Renewable Material-derived Biochars for the Efficient Removal of 2,4-Dichlorophen from Aqueous Solution: Adsorption/Desorption Mechanisms

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This study investigated the efficiency of peanut hull (PBC), bush branch (BBC), *Spartina alterniflora* (SBC), and rape straw (RBC) in removing 2,4-dichlorophen (2,4-DCP) from an aqueous solution. The 2,4-DCP removal efficiency of the four kinds of biochars (BCs) increased in the order BBC > PBC > SBC > RBC. The adsorption process was affected by the pH, contact time, temperature, BC's particle size, and dosage. Based on the results of Fourier transform infrared spectrometry (FTIR) and scanning electron microscope (SEM), the adsorption mechanism of 2,4-DCP was associated with the functional groups and the microtissue and structure of BCs. Furthermore, the organic components of the BCs played an essential role during the adsorption process of the 2,4-DCP. The remediation of organic pollutants by BCs is a complicated process that is characterized by the physical-chemical reaction between the two components (organic pollutants and BCs).

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INTRODUCTION

Chlorophenols (*e.g.* 4-chlorophenol, 2,4-dichlorophen, 2,4,6-trichlorophenol) are organochlorides of phenol that contain an aromatic structure bonded with one or more chlorine atoms. They are widely used as intermediates in manufacturing insecticides, papers, print-dyes, and pharmaceuticals (Rashid *et al.* 2014). Among chlorophenols, the 2,4-dichlorophen (2,4-DCP) is considered a priority pollutant (Li *et al.* 2011). It is extensively used to control insects and weeds globally (Peng *et al.* 2016). The excessive use of chlorophenols leads to the pollution of surface water, underground water, air, and agricultural fields (Shih *et al.* 2012; Xiao *et al.* 2016). Vlastos *et al.* (2016) reported that 2-chlorophenol (only one Cl element) with the concentrations up to 1 μg mL^{-1} could cause chronic toxicity to microbes and fish. Chlorophenols also produce unpleasant and excitant odors; they are potentially carcinogenic and mutagenic that induce a negative impact on the human health (Wang *et al.* 2014).

Due to its toxic effects, which harm public health and the environment, various technologies have been reported for the degradation of chlorophenols in soil or removal from the effluent, such as adsorption (Devi and Saroha 2014), membrane filtration (Du *et al.* 2013), and bioremediation (Dos Reis *et al.* 2013). Among the remediation technologies, adsorption is an efficient, cost-effective, and simple process for the removal of the organic pollutants from the wastewater (Devi and Saroha 2014).

Biochar (BC) is a stable and environmentally friendly carbonaceous material that has attracted broad attention in recent years for its adsorption properties to remediate various contaminants (Lehmann 2007; Ahmad *et al.* 2014). Biochar prepared from agricultural wastes through pyrolysis is a potentially attractive adsorbent for the organic pollution control because of its high sorptivity, rich carbon source, small ecological risk, and minimal secondary contamination (Lehmann *et al*. 2011; Lou *et al.* 2011). The BC contains various functional groups and microcellular structures, which enhances its efficiency to remove and remediate various organic and inorganic pollutants (Lou *et al.* 2012; Cui *et al.* 2016). Many studies have reported that biochar is an efficient adsorbent for the remediation of various organic pollutants, such as phenol (Liu and Zhang 2011), 4-chlorophenol (Shih *et al.* 2012), and polycyclic aromatic hydrocarbons (Oleszczuk *et al.* 2012). Devi and Saroha (2015) reported that modified biochar was efficient to adsorb pentachlorophenol (PCP) from water. The modified biochar simultaneously degraded PCP by dechlorination (Devi and Saroha 2015). Oh and Seo (2016) reported that bio-solid derived biochar had maximum adsorption capacity (34.4 mg g^{-1}) for 2,4-DCP in an aqueous solution compared to other biochars (rice straw, oak tree leaves, corn stalks, and coffee grounds). However, very limited knowledge is available regarding the potential of plant biomass derived biochars with varying physico-chemical properties to remove the 2,4-DCP from an aqueous solution. Hence, this study was conducted to confirm the mechanism of different plant biomass derived biochars on the adsorption of 2,4-DCP in an aqueous solution. The variation in the surface and chemical characteristics of different biochars was also evaluated after the 2,4-DCP adsorption at different temperatures. Moreover, the impact of different factors (pH, temperature, biochar dosage, and reaction time) on the adsorption of 2,4-DCP onto biochar was estimated with different models.

EXPERIMENTAL

Materials

Four kinds of BCs were produced in the laboratory by pyrolyzing the raw materials peanut hull (PBC), bush branch along the road side (BBC), *Spartina alterniflora* from the sea coast of Yancheng, Country (SBC), and rape straw (RBC) at 450 °C in a vacuum tube furnace (NBD-O1200, Nobody Materials Science and Technology CO., LTD, Zhengzhou, China). The BCs were ground and separated into different particle sizes (0.15 mm to 2 mm) through a mesh sieve. The organic matter content, CEC, total N and P were determined according to procedures described by Lu (2000). The pH of each mixture of biochar and distilled water (1:10, W:V) was measured with the electrode method (Jindo *et al.* 2014). The specific surface area was determined using N$_2$ sorption isotherms (Zhang *et al.* 2011). The biochar materials were digested with HF, HNO$_3$, and HClO$_4$ (2:1:1, V:V:V) and K, Ca, Mg determined by using flame atomic absorption spectrophotometer (FAAS, TAS-986, Persee, China). The basic properties of BCs are presented in Table 1. The functional groups (*e.g.* –OH, C=O) were identified using a Fourier transform infrared spectrometer (Nexus-

670, Thermo Nicolet Corporation, Waltham, USA). The morphological structure and relative elemental composition of the BCs were observed by scanning electron microscopy and energy dispersive spectroscopy (SEM- EDS) (Quanta200, Field Electron and Ion Co., Hillsboro, USA). The degradation matter of 2,4-DCP was detected by Thermo Trace DSQ II Gas Chromatography-Mass Spectrometer (GC-MS) (TRACE 1310- ISQ, Thermo Fisher Scientific, Waltham, USA).

Table 1. Basic Properties of BCs

	pH (H_2O)	Organic Carbon (g kg⁻¹)	Surface Area (m² g⁻¹)	CEC (cmol kg⁻¹)	Total N (g kg⁻¹)	Total P (g kg⁻¹)	Total K (g kg⁻¹)	Total Ca (g kg⁻¹)	Total Mg (g kg⁻¹)
PBC	9.16	558.2	9.54	9.54	10.52	44.73	15.51	4.25	1.52
BBC	9.51	671.5	18.01	14.63	8.96	33.25	18.06	10.38	6.49
SBC	10.13	699.1	6.41	6.70	10.35	55.63	15.87	8.65	4.56
RBC	10.35	574.3	7.52	9.86	6.32	20.53	19.65	20.31	5.83

The 2,4-DCP was purchased from Sigma–Aldrich (Shanghai, China) with analytical purity ≥ 99%. The stock solution of 2,4-DCP (1000 mg L⁻¹) was prepared daily with pure water and its pH was adjusted with 0.1 mol L⁻¹ HCl or NaOH. The stock solution was kept in a refrigerator to prevent the degradation. The 2,4-DCP stock solution was further diluted to achieve the target concentration.

Methods

Sorption experiments

A series of batch experiments was performed in triplicates to evaluate the 2,4-DCP adsorption capacity of BCs. The 2,4-DCP adsorption concentrations were prepared from the stock solution with a range from 5 mg L⁻¹ to 160 mg L⁻¹. The biochar (0.1, 0.2, 0.4, 0.8 g 50 mL⁻¹) to solution ratios were adjusted to obtain 30% to 70% 2,4-DCP adsorption after reaching equilibrium. The BCs and 2,4-DCP solution were mixed in a 250-mL glass flask, and sealed with tape and shaken at 180 rpm for 0, 10, 30, 60, 120, 240, 480 min in a water bath at 25 °C, 35 °C, and 45 °C. The background electrolyte of the mixed solution was 0.01 mol L⁻¹ CaCl₂, and the pH (1, 3, 6, 8, and 10) was adjusted with 0.1 M NaOH and HCl (Lou *et al.* 2013). After reaching the equilibrium during the sorption experiment, the solution was filtered through a 0.22-μm nylon membrane. The 2,4-DCP concentrations were analyzed by high performance liquid chromatography (HPLC, Perkin Elmer Flexar-15, PerkinElmer Inc., Waltham, USA) with a UV detector equipped with a reverse phase column, 4.6 mm × 150 mm XDB-C18 column (Agilent Technologies Inc., Santa Clara, USA) (Shih *et al.* 2012; Lou *et al.* 2013).

In the desorption experiments, the 2,4-DCP loaded BCs were washed with distilled water three times to remove the surface 2,4-DCP. Then, 50 mL 0.01 mol L⁻¹ CaCl₂ was added to the 2,4-DCP loaded BCs and shaken for 16 h at 25 °C. After shaking the solution was filtered, and the 2,4-DCP concentration in the filtrate was measured as described above.

To evaluate the adsorption capacities of 2,4-DCP by the BCs, the Langmuir model was used to fit the experimental data. The Langmuir model was expressed as,

$$Q_e = C_e \times K \times X_{max} / (1 + C_e \times K) \tag{1}$$

where Q_e is the 2,4-DCP adsorption capacity (mg g^{-1}), C_e is the 2,4-DCP concentration after the equilibrium (mg L^{-1}), X_{max} is the maximum adsorption capacity (mg g^{-1}), and K is the adsorption equilibrium coefficient (Cui *et al.* 2013; Peng *et al.* 2016).

RESULTS AND DISCUSSION

FTIR of BCs

Fourier transform infrared spectrometry (FTIR) was employed to identify the functional groups that BCs contained before and after the 2,4-DCP adsorption (Fig. 1). The FTIR spectrum of BCs showed the various functional groups, such as −OH (3425 cm^{-1} to 3431 cm^{-1}), C-H (2924 cm^{-1} to 2922 cm^{-1}), aromatic rings C=C (1615 cm^{-1} to 1630 cm^{-1}), aliphatic C−O−C (1258 cm^{-1} to 1261 cm^{-1}), and C−OH (1418 cm^{-1} to 1439 cm^{-1}). Li *et al.* (2016) showed that the abundant functional groups on the surface of biochar were due to the carbonation process. The peaks changed slightly after the 2,4-DCP adsorption onto the BCs, which formed organic C−Cl stretching (704 cm^{-1} to 762 cm^{-1}). Similarly, the peak that appeared at 1383 cm^{-1} to 1449 cm^{-1} was a methylene stretching that linked to the C−C groups in the BCs. The FTIR results revealed that the different BCs had different functional groups, which could be attributed to the biochar species (Xiao *et al.* 2016). The biochar properties considerably affect the interactions between 2,4-DCP and the functional groups during the sorption process (Cui *et al.* 2016). Fang *et al.* (2015) found that the persistent free radicals (-OH) could be activated on carbonaceous materials, such as biochar, and that the oxygenated functional groups were key factors in the formation of persistent free radicals. Part of molecular substance in the biochar formed extra functional groups (as shown in the FTIR results) during the adsorption process, which provided more sites and improved the adsorption capacity of BCs (Lou *et al.* 2013).
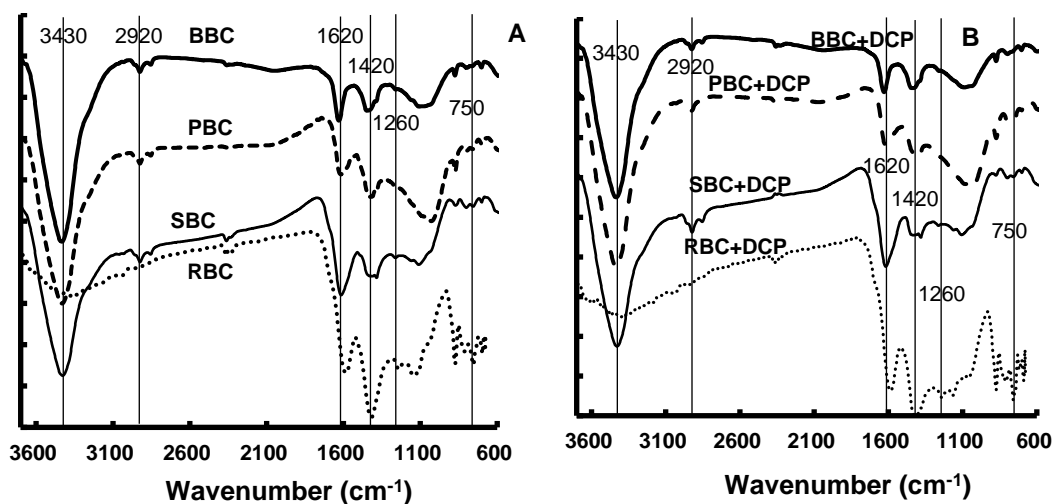

Fig. 1. FTIR spectra of BCs before (A) and after 2,4-DCP adsorption (B)

SEM-EDS of BCs

Map A is the SEM image of the BBC that shows the exterior surface containing various vessels. The EDS analysis further indicated that BBC contained relatively more C than Si element. Map B showed that the surface of peanut biochar was irregular and element distribution was like that of BBC. Moreover, the SBC map indicated relatively

abundant Si particles on its surface (high Si element peak) than other elements (Map D). The SEM-EDS analysis indicated that the BCs adsorption capacity was associated with the high percentage of C, O, and Si elements, which formed the micritic carbon structure and small nanopores (Bian *et al.* 2014).
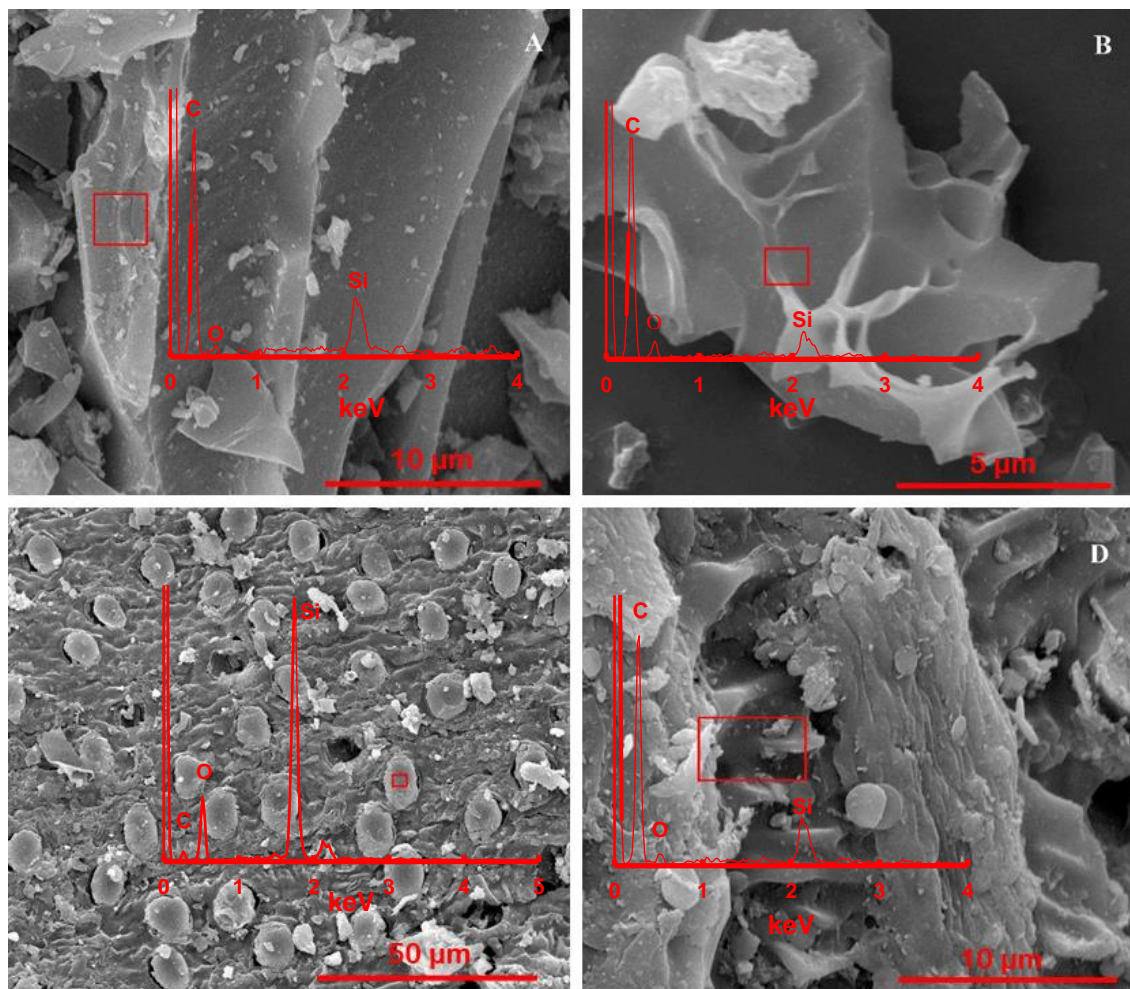

Fig. 2. SEM images of four kinds of BCs and the EDS elemental maps of the main elements in the red boxed area; (A, BBC; B, PBC; C, SBC; and D, RBC)

Effects of Solution's pH and BCs Dose/Particle Size

The 2,4-DCP adsorption was affected by various factors, such as the solution pH, BC's dosage, and BC's particle size. The solution pH was a key factor affecting the 2,4-DCP state and BC's surface and inner structure, such as electrostatic effects and π–π interactions (Peng *et al.* 2016). Wang *et al.* (2007) found that activated carbon was most efficient in removing the 2,4-DCP from water at pH 3 and concluded that an increase of electrostatic repulsion exists between activated carbon and dichlorophenate anions in solution at high pH. Kalderis *et al.* (2017) used different biochars materials for the removal of 2,4-DCP from aqueous media and found that the maximum adsorption percentage was achieved at pH 2. Similarly, in our study, all BCs were efficient in removing the 2,4-DCP, especially at the initial pH of 1 (Fig. 3 A). When the solution pH was higher than 6, the adsorption capacity decreased by 36.6% to 58.6% (BBC), 53.1% to 73.0% (PBC), 29.0% to 66.3% (SBC), and 38.5% to 93.7% (RBC) at pH of 6, 8, and 10 compared with pH 1

(Fig. 3 A). Overall, the 2,4-DCP adsorption capacity of BBC increased 31.3% to 94.0% compared to the other BCs. This negative correlation between 2,4-DCP adsorption and solution pH could be due to the reason that at very low pH, H_3O^+ ions surround the biochar surface, which promotes the interactions between the ionizable chlorophenols and the biochar surface (Wang *et al.* 2007). At elevated pH (> 7), it is possible that the negative charge of 2,4-DCP increases due to loses of H^+ and therefore reducing the adsorption due to repulsion phenomena of the anionic dichlorophenate (Müller *et al.* 1998; Cui *et al.* 2013). Moreover, the functional groups and adsorption sites of the BCs might have changed with increased solution pH and thus could have resulted in the decrease adsorption of BCs (Lou *et al.* 2011). At the same time, the water solubility of 2,4-DCP increases with high pH (pH > 7), which could exert a great environmental toxic effect (Vlastos *et al.* 2016).
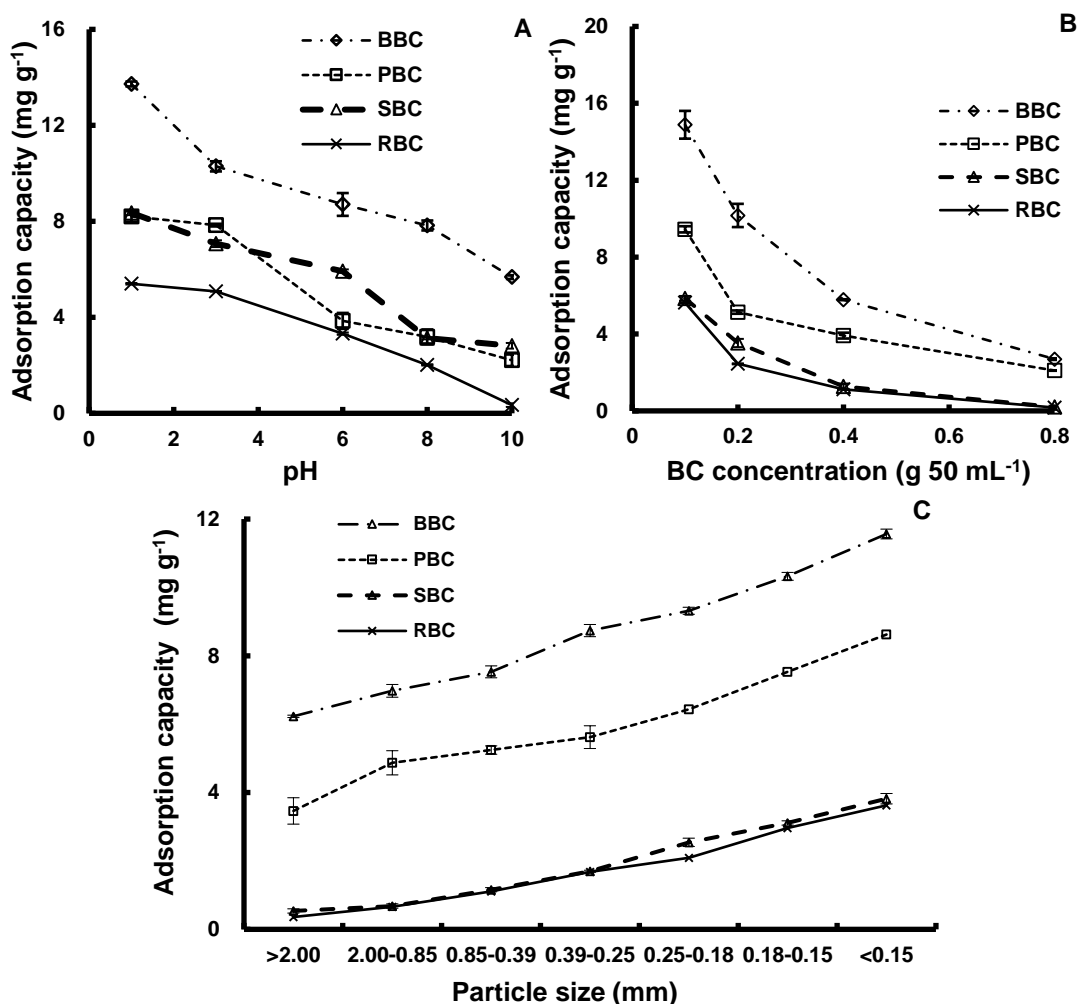
Fig. 3. Effect of pH (A), biochar dosage (B), and particle size (C) on 2,4-DCP adsorption capacities by four kinds of BCs (All data is shown as the mean ± standard deviation (SD))

The removal rate of 2,4-DCP increased by 37.8% to 92.5% with the increase in BCs dosage (except SBC and RBC) (Fig. 3B). Similar to our results, Ma *et al.* (2010) found that at adsorption equilibrium, 2,4-DCP removal (95.5% to 99.5%) increased with doses of bamboo charcoal. The increase in adsorption with the BCs dosage can be due to increased surface area and the availability of more adsorption sites. However, the decrease in

adsorption capacity of SBC and RBC with increased dosage could be due to the decrease number of 2,4-DCP molecules per adsorption site (Nguyen and Lee 2015). Moreover, once the dose of SBC and RBC exceeded 0.4 g 50 mL^{-1}, the pH of the mixed solution remarkably increased even at the low initial pH.

The BC's particle size was also found to be an important factor that affected the 2,4-DCP adsorption (Fig. 3 C). The adsorption capacity increased with the smaller BCs particle size. The 2,4-DCP adsorption increased by 10.7% to 90.1% with the particle size > 2 mm compared with the size < 0.15 mm for the four kinds of biochars. At the same particle size, the adsorption capacity of BBC and PBC was > 50% higher than SBC and RBC. The removal rate of 2,4-DCP increased with smaller biochar size particles, which provided the higher specific surface area and more adsorption sites (Lin *et al.* 2009).

Effects of Contact Time

The effects of the contact time on 2,4-DCP adsorption by four BCs are shown in Fig. 4.
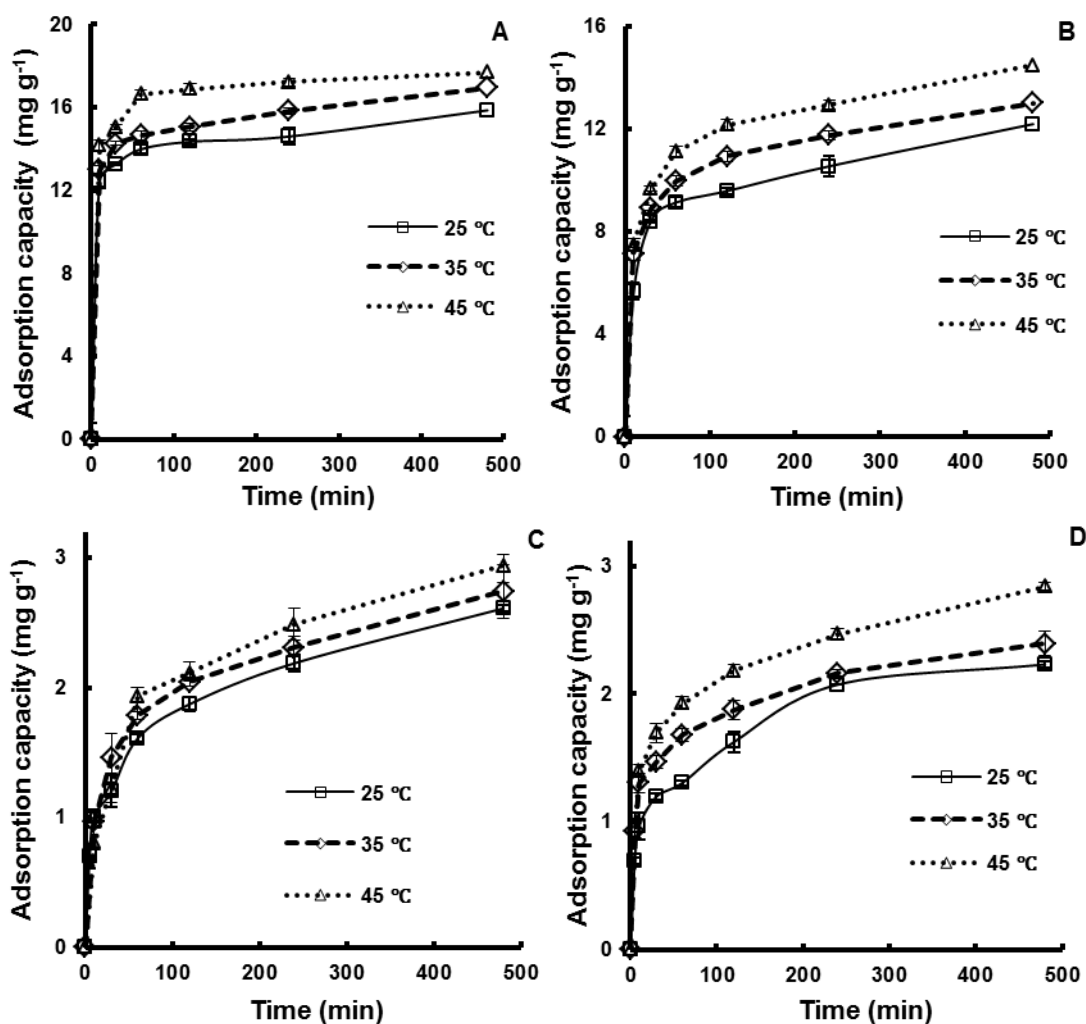
Fig. 4. Effect of contact time on 2,4-DCP adsorption capacities by BBC (A), PBC (B), SBC (C), and RBC (D)

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The 2,4-DCP adsorption capacities of BCs increased with the passage of time. Ma *et al.* (2010) reported that activated charcoal removed about 90% of 2,4-DCP from the solution within the first 5 min. As time increased above 5 min the adsorption capacity of the adsorbent increased slowly with the contact time and eventually reached equilibrium in less than 100 min. However, in the present study, the removal rate of 2,4-DCP was the fastest with BBC, and over 80% of 2,4-DCP was removed from solution within 10 min. The other three BCs showed a slower adsorption rate and nearly achieved equilibrium during the first 120 min. This is simply due to the reduction of driving force after a longer period of operation.

Adsorption Isotherms

The effect of four BCs on the adsorption isotherms of 2,4-DCP is shown in Fig. 5. The Langmuir model was employed to estimate the maximum adsorption capacity with the initial concentration in the range from 10 mg L^{-1} to 160 mg L^{-1}. The results showed that the maximum adsorption capacity was 24.48 mg g^{-1} (BBC), 23.42 mg g^{-1} (PBC), 18.46 mg g^{-1} (SBC), and 11.84 mg g^{-1} (RBC) at 45 °C.
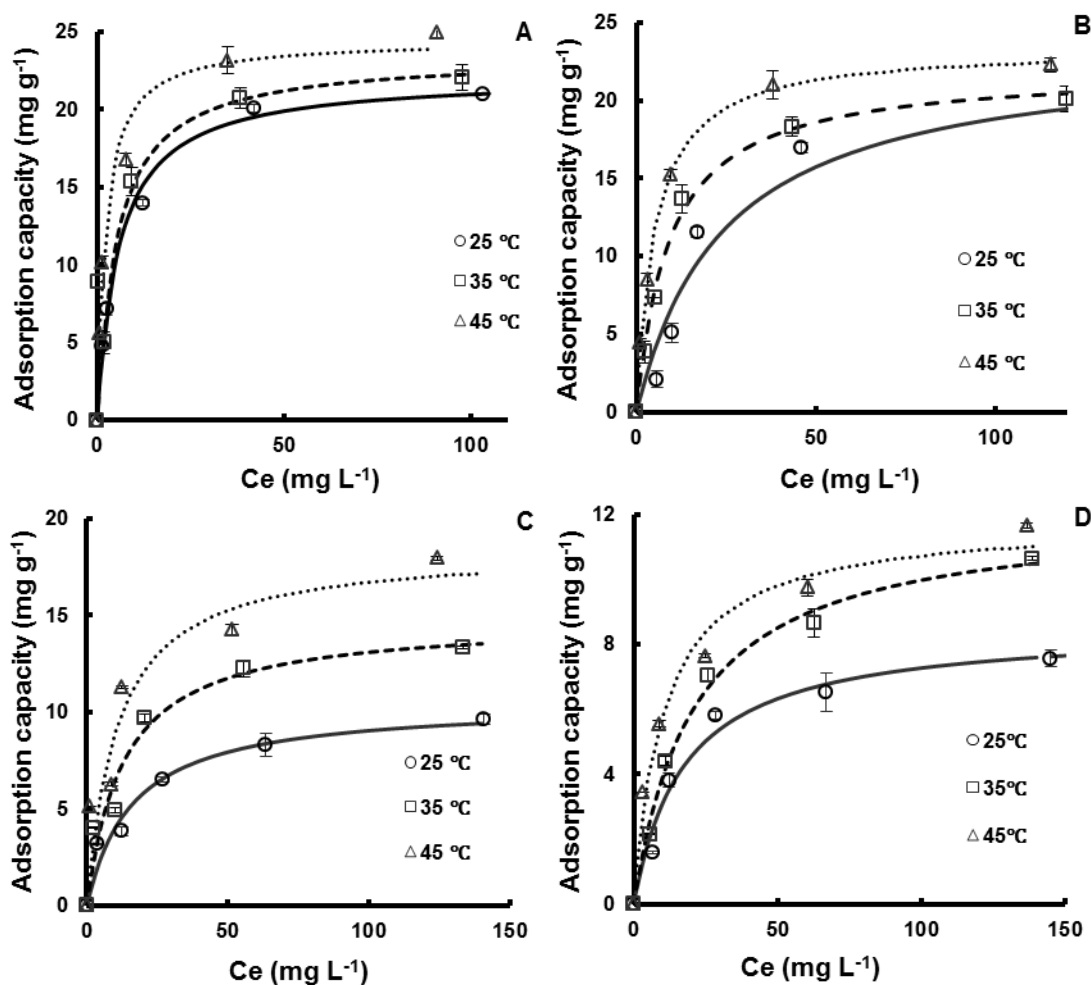

Fig. 5. Sorption isotherms of 2,4-DCP adsorption capacities by BBC (A), PBC (B), SBC (C), and RBC (D)

The K value from the equation (1) was substantially increased from 7.0% to 388.0% with the increase in temperature. The K values of BBC and PBC were much higher than RBC and SBC at 45 °C, which showed that the BBC and PBC had larger adsorption ability compared with RBC and SBC, and the surface area also proved this point (Table 1). Kalderis *et al.* (2017) found that the 2,4-DCP adsorption capacity at equilibrium (9.28 mg g^{-1}) of paper sludge/wheat husk biochar was highest compared with that of other biochars derived from different materials such wood chip, hog fuel/demolition wastes, and sewage sludge (1.57−2.96 mg g^{-1}). They concluded that π-electron donor-acceptor (non-covalent) and electrostatic interactions (pH-dependent) were primary mechanisms that played the most significant roles in the adsorption of 2,4-DCP onto biochars. BBC, which had the highest surface area, exhibited the maximum adsorption capacity for the 2,4-DCP. The surface area is closely linked to average pore size, and the very small size (0.482 nm) of 2,4-DCP molecule promoted the pore-filling process in the microporous biochar and resulted in the highest adsorption (Yang *et al.* 2016).

The organic components in the solution were analyzed by GC/MS after the biochar adsorption experiment (Fig. 6). The pyrograms of the GC-MS fingerprint of BCs adsorption was mainly attributable to that portion of 2,4-DCP that was not adsorbed. The other dominant components were of the mixture of benzene derivatives and low molecular weight organic matter, which came from the biochar or were produced from the interaction of 2,4-DCP and biochar. The different kinds of organic compound except the 2,4-DCP appeared in the solution, which could have been attributed to the enhanced effects of BCs (Ghidotti *et al.* 2017). Several low molecular weight organic compounds produced during the pyrolysis could also have been responsible for 2,4-DCP sorption by BCs (Buss *et al.* 2015).
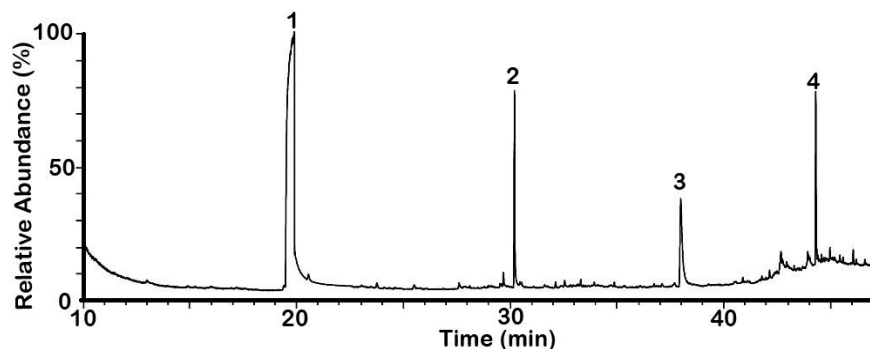
Fig. 6. GC/MS total ion chromatograms of solution after BCs adsorption; peak attribution: 1: 2,4-DCP; 2: 2, 6-Di-tert-butyl-4-methylphenol; 3: Dibutyl phthalate; and 4: 2, 2`-methylenebis (6-tert-butyl-4-methylphenol)

Thermodynamic Studies

The solution temperature was another important factor affecting the 2,4-DCP adsorption onto BCs. The BCs adsorption capacity of 2,4-DCP increased with increasing temperature, which provided enough energy for adsorption onto the BCs' interior structure and increased the reaction rate. The 2,4-DCP adsorption on the BCs was a spontaneous and endothermic reaction, which accelerated with increased temperature during the isotherm process (Cui *et al.* 2015). At the same time, the solution temperature affected the 2,4-DCP activity and heterogeneous BC's properties including the physico-chemical adsorption, rearrangement of the microcellular structure, and the interaction between the carbonized inorganic structural and non-carbonized organic functional groups (Zheng *et al.* 2010).
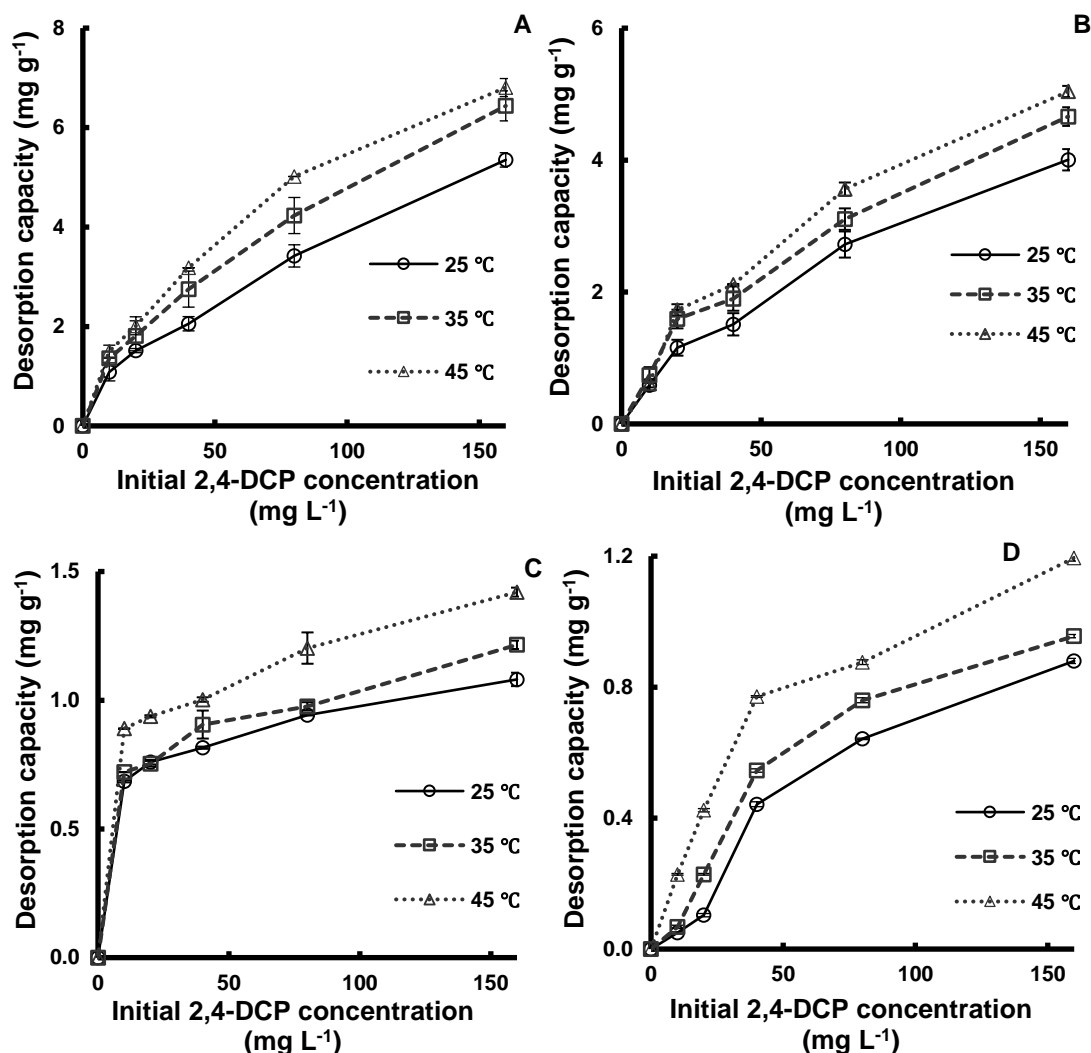
Fig. 7. Desorption of 2,4-DCP capacities by BBC (A), PBC (B), SBC (C), and RBC (D)

Effects of 2,4-DCP Desorption

The 2,4-DCP desorption rate is shown in Fig. 7. The 2,4-DCP desorption rate ranged from 13.0% to 27.8%. The desorption concentration of 2,4-DCP from biochar increased with high adsorption solution temperature. The more 2,4-DCP adsorption on BC, and more 2,4-DCP probability were easy elution down from BC. Over two-thirds proportion 2,4-DCP was firmly adsorbed on the BC and difficult to remove.

CONCLUSIONS

1. The 2,4-DCP was efficiently adsorbed by four kinds of BCs in the solution. The process of the adsorption was influenced by solution pH, contact time, temperature, BC's dose, and BC's particle size.

2. The adsorptions were mainly attributed to the physical-chemical interaction between 2,4-DCP and biochar.

3. The mechanism of 2,4-DCP adsorption on BCs involved the functional groups, amorphous carbon, silicon microcrystallite, and the complex microcellular nanostructure.

4. The biochar could be produced by various raw materials, which have a great potential for the remediation of organic pollutants.

ACKNOWLEDGMENTS

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