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# Production and use of biochar from buffalo-weed (*Ambrosia trifida* L.) for trichloroethylene removal from water

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# Abstract

BACKGROUND: Ambrosia trifida L. (buffalo-weed) is a ubiquitous invasive plant species in Korea, causing severe allergy problems to humans and reduction in crop yields. Converting buffalo-weed biomass to biochar and its use as an adsorbent for the depuration of trichloroethylene (TCE) contaminated water could help resolve two existing environmental issues simultaneously.

RESULTS: The plant biomass was converted to biochar at 300 °C (BC300) and 700 °C (BC700). The pyrolysis temperature strongly influenced the properties of resulting biochars. The higher temperature resulted in a higher degree of C-enrichment. The loss of H- and O-containing functional groups shifted the BC700 composition towards a less polar, more aromatic carbon structure evidenced by lower O/C (0.06) and H/C (0.15) values compared with those of BC300 (0.07 and 0.65, respectively). These properties of BC700 further highlighted its greater efficiency of TCE removal (88.47%) from water, compared with that of BC300 (69.07%). The TCE adsorption data was well described by the Hill isotherm model indicating the mechanism of adsorption to be cooperative interaction. Linear correlations between model parameters and biochar properties were also observed.

CONCLUSIONS: Buffalo-weed can be converted to value-added biochar that can be used as an effective adsorbent for the treatment of TCE contaminated groundwater. © 2013 Society of Chemical Industry

Keywords: invasive plant species; weed biomass; thermal decomposition; black carbon; biosorption; chlorinated hydrocarbon

# INTRODUCTION

Invasive plants are species that are non-native to an ecosystem resulting in adverse economic, environmental, and/or ecological effects.<sup>1</sup> Rapid growth rate, fewer natural predators, and strong survival ability are the salient characteristics of invasive plant species that can cause serious environmental damage such as loss of biodiversity, extinction of indigenous plant species, and the spread of human or animal diseases. Ambrosia trifida L., commonly known as buffalo-weed or raqweed, has been designated as one of the 11 most harmful invasive plants by the Ministry of Environment in Korea. It was introduced in Korea from North America in the 1970s and is now widely distributed throughout the country.<sup>2</sup> Buffalo-weed has been reported to cause reduction in crop yields in agricultural fields and severe allergy problems for humans.<sup>3</sup> Several strategic attempts have been undertaken to eradicate this noxious weed, however, there is currently no beneficial way of reusing the eradicated buffalo-weed biomass in a sustainable manner.

Biochar (BC) is a form of black carbon produced when biomass (BM) is pyrolyzed in a low/no oxygen environment.<sup>4</sup> Depending on initial feedstock and pyrolysis conditions, the quality of BC is highly variable. Slow pyrolysis of BM minimizes the risk of producing dioxins and other harmful polyaromatic hydrocarbons.<sup>5</sup>

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Therefore, the physical, chemical and biological properties of BCs tend to be influenced by the process variables, which in turn, determine the potential use of BCs. In recent years, BC has received a great deal of attention for a variety of applications including as an amendment for soil fertilization, a carbon sequestration approach, and an environmental control process for contaminant immobilization.<sup>6–10</sup> However, little information is available on using BC as a carbonaceous adsorbent for removing organic contaminants from water and wastewater, as well exploring the associated sorption mechanism.

Trichloroethylene (TCE) is the most frequently occurring chlorinated hydrocarbon in groundwater in industrial/urban areas around the world, and is classified as a priority pollutant by the US Environmental Protection Agency. In Korea, the groundwater of an industrial estate at Wonju city has recently been reported to be highly contaminated with TCE.<sup>11</sup> An estimated area of 300 000 m<sup>2</sup> in Wonju city was found to be contaminated with ~51 times the safety limit of 0.03 mg L<sup>-1</sup> proposed for TCE by the Ministry of Environment in Korea.<sup>12</sup> As a result of similar pollution incidents involving a host of other organic contaminants, appropriate, cost-effective, and environment friendly remediation techniques are continuously in demand.

Adsorption is the simplest, most effective and most widely used technology for TCE remediation, and activated carbon is the most commonly used adsorbent in this technology.<sup>13</sup> Recently, the high cost of activated carbon as well as the associated disadvantages of non-biodegradability and expensive regeneration has led researchers to explore alternative and more cost effective adsorbents. BC produced from buffalo-weed biomass may prove to be an alternative adsorbent because of its similarity to activated carbon in exhibiting a fairly structured carbon matrix and high surface area.

This study was aimed at reusing plant biomass originating from eradicated buffalo-weed by converting it to value-added BC in a slow pyrolysis process. The effect of temperature on BC production and its resulting characteristics were evaluated in batch adsorption experiments where the BCs produced were tested for their effectiveness in removing TCE from groundwater. This approach manages to use an invasive species biomass as a renewable material resource to address remediation of organocarbon contamination thus addressing two existing environmental issues simultaneously, enabling an integrated sustainable outcome.

# **EXPERIMENTAL**

# **Biochar production**

Buffalo-weed plants were collected from Namyangju city in Gyeonggi province, Korea. The plant shoots were dried, first under the sun for 1 week, and subsequently in a fan-forced oven at 60 °C for 24 h. The dried shoots were crushed and ground to <1.0 mm particle size. Portions of this BM were pyrolyzed at two temperatures, namely 300 and 700 °C in a muffle furnace (MF 21GS, Jeio Tech, Korea) under a limited supply of air. To achieve slow pyrolysis, BM was heated to the desired temperature at the rate of 7 °C min<sup>-1</sup>. For the complete carbonization of BM, a holding time of 3 h was applied for each peak temperature. The BCs produced at 300 and 700 °C were allowed to cool inside the furnace overnight, and are hereinafter referred to as BC300 and BC700, respectively. From a practical application standpoint, no pre- or post-treatments of BM or BC were performed in order to minimize the cost of the product. The production yield of the pyrolyzed BC was determined as a mass fraction of the initial BM.

## **BM and BC characterization**

Moisture contents of BM and BCs were measured by heating the samples at 105 °C for 24 h in a convection oven. Determination of the mobile matter was made by heating samples in covered crucibles in a furnace operating at 450 °C for 1 h. The ash content was measured by heating the samples in open-top crucibles at 750 °C for 1 h. Resident matter was finally calculated from ash, mobile matter and moisture contents. The elemental composition (C, H, N, and O) of BM and BCs was determined by an elemental analyzer (Flash EA 1112 series, CE Instruments, UK). Molar H/C and O/C ratios were also calculated from the elemental analysis. Specific surface area, pore volume and pore diameter were determined using an adsorption apparatus (Micromeritics, ASAP 2010 v 5.02 H, USA).

Spectral characteristics of BM and BCs were examined by Fourier transform infrared spectroscopy (FT-IR) (Bio-Rad Excalibur 3000MX spectrophotometer, Hercules, CA, USA). The Essential FT-IR software (v 2.00.045) was used for baseline correction and normalization of the absorption intensities of the FT-IR spectra.

#### **Sorption experiments**

To evaluate the effectiveness of BCs produced at different pyrolytic temperatures in comparison with BM, batch sorption experiments were performed. TCE contaminated water was prepared by dissolving reagent grade TCE (99% purity; Wako Pure Chemical Industries, Osaka, Japan) in ultrapure water (Arium Pro UV/DI Water Purification System; Sartorius Stedium Biotech, Goettingen, Germany). The initial concentration of TCE solution was set to  $20 \text{ mg L}^{-1}$ . The ultrapure water was buffered at pH7 with 0.5 mmol L<sup>-1</sup> Na<sub>2</sub>HPO<sub>4</sub>.H<sub>2</sub>O and 0.5 mmol L<sup>-1</sup> NaH<sub>2</sub>PO<sub>4</sub> prior to TCE addition, to reduce the impact of pH induced by the sorbents on TCE adsorption.<sup>14</sup> Incremental adsorbent loading weight from 0 to 1.2 g L<sup>-1</sup> was applied to TCE solutions in Teflon-lined screwcapped glass vials. There was no free head space in the vials to reduce the volatilization loss of TCE. Three replicates of each sorbent (BM or BC300 and BC700) were performed. A control, without any sorbent, was also determined in triplicate. The vials were shaken on a mechanical shaker at 50 rpm for 48 h at 25 °C, after which an aliquot of TCE solution from each vial was filtered through a 0.45 µm pore size syringe filter for aqueous phase TCE analysis. A high performance liquid chromatograph (HPLC) (SCL-10A, Shimadzu, Japan) equipped with an autosampler (SIL-10 AD; Shimadzu, Japan) and UV-VIS detector (SPD-10A; Shimadzu, Japan) was used for TCE analysis.

The removal percentage of TCE from water was calculated using Equation (1):  $^{15}\,$ 

% TCE removed = 
$$\left[ \left( C_0 - C_e \right) / C_0 \right] \times 100$$
 (1)

where  $C_0$  and  $C_e$  are the initial and equilibrium aqueous phase concentrations of TCE in mg L<sup>-1</sup>.

The amount of TCE adsorbed onto the sorbents was calculated as a function of the TCE concentration remaining in solution at equilibrium by following Equation (2):<sup>16</sup>

$$Q_e = [(C_0 - C_e)] \times V/M$$
<sup>(2)</sup>

where  $Q_e$  is the solid phase TCE equilibrium concentration in mg  $g^{-1}$ ; V is the volume of TCE solution in L; and M is the sorbent mass in g.

## Freundlich isotherm model

In this study, one of the most commonly used isotherm models, the Freundlich, was applied to the TCE adsorption experimental data. The sorption equilibrium was described by following the Freundlich Equation (3):<sup>17</sup>

$$\log Q_{e} = \log K_{f} + 1/n \log C_{e}$$
(3)

where  $K_f$  is the Freundlich constant representing adsorptive capacity in  $(mg g^{-1})/(mg L^{-1})^{-1/n}$ ; and n is a constant related to adsorption intensity.<sup>18</sup> Values of the constants  $K_f$  and n were determined by linear regression.

#### Hill isotherm model

Most organic contaminants are sorbed onto organic sorbate surfaces by a cooperative sorption mechanism, which is represented by the Hill isotherm Equation (4):<sup>19</sup>

$$Q_{e} = Q_{max} \left(K_{H}C_{e}\right)^{b} / \left[1 + \left(K_{H}C_{e}\right)^{b}\right]$$
(4)

where  $K_H$  is Hill constant,  $Q_{max}$  is the maximum adsorption capacity, and b is an empirical parameter which varies with the degree of heterogeneity.

#### Statistics

Mean values of three replicates were applied to calculate the TCE percentage removal and to determine the Freundlich and Hill adsorption isotherm parameters. Linear regression was used to plot the adsorption isotherms and to determine the correlation between sorbent properties and model parameters.

# **RESULTS AND DISCUSSION** BC characterization

#### Proximate and ultimate analyses

Table 1 presents the proximate and ultimate analyses results of buffalo-weed BM and the BCs derived at the two pyrolysis temperatures. The temperature strongly influenced BC yields and their properties. At 300 °C the BC yield was 50%, which was reduced to 29% at 700 °C. This decrease in the BC yield at high pyrolysis temperature is expected due to a greater loss of volatile matter at the higher temperature. Similar observations of the decrease in BC yield with increasing pyrolysis temperature have been reported by other studies<sup>20,21</sup> which emphasized that at the higher temperature of 700 °C, secondary decomposition of char produced at a lower temperature of 300 °C could occur, causing a further decrease in the BC yield. This was further supported by the greater loss in mobile matter at 700  $^{\circ}$ C (73%) compared with at 300 °C (42%) as indicated by 76.44, 44.22 and 20.88% mobile matter contents of BM, BC300 and BC700, respectively. High mobile matter in a material is indicative of high susceptibility towards biodegradation. BCs having sufficient mobile matter could improve the microbial activity in soils resulting in soil quality improvement.<sup>22</sup> In contrast to mobile matter, the resident matter, which indicates the fixed or non-biodegradable matter, increased in BCs. The increase was determined to account for 46.77% of BC700 compared with 30.42% of BC300 and 7.59% of BM. This suggested that compared with BM, BCs have higher fixed C **Table 1.** Proximate and ultimate analyses of buffalo-weed biomass (BM) and derived biochars at 300  $^\circ$ C (BC300) and 700  $^\circ$ C (BC700)

	BM	BC300	BC700
Proximate analysis			
Yield (%)	_	50.00	29.00
Moisture (%)	5.51	5.00	0.01
Mobile matter (%)	76.44	44.22	20.88
Resident matter (%)	7.59	30.42	46.77
Ash (%)	10.46	20.36	32.34
Ultimate analysis			
C (%)	66.55	78.09	84.96
H (%)	6.42	4.26	1.09
O (%)	15.84	7.44	6.56
N (%)	11.20	10.21	7.40
Molar H/C	1.15	0.65	0.15
Molar O/C	0.18	0.07	0.06
Surface area ( $m^2 g^{-1}$ )	6.30	3.98	9.25
Pore volume (cm <sup>3</sup> g <sup><math>-1</math></sup> )	0.01	0.01	0.02
Pore diameter (nm)	4.21	4.56	5.63

contents, making them more stable and possibly more useful in sequestering C. Ash contents were also increased from 10.46% in BM to 20.36% in BC300 and 32.34% in BC700, showing the resultant concentration of alkaline minerals and organic matter residues due to the removal of organics.<sup>23</sup>

Changes in the elemental composition of BM and BCs were observed with different pyrolysis temperatures. Total C contents of BCs increased with increasing temperature. A maximum of 27.66% increase in the C content of BC700 was observed. Depolymerization of cellulose in BM at 300 °C caused amorphous C to develop, while carbonization at 700 °C resulted in the further removal of non-C atoms and growth of graphene sheets.<sup>24</sup> The formation of graphene sheets in BC700 indicated a greater stability. Several other studies have also reported that BC produced at higher pyrolysis temperatures is more stable because of its condensed aromatic nature.<sup>3,25</sup> The H content was lowered in BC300 (4.26%) and BC700 (1.09%) compared with BM (6.42%), showing a maximum reduction of 83.02% in BC700 compared with BM, which is understandable due to the fact that H is primarily associated with plant organic matter.<sup>26</sup> The O content also decreased in BC300 (7.44%) and BC700 (6.56%) compared with BM (15.84%). This decrease in H and O contents with increasing pyrolysis temperature is attributed to the loss of water, hydrocarbons, H<sub>2</sub>, CO and CO<sub>2</sub>.<sup>27</sup> The N content was also lowered to 10.21% in BC300 and 7.40% in BC700 compared with 11.20% in BM. Decrease in N contents with increasing pyrolysis temperature has also been reported by several workers.<sup>28,29</sup>

Molar ratios of H/C and O/C have been reported to provide a reliable analysis of both the extent of pyrolysis and the level of oxidative alteration of BCs.<sup>30</sup> Molar H/C ratios, related to the degree of aromaticity, were found to be 1.15, 0.65 and 0.15 for BM, BC300 and BC700, respectively, indicating that higher pyrolysis temperatures imparted a higher aromaticity to BC700. Likewise, molar O/C ratios, related to the degree of maturity, were found to be 0.18, 0.07 and 0.06 for BM, BC300 and BC700, respectively, suggesting greater stability of BCs produced at high pyrolysis temperatures. Spokas<sup>31</sup> expected a half- life of 1000 years for BCs with an O/C ratio <2.0. Another aspect of molar O/C ratio is its relationship with polarity. Low O/C values suggest a lower degree of polarity, which implies that BC700 is less polar or more hydrophobic than BC300 and BM.

The pyrolysis temperature also affected the morphological properties of BCs, such as surface area, pore volume and pore diameter. However, the surface areas of BCs were unexpectedly lower than usual with an increasing trend with increasing pyrolysis temperature. At the higher temperature of 700 °C, BC700 exhibited a surface area of  $9.25 \text{ m}^2 \text{ g}^{-1}$ . The lower surface area may have resulted from the lack of pore size within hexagonal carbon layers, as indicated by high pore diameter of BCs (>4 nm). It has been widely described that surface area is primarily related to micropores (<2 nm) rather than mesopores (2 – 50 nm), which were abundant in BCs derived from buffalo-weed.<sup>32</sup>

#### Spectral characteristics

Changes in essential functional groups of BCs were estimated by FT-IR spectroscopy. The FT-IR spectra of BM, BC300 and BC700 are shown in Fig. 1. The peak assignments are based on those of Coates.<sup>33</sup> The band observed at 3360 cm<sup>-1</sup> in BM corresponds to the stretching vibration of -OH group showing the presence of bonded water. The band intensity is markedly reduced in BC300 and BC700 (Fig. 1(b)) indicating removal of water molecules as a result of heating. The bands at 2920 and 2850 cm<sup>-1</sup> are assigned to -CH<sub>2</sub> stretching vibration suggesting the presence of long linear aliphatic groups in BM, which are reduced in BC300 and even disappear in BC700. This suggests the removal of polar functional groups from BCs.<sup>34</sup> The broad peak at 1504–1630 cm<sup>-1</sup> is related to the lignin content of BM. Reduction of this peak in BC300 and its disappearance in BC700 suggests the loss of the original plant structure of buffalo-weed. Specifically, the band at 1650 cm<sup>-1</sup> in BM corresponds to an amine NH group, which is reduced in BC300 and BC700 during pyrolysis. The absorption bands at 1420 and 1240 cm<sup>-1</sup> are assigned to CO<sub>3</sub><sup>2-</sup> and aromatic CH stretching, respectively. Aliphatic C-O-C representing oxygenated functional group of cellulose, hemicellulose, and lignin is assigned at 1050 cm<sup>-1</sup>. Appearance of a new peak at 874 cm<sup>-1</sup> in BC300 and BC700 is assigned to the aromatic –CH out of plane bending, predicting the condensation of smaller aromatic units into larger sheets.<sup>35</sup> Differences in FT-IR spectra (Fig. 1(b)) indicate a greater loss in –OH stretching of hydrogen bonding at 3300 cm<sup>-1</sup>, –CH<sub>2</sub> stretching of polar groups at 2800–3000 cm<sup>-1</sup>, C = O and C = C stretching of lignin at 1600–1750 cm<sup>-1</sup> and C-O-C stretching of cellulose at 1030–1260 cm<sup>-1</sup> in BC700 compared with BM. Removal of the aforementioned functional groups at high pyrolysis temperatures is in agreement with the C, H, O and N elemental contents of BCs (Table 1). The overall spectral identification suggests dehydration of cellulosic and ligneous contents, and an increase in the condensation of aromatic units in BCs with increasing pyrolysis temperature.

The pyrolysis temperature during production of BC from buffaloweed BM was the most critical factor in determining BC properties. Removal of O- and H-containing functional groups with increasing pyrolysis temperature gives rise to BCs having high aromaticity and low polarity, which can further influence adsorption properties.

## **TCE** adsorption

BCs produced from buffalo-weed, possessing different characteristics, were tested for the adsorption of TCE from water. Percentage removals of TCE from water with different adsorbent loadings (BM and BCs) are shown in Fig. 2. An increase in TCE removal is observed with increasing loading weight of BM or BCs. With BM, TCE removal is increased from 24.21% to a maximum of 58.65%, whereas with BC300, the TCE removal was increased from 35.78% to 69.07%, as the adsorbent dose was increased from 0.1 to  $1.2 \text{ g L}^{-1}$ . Maximum TCE removal is observed in the case of BC700, specifically a 45.57–88.47% removal with increasing loading weights of  $0.1-1.2 \text{ g L}^{-1}$ . Conversely, the solid phase equilibrium concentration of TCE (Q<sub>e</sub>) decreases with increasing adsorbent dosage, indicating high adsorption capacities of the sorbents at low equilibrium concentration of TCE in the



Figure 1. FT-IR spectra of (a) buffalo-weed biomass (BM), and derived biochar at 300°C (BC300) and 700 °C (BC700). The shaded areas (b) show reduction in absorbance intensities related to specific spectral regions, as affected by pyrolysis temperature.



Figure 2. Percentage removal of TCE from water by buffalo-weed biomass (BM), and its biochars derived at 300  $^\circ$ C (BC-300) and 700  $^\circ$ C (BC-700). TCE initial concentration is 20 mg L<sup>-1</sup> and equilibrium time is 48 h at 25  $^{\circ}$ C.

aqueous phase. The Qe values of BM, BC300 and BC700 at approximately 13.0 mg L<sup>-1</sup> TCE equilibrium concentration are 48.42, 71.57 and 91.15 mg  $g^{-1}$ , respectively. The increase in TCE removal with increase in the adsorbent loading may be attributed to more available adsorption sites.<sup>36</sup> However, it is observed that above a certain dose of adsorbent ( $\sim$ 1.0 g L<sup>-1</sup>), there is little or no increase in the removal of TCE from water, suggesting that maximum adsorption is attained at this adsorbent loading. Thus, the adsorbed and free TCE molecules become constant with further addition of the adsorbent. In other words, adsorption density decreases with increasing adsorbent loading weight, which is attributed to the fact that some of the adsorption sites remain unsaturated during the adsorption process.<sup>37</sup>

#### Adsorption isotherms

Simple equations such as Freundlich and Langmuir are commonly used to describe adsorption isotherms. These sorption isotherms are classified into different categories based on their slopes curvatures.<sup>38</sup> Lack of accurately described data using isotherms may generate considerable errors in the real application and hence, it is essential to describe data adequately using a best fitted model. In this case, fitting was done for Freundlich and



Figure 3. Linearized Freundlich isotherm on TCE adsorption for buffaloweed biomass (BM) and biochars derived at 300  $^{\circ}$ C (BC-300) and 700  $^{\circ}$ C (BC-700). TCE initial concentration is  $20 \text{ mg L}^{-1}$  and equilibrium time is 48 h at 25 °C.

Hill isotherms based on the experimental data. Figure 3 shows the linear regression between  $Q_{e}\xspace$  and  $C_{e}\xspace$  with a linearized Freundlich adsorption model. A comparison of the adsorption capacities of different BCs and BM indicated that BC700 is the most effective sorbent in removing TCE from water, followed by BC300 and BM. Table 2 presents the Freundlich isotherm constants and correlation coefficients of TCE adsorption onto different adsorbents.  $R^2$  values of  $\sim$ 0.9 predict that the adsorption data is adequately described by the Freundlich isotherm model. The K<sub>f</sub> values, representing the adsorptive capacity, are in the order BC700  $(5.461 \text{ mg g}^{-1}) > BC300 (0.038 \text{ mg g}^{-1}) > BM$  $(0.004 \text{ mg g}^{-1})$ , indicating the higher adsorption ability of BC700. The value of n in the Freundlich isotherm model describes the deviation from linearity, i.e. n values close to 1 indicate linearity in the isotherm. In this study, the n value of BC700 was 0.931 suggesting that BC700 could be an effective adsorbent even at higher equilibrium concentrations of TCE, whereas relatively lower n values for BC300 (0.343) and BM (0.284) indicate that these adsorbents could be effective at lower TCE concentrations.<sup>39</sup> The n parameter of the Freundlich isotherm model also relates to the degree of heterogeneity on the adsorption sites. Values of n close to 1 indicate greater heterogeneity of the surface of the

derived at 300 °C (BC300) and 700 °C (BC700)							
	Freundlich						
Adsorbent	$K_{\rm f}$ ([mg g <sup>-1</sup> ] /[mg L <sup>-1</sup> ] <sup>-1/n</sup> )	n		R <sup>2</sup>			
BM	0.004	0.284		0.992			
BC300	0.038	0.343		0.988			
BC700	5.461	0.931		0.875			
Hill							
Adsorbent	K <sub>H</sub>	b	$Q_{max}$ (mg g <sup>-1</sup> )	R <sup>2</sup>			
BM	0.078	5.845	62.61	0.953			
BC300	0.092	4.777	86.82	0.959			
BC700	0.265	4.02	92.52	0.997			



**Figure 4.** Adsorption isotherm fitted with Hill equation for buffalo-weed biomass (BM) and biochars derived at 300 °C (BC-300) and 700 °C (BC-700). TCE initial concentration is 20 mg L<sup>-1</sup> and equilibrium time is 48 h at 25 °C.

adsorbent,<sup>40</sup> as was observed in the case of BC700. Moreover, in this study, values of n<1 indicated a cooperative sorption rather than normal sorption.  $^{41}$ 

In certain instances, especially in the case of adsorption of organic pollutants, cooperative interaction occurs between the surface and sorbent and the sorption pattern corresponds to an S-curve.<sup>38</sup> It indicates a cooperative as well as a strong adsorption.<sup>42</sup> Hill isotherm constants and correlation coefficients of TCE adsorption onto BM and two different BCs are tabulated in Table 2. The isotherms of TCE in this case are best represented by the Hill isotherm model resulting in an R<sup>2</sup> of 0.997 for BC700, whereas for Freundlich it is less well fitted, with  $R^2 = 0.875$  (Fig. 4 and Table 2). Best goodness of fit was observed for BC700 for the Hill equation fitting compared with that of BC300 and BM, while this was reversed for Freundlich fitting. Hill fitting indicates that the adsorbed TCE molecules may tend to be packed in rows or clusters on the BC surfaces.<sup>43</sup> The Hill coefficient b gives a quantitative measure of the degree of cooperativity. Generally, if Hill coefficient b > 1, cooperativity is defined as positive; if b < 1cooperativity is negative.<sup>44</sup> These data showed that cooperative adsorption is the most probable mechanism for TCE sorption on different BCs and BM.

# Correlation between BC/BM characteristics and TCE adsorption

TCE adsorption experiments with BM and BCs showed that, among the different adsorbents, BC700 was the more effective sorbent in removing TCE from water. To determine the cause of this higher efficiency of BC700, correlations were made between different BM or BC properties versus Freundlich adsorptive capacity (K<sub>f</sub>) and Hill maximum adsorption capacity (Q<sub>max</sub>) (Fig. 5). Strong negative correlation were observed between H/C molar ratios of sorbents versus K<sub>f</sub> (R<sup>2</sup> = 0.754) and Q<sub>max</sub> (R<sup>2</sup> = 0.887). Likewise, negative correlations between molar O/C ratios of sorbents versus K<sub>f</sub> (R<sup>2</sup> = 0.349) and Q<sub>max</sub> (R<sup>2</sup> = 0.994) were observed. This implies that the high aromaticity and low polarity of BCs, particularly of BC700 (H/C of 0.15 and O/C of 0.06 in Table 1), result in greater adsorption of TCE. As mentioned earlier that higher pyrolysis temperatures result in the removal of O- and H-containing functional groups in BC700, making the carbon surfaces more hydrophobic.<sup>45</sup> Consequently, lack of H-bonding impairs the formation of water clusters while facilitating the attraction of hydrophobic organic contaminants such as TCE.<sup>45</sup> The importance of hydrophobic carbon surfaces in adsorption of TCE by activated carbons has been reported by Karanfil and Dastgheib.<sup>46</sup> Additionally, TCE adsorption onto BC700 may depend on the electrostatic interaction between the delocalized  $\pi$ -electrons of the graphene sheets and TCE molecule.<sup>47</sup>

The relatively higher surface area of BC700 (9.25 m<sup>2</sup> g<sup>-1</sup>; Table 1) compared with that of BC300 (3.98 m<sup>2</sup> g<sup>-1</sup>) and BM (6.30 m<sup>2</sup> g<sup>-1</sup>) justifies its high adsorption capacity, as indicated by positive correlations between the surface area of the sorbents versus K<sub>f</sub> (R<sup>2</sup> = 0.803) (Fig. 5). Similar linear regressions between surface area and Freundlich isotherm parameters have also been reported by Uchimiya *et al.*<sup>6</sup> Furthermore, relatively high pore volume (0.02 cm<sup>3</sup> g<sup>-1</sup>) of BC700 compared with BM and BC300 (0.01 cm<sup>3</sup> g<sup>-1</sup>) favors greater uptake of TCE from water.<sup>46</sup>

BC characteristics affected by pyrolysis temperature also influences TCE removal from water. The presence or absence of O- and H-containing functional groups provides an estimation of the hydrophobicity of BCs that further relate to adsorption efficiencies.

#### **Future implications**

Although activated carbon has proven to be one of the most efficient adsorbents in removing TCE from water because of its high surface area, certain disadvantages are making this a less attractive option for many applications. High costs due to the activation process, non-biodegradation of adsorbed TCE by microbes, and high regeneration cost of activated carbon are some examples.<sup>17</sup> Under these circumstances, BC could serve as an alternative to activated carbon. The advantages associated with BC include its relatively low cost due to the absence of preor post-activation, enhanced microbial activity for adsorbed TCE biodegradation, and high availability of a variety of biomass for BC production. The estimated breakeven price of BC is US\$246 per ton, which is approximately 1/6 of commercially available activated carbon (~US\$1500 per ton).<sup>18,47</sup> Additionally, during pyrolysis, the evolved gases and volatile matter can easily be converted to biofuel and bio-oil, respectively. Unlike activated carbon, BC contains essential nutrients such as P, N, K, Na and Ca that can also increase soil fertility. Production of BC from buffalo-weed can also provide an environment friendly method of processing harvested residues of harmful invasive plant species. Depuration of TCE contaminated groundwater with BC produced from buffalo-weed can provide a cost effective sustainable remedial technology.

# CONCLUSIONS

The invasive plant species buffalo-weed was converted into BC by slow pyrolysis at two different temperatures. BC yield and properties were influenced by the corresponding pyrolysis temperature. High temperature resulted in C-enrichment and removal of O- and H-containing functional groups, giving rise to less polar and more aromatic BC. These particular properties also affected the effectiveness of BCs in removing TCE from water. BC700 produced at a higher temperature of 700 °C was more effective than BC300 produced at a lower temperature of 300 °C because of its low polarity (lower O/C molar ratio), high aromaticity (lower H/C molar ratio) and high surface area. A strong



Figure 5. Correlation between molar H/C, O/C and surface area of buffalo-weed biomass and its derived biochars versus Freundlich adsorptive capacity ( $K_f$ ) and Hill maximum adsorption capacity ( $Q_{max}$ ).

and cooperative sorption mechanism was predicted by modeling isotherm data. It is, therefore, suggested that BC produced from buffalo-weed, specifically at higher pyrolysis temperatures, could serve as an efficient adsorbent of TCE from water. However, field studies are required to demonstrate the practical applicability of BC for removing TCE from groundwater.

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