).

adsorbent and consequently results in a higher removal of CBZ (Amarasinghe and Williams, 2007). However, after a certain dose, further increase in adsorbent dose did not show any improvement which can be due to the overlapping of adsorption sites and also possibility of particle aggregation (Garg et al., 2003).

3.4.4. Surfactant concentration

Surfactants are widely used in daily life products, such as detergents and food stabilizers. They find their way into wastewater and due to their amphiphilic properties, they can affect the removal of micropollutants through adsorptive systems (Kibbey and Hayes, 1993; Shiau et al., 1995). In this work, the effect of addition of a widely-used surfactant (Tween 80) on adsorption of CBZ on nanobiochar was investigated and the results are illustrated in Fig. 8. It was found that with increasing Tween 80 to CBZ molar ratio from 0 to 1, the adsorption efficiency increased from 42% to 66%. It is in agreement with the results of Hari et al. who related this enhancement to the strong affinity of compounds for adsorbed surfactant aggregates (Hari et al., 2005). Also, there is another report on improvement of CBZ adsorption onto modified zeolite with surfactant (Cabrera-Lafaurie et al., 2014).

Tween 80 is a nonionic surfactant which in comparison with its ionic counterparts is less sensitive to the widely found divalent cations in water and wastewater (Stellner and Scamehorn, 1989). Each molecule of Tween 80 has several hydrophilic functional groups and one hydrophobic tail and therefore it can link carbamazepine to nanobiochar. The possible interactions between CBZ, nanobiochar and Tween 80 are illustrated in Fig. 9. Oxygen and nitrogen in amide group of CBZ can form a hydrogen bonding with the hydrophilic head of Tween 80 and its hydrophobic tail can enter a hydrophobic interaction with graphite-like structure of nanobiochar.

4. Conclusions

CBZ is a pharmaceutically active compound present in water sources at very low concentration (up to several μg/L) and its removal is difficult through conventional water treatment technologies in water and wastewater treatment plants. In this paper, removal of CBZ at environmentally relevant concentration range (0.5–20 ppb) was studied through adsorption on as-produced pinewood nanobiochar that can be obtained from low-cost resources using a green production technique. The results showed that nanobiochar can remove up to 74% and 95% of CBZ after 1 and 6 h contact time, respectively. It indicated that nanobiochar has a faster adsorption compared to other carbonaceous materials, such as activated carbons, carbon nanotubes and graphene oxides. Among examined isotherms and kinetic models, adsorption of CBZ on nanobiochar showed better fitting parameters with Freundlich isotherm model (R^2 = 0.9822) and pseudo-second order kinetic model (R^2 = 0.9994). Calculation of adsorption energy showed that adsorption of CBZ on nanobiochar is a physical process. Increasing pH from 3 to 6 enhanced the adsorption efficiency by 2.3 folds. The addition of Tween 80 as a model surfactant was studied in the range of 0–1 (Tween 80 to CBZ molar ratio) and the results

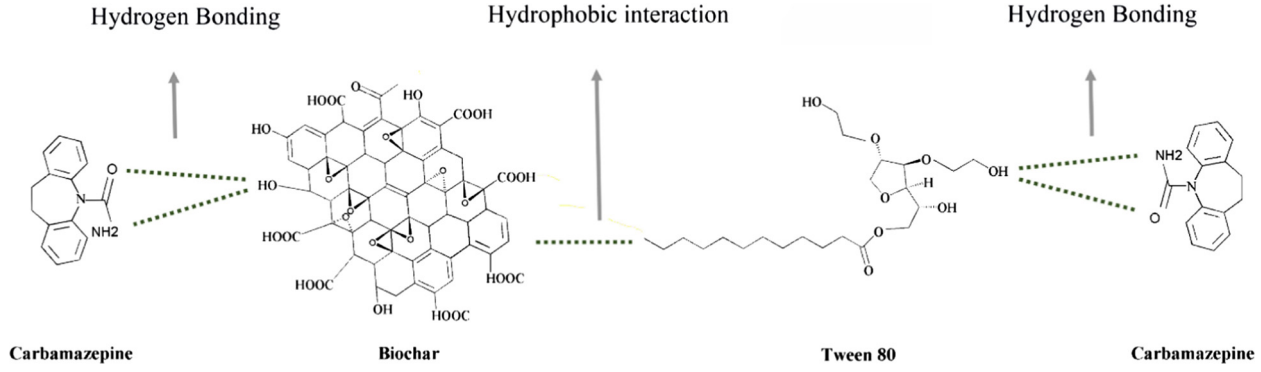

Figure 9 Illustration of possible interaction between Tween 80, nanobiochar and carbamazepine.

showed that adsorption efficiency can be enhanced by 57%. It indicated that nanobiochar can have better performance in wastewater containing surfactants. Thus, nanobiochar can be a promising adsorbent for removal of micropollutants from aqueous media and compete with conventional activated carbon filters in terms of production cost, equilibration time and environmental friendliness.

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