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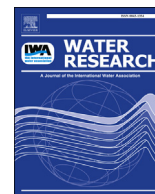
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# Granular biochar compared with activated carbon for wastewater treatment and resource recovery



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## ABSTRACT

Granular wood-derived biochar (BC) was compared to granular activated carbon (GAC) for the treatment and nutrient recovery of real wastewater in both batch and column studies. Batch adsorption studies showed that BC material had a greater adsorption capacity at the high initial concentrations of total chemical oxygen demand (COD<sub>T</sub>) (1200 mg L<sup>-1</sup>), PO<sub>4</sub> (18 mg L<sup>-1</sup>), and NH<sub>4</sub> (50 mg L<sup>-1</sup>) compared to GAC. Conversely the BC material showed a lower adsorption capacity for all concentrations of dissolved chemical oxygen demand (COD<sub>D</sub>) and the lower concentrations of PO<sub>4</sub> (5 mg L<sup>-1</sup>) and NH<sub>4</sub> (10 mg L<sup>-1</sup>). Packed bed column studies showed similar average COD<sub>T</sub> removal rate for BC with 0.27 ± 0.01 kg m<sup>-3</sup> d<sup>-1</sup> and GAC with 0.24 ± 0.01 kg m<sup>-3</sup> d<sup>-1</sup>, but BC had nearly twice the average removal rate (0.41 ± 0.08 kg m<sup>-3</sup> d<sup>-3</sup>) compared to GAC during high COD<sub>T</sub> concentrations (>500 mg L<sup>-1</sup>). Elemental analysis showed that both materials accumulated phosphorous during wastewater treatment (2.6 ± 0.4 g kg<sup>-1</sup> and 1.9 ± 0.1 g kg<sup>-1</sup> for BC and GAC respectively). They also contained high concentrations of other macronutrients (K, Ca, and Mg) and low concentrations of metals (As, Cd, Cr, Pb, Zn, and Cu). The good performance of BC is attributed to its macroporous structure compared with the microporous GAC. These favorable treatment data for high strength wastewater, coupled with additional life-cycle benefits, helps support the use of BC in packed bed column filters for enhanced wastewater treatment and nutrient recovery.

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## 1. Introduction

Modern wastewater treatment facilities are particularly good at removing bulk organic contaminants and buffering the contamination of local waterways, but current processes have high energy, material, and capital requirements. Systems that are designed with reduced operational costs, direct water reuse capabilities, and value added processes such as the recovery of nutrients, could aid in the development of a sustainable wastewater treatment infrastructure (Li et al., 2015; Ren and Umble, 2016). Biologically activated carbon (BAC) trickling filters have been used in wastewater treatment and reuse due to their high treatment efficiency and resource recovery potential (Henze, 2008). These benefits are largely due to the combined effects of adsorption of non-biodegradable matter and

the oxidation of biodegradable contaminants on the surface of a carbon-based material (Weber et al., 1978). However, BAC application has been limited to low influent concentrations such as municipal wastewater tertiary treatment, because fouling has been a big challenge under high organic loading. The use of carbon materials that reduce fouling by mitigating the effects of complex wastewaters could help expand the application range.

Generally BAC systems are constructed with activated carbon granules arranged in packed bed columns. Contaminants are removed through adsorption onto the surface of the carbon material during advective transport through the reactor as well as biological degradation (Cooney, 1998). Once the available adsorption sites are filled the removal efficiency is significantly diminished. Common granular activated carbon (GAC) materials are comprised primarily of micropores (>1 nm) which are highly effective at adsorbing dissolved contaminants, but are easily blocked by suspended solids (Matsui et al., 2012). The development of a bacterial biofilm can aid in the bioregeneration of adsorption sites but this is also limited and eventually the carbon material will need to be replaced (Simpson, 2008). The life span of the carbon

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material depends on the contaminant concentration, flowrate, and its adsorption capacity. Consequently, the selection of a carbon material with the highest adsorption capacity for a targeted contaminant could aid in lengthening treatment capability. Given that disposal of spent material is inevitable, initial cost and method of replacement should also be considered.

BC is carbon-based material formed from the pyrolysis of woody biomass and has recently shown great potential as a low-cost GAC replacement material for contaminant removal (Ahmad et al., 2014). When lignocellulosic biomass is thermally converted it maintains an interconnected 3-dimensional structure resembling its original physical morphology, resulting in a high surface area ( $>300 \text{ m}^2 \text{ g}^{-1}$ ) and large pore size distribution, including macro-, meso-, and nano-pores (Huggins et al., 2014). BC is often used directly with little post treatment modification and is generally less resource, energy, and capital intensive to manufacture compared to highly refined GAC. Furthermore, BC has also been shown to have additional carbon sequestration and agronomic benefits when used as a soil amendment (Woolf et al., 2010). Using spent BC material after wastewater treatment as an agricultural amendment could further increase its life-cycle benefits. Porosity, cost, and nutrient recovery potential makes BC an ideal carbon-based material, however its performance during real wastewater treatment has yet to be evaluated.

In this study we compared the maximum contaminant ( $\text{COD}_T$ ,  $\text{COD}_D$ ,  $\text{NH}_4$ , and  $\text{PO}_4$ ) adsorption capacity of BC with GAC from real wastewater. We then tested the wastewater treatment efficiency and nutrient recovery capability of BC and GAC granules in a packed bed column filters. Our findings demonstrate the advantage of the macroporous BC with increased contaminant adsorption capacity at high  $\text{COD}_T$  concentrations ( $1200 \text{ mg L}^{-1}$ ) when compared to microporous GAC. BC also had a slightly higher  $\text{COD}_T$  removal rate ( $\text{kg m}^{-3} \text{ d}^{-1}$ ) than GAC during high  $\text{COD}_T$  concentrations ( $>500 \text{ mg L}^{-1}$ ) in a column study. Nutrient retention for both materials was satisfactory with BC having a final phosphorous ( $\text{PO}_4$ ) concentration of  $2.6 \text{ g kg}^{-1}$ , GAC with  $1.9 \text{ g kg}^{-1}$ , and both materials retaining high levels of other macronutrients (K, Ca, and Mg) and low levels of metals (As, Cd, Cr, Pb, Zn and Cu). This study helps to support the use of macroporous, low cost, and renewable BC granules for mainstream wastewater treatment and nutrient recovery.

## 2. Experimental section

### 2.1. Carbon material characterization and manufacturing process

The BC material was prepared from lodgepole pine wood and was thermally converted at a highest heat temperature of  $1000^\circ\text{C}$  for 1 h, in a top-lit up-draft (TLUD) gasifier. The larger pieces of BC material were crushed to a size range between 4.8 and  $8.0 \text{ mm}^3$  without any further activation step. The GAC was purchased from Grainger® and was manufactured from coal using standard industrial methods. Common GAC manufacturing steps include the grinding, blending, and agglomerating of coal followed by carbonization and activation. A flow diagram illustrating the difference in manufacturing between BC and GAC can be seen in Fig. 1.

### 2.2. Physical and chemical analysis

The morphology and structure of the BC and GAC materials were investigated using scanning electron microscopy (SEM; Jeol JSM-6480LV, 30 kV). Elemental composition of each material was determined by inductively coupled plasma mass spectrometry (ICP-MS) using a Perkin Elmer SCIEX inductively coupled plasma mass spectrometer (Table 1). Specific surface area was determined

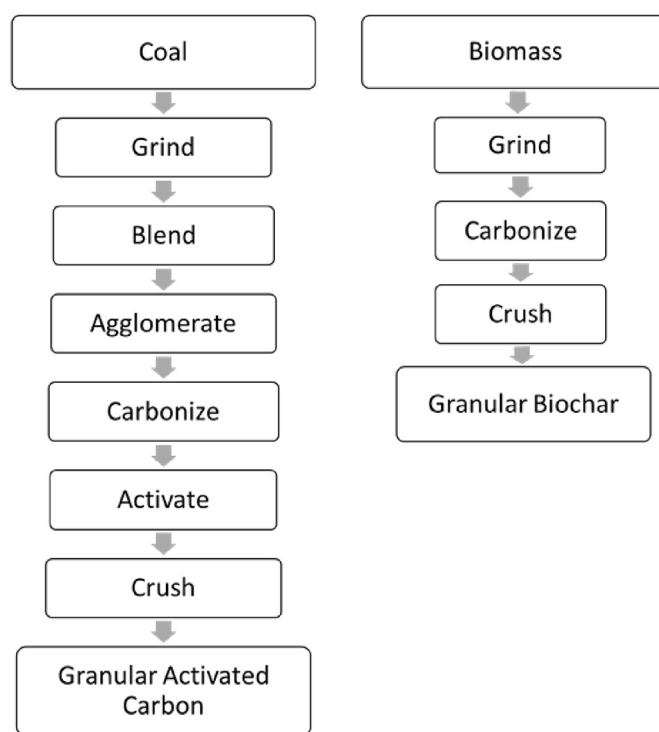


Fig. 1. Flow diagram for the manufacturing of GAC and BC materials.

using the Brunauer–Emmett–Teller (BET) method via a five-point  $\text{N}_2$  gas adsorption technique (ASAP 2020; Micromeritics, Norcross, GA) (Wang, et al., 2011) (Huggins et al., 2015). Wastewater quality measurements (total COD ( $\text{COD}_T$ ), dissolved COD ( $\text{COD}_D$ ), phosphate ( $\text{PO}_4$ ), and ammonia ( $\text{NH}_4$ )) were taken for all experiments (Table 2) and were measured with digester vials (Hach Co.), according to APHA standards (Huggins et al., 2013). Total suspended solids (TSS) were measured by filtering wastewater through a dry weighed  $1 \mu\text{m}$  filter and then drying the filter at  $105^\circ\text{C}$ . After drying, the filter was weighed and the TSS concentration was calculated using Equation (1):

$$\text{TSS} (\text{mg L}^{-1}) = ((A-B) \times 1000 / C) \quad (1)$$

where A is the end weight of filter (mg); B is the initial weight of filter (mg); and C is the volume of water filtered (L).

### 2.3. Batch adsorption study

Batch adsorption studies were carried in 55 mL polyethylene tubes using 50 mg of adsorbent and 50 mL of real industrial wastewater solution at room temperature. Brewery wastewater was collected from Coors® wastewater treatment plant in Golden, Colorado. Trials were set up with  $\text{COD}_T$  concentrations of  $1200 \text{ mg L}^{-1}$ ,  $600 \text{ mg L}^{-1}$ , and  $300 \text{ mg L}^{-1}$  and  $\text{COD}_D$  concentrations of  $990 \text{ mg L}^{-1}$ ,  $495 \text{ mg L}^{-1}$ , and  $248 \text{ mg L}^{-1}$ . The  $\text{COD}_T$  concentrations had TSS concentrations of  $300 \text{ mg L}^{-1}$ ,  $150 \text{ mg L}^{-1}$  and  $75 \text{ mg L}^{-1}$ , respectively. Nutrient adsorption capacity corresponding to  $\text{COD}_T$  concentrations were also monitored for  $\text{PO}_4$  ( $18 \text{ mg L}^{-1}$ ,  $9 \text{ mg L}^{-1}$ , and  $4.5 \text{ mg L}^{-1}$ ) and  $\text{NH}_4$  ( $50 \text{ mg L}^{-1}$ ,  $25 \text{ mg L}^{-1}$ , and  $12 \text{ mg L}^{-1}$ ). Adsorption equilibrium was achieved after shaking for 24 h in a rotary shaker at room temperature ( $20 \pm 2^\circ\text{C}$ ). The tubes were then centrifuged at 4000 rpm for 10 min. All adsorption experiments were run in duplicates, and a blank solution was measured as control. The filtered trials, using

**Table 1**  
Physical and elemental characteristics of BC and GAC materials.

Material	pH	Particle size mm <sup>3</sup>	Specific gravity g cm <sup>−3</sup>		BET N <sub>2</sub> -total m <sup>2</sup> g <sup>−1</sup>		Pore size range (μm)		Material cost (\$ ton <sup>−1</sup> ) <sup>a</sup>	
BC	9.66	8.0–4.8	0.32		152.3		>1 - 40		51–381	
GAC	8.22	4.5–3.7	1.83		895.5		>1 - 5		800–2500	
Elemental composition (mg kg <sup>−1</sup> )										
	P	K	Ca	Mg	As	Cd	Cr	Pb	Zn	Cu
BC	106	26,143	7305	878	14.3	0.16	30.0	2.3	79.4	2.9
GAC	196	673	3987	2288	16.3	0.21	14.3	11.3	17.0	9.0

<sup>a</sup> Material costs were determined from (Meyer et al., 2011), <http://www.alibaba.com>, and personal communications with retailers.

**Table 2**  
Wastewater characteristics.

Contaminants (mg L <sup>-1</sup> )	Average (mg L <sup>-1</sup> )
COD-total (COD <sub>T</sub> )	1243 ± 55
COD-dissolved (COD <sub>D</sub> )	989 ± 21
Phosphate (PO <sub>4</sub> )	18 ± 2
Ammonia (NH <sub>4</sub> )	24 ± 3
Total suspended solids (TSS)	320 ± 20
<b>Metals</b>	<b>(μg L<sup>-1</sup>)</b>
Arsenic (As)	4.8
Cadmium (Cd)	0.07
Chromium (Cr)	92
Lead (Pb)	0.76
Zinc (Zn)	27
Copper (Cu)	38

1 μm filter paper, were established to test COD<sub>D</sub> adsorption capacity and to determine the effect of TSS on COD<sub>T</sub> adsorption capacity. The variations in the batch study were established to determine the effect of complexity and pollutant concentration on the adsorption capacities and how that may relate to the different characteristics of each electrode material.

The amount of adsorbed contaminant per unit sorbent mass and the removal percentage were calculated using Equations (2) and (3).

$$q_e = (C_0 - C_e)/C_0 \times 100\% \quad (2)$$

$$R = (C_0 - C_e)/m \times 100\% \quad (3)$$

where  $q_e$  is the adsorbent removal capacity of the given contaminant;  $C_0$  is the initial and  $C_e$  is the equilibrium concentration of the given contaminant (mg L<sup>-1</sup>);  $R$  is the removal percentage (%);  $V$  is the volume of solution (mL) and  $m$  is the weight of the adsorbent (mg).

#### 2.4. Column construction and operation

Each material was tested as media in a packed bed column with a height of 50.8 cm, a diameter of 5.1 cm, and a total bed volume of approximately 1 L. The columns were fed wastewater continuously and recirculated at a rate of 400 mL min<sup>-1</sup> in a down flow configuration to provide mixing and aeration. Each batch study consisted of treating 19 L of wastewater with a hydraulic retention time (HRT) of 72 h<sup>-1</sup>. The HRT was selected to evaluate the performance of each material over a range of COD concentrations (>1200 mg L<sup>-1</sup> to <100 mg L<sup>-1</sup>) and to determine the average removal efficiency (%) and rate (kg m<sup>-3</sup> d<sup>-1</sup>) over the entirety of the treatment process. Column experiments were carried out at room temperature in a temperature controlled environment. The wastewater characteristics (COD<sub>T</sub>, PO<sub>4</sub>, NH<sub>4</sub>, temperature, and pH) were tested daily until the end of each trial. Removal rate was calculated from the

difference in initial ( $C_0$ ) and final ( $C_f$ ) concentration over the HRT and normalized by the bed volume (BV). After the final of five trials, the BC and GAC material from each column were collected and tested for final nutrient and metal concentration.

### 3. Results and discussion

#### 3.1. Physical and chemical characterization of BC and GC materials

Carbon-based adsorbent materials play a large role in the remediation of contaminated waters. However, it is important to consider the physical form of the adsorbent and how that relates to its specific application. The overall performance of the materials was determined by comparing the physical and chemical analysis of each carbon material under identical conditions. The major physical characteristics and elemental composition are presented in Table 1. Based on BET surface area, measuring pore sizes up to 100 nm, we observed that the BC had a much lower surface area (152 m<sup>2</sup> g<sup>-1</sup>) compared to GAC (895 m<sup>2</sup> g<sup>-1</sup>). The SEM images reveal macropores in the size range of 1–40 μm for BC and less than 1 μm for GAC (Fig. 2). The large macroporosity of BC is mainly attributed to the intrinsic physical structure of the precursor biomass. Biochar can be made using a variety of different biological materials and heat treatments, so it is important that the most appropriate feedstock and thermal conversion temperature were used to match form to function (Zhao et al., 2013). Previous studies on both wood- and coal-based carbons determined that macroporosity was primarily caused by the pit fields and cell cavities of the source material and that further refinement in GAC manufacturing destroys these courser features (Wildman and Derbyshire, 1991). A more detailed analysis conducted on the change in molecular structure during the thermal conversion of biomass showed distinct phase changes in the amorphous biomass to more ordered turbostratic char and an increase in BET<sub>N<sub>2</sub></sub> surface area with increased temperature (>600 °C) (Keiluweit et al., 2010).

Given the importance of the physical features of carbon materials, both the feedstock material and manufacturing methods should be taken into consideration in order to fit “form to function” in terms of wastewater treatment. Although the manufacturing and activation step greatly increases the microporosity of GAC, nearly all macropores greater than 1 μm are lost. In the case of fixed biofilm processes for the treatment of industrial wastewaters, long term exposure to bacterial colonization and complex contamination should be taken into consideration. Since bacteria range from 0.4 μm to 4 μm in diameter, they cannot access the smaller micropores and the formation of a biofilm can thus limit overall surface area for adsorption (Simpson, 2008). The larger macropores of the BC material play an important role in harboring bacterial growth while allowing enough area for convective forces to facilitate physical and biological adsorption. This is a significant advantage over GAC-type materials for wastewater treatment (Lehmann et al., 2011).



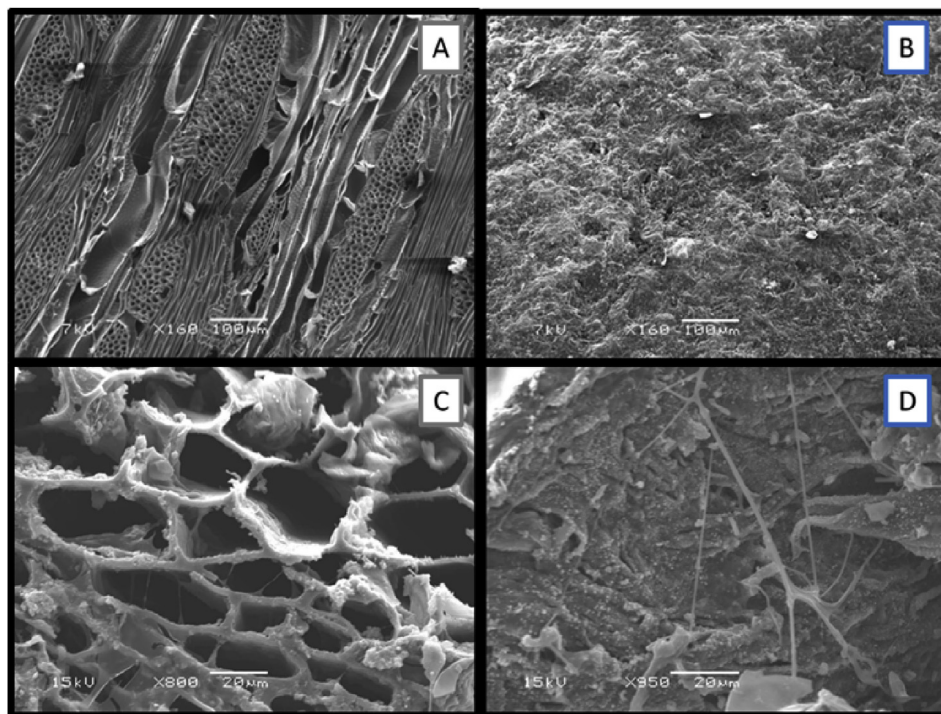


Fig. 2. Scanning electron microscope images of BC (A) and GAC (B) before and BC (C) and GAC (D) after wastewater treatment.

Elemental composition measurements of each material showed a variety of different trace elements imbedded in the carbon matrix. Most noticeably BC had a high concentration of  $K^+$  ( $26.1 \text{ g kg}^{-1}$ ),  $Ca^{2+}$  ( $7.3 \text{ g kg}^{-1}$ ), and  $Na^+$  ( $1.9 \text{ g kg}^{-1}$ ), while GAC had high concentrations of  $Ca^{2+}$  ( $4.0 \text{ g kg}^{-1}$ ),  $Mg^{2+}$  ( $2.3 \text{ g kg}^{-1}$ ),  $Fe^{3+}$  ( $8.3 \text{ g kg}^{-1}$ ), and  $Al^{3+}$  ( $10.0 \text{ g kg}^{-1}$ ). The mineral composition of carbon materials can play an important role in the adsorption of various contaminants through both co-precipitation and inner sphere complexation (Lu et al., 2012). Carbon materials with the appropriate mineral composition should be selected to avoid toxic leaching of both metals and the target specific contaminants (Wang and Ren, 2015).

### 3.2. Batch adsorption capacity of BC and GAC materials

The results from the batch adsorption studies are illustrated in Fig. 3. Adsorption measurements of  $COD_T$  at  $1200 \text{ mg L}^{-1}$  show that the BC material had a 30% higher adsorption capacity of  $70.0 \text{ mg } COD_T \text{ g}^{-1}$  compared to GAC at  $49.3 \text{ mg } COD_T \text{ g}^{-1}$ . At  $1200 \text{ mg } COD_T \text{ L}^{-1}$  and  $PO_4$  and  $NH_4$  concentrations of  $18 \text{ mg L}^{-1}$  and  $50 \text{ mg L}^{-1}$ , respectively, BC also showed more than twice the  $PO_4$  and  $NH_4$  adsorption of  $1.0 \text{ mg g}^{-1}$  and  $3.6 \text{ mg g}^{-1}$  respectively, compared to  $0.49 \text{ mg g}^{-1}$  and  $1.4 \text{ mg g}^{-1}$ , respectively for GAC. At the middle ( $600 \text{ mg L}^{-1}$ ) to lower ( $300 \text{ mg L}^{-1}$ )  $COD_T$  concentrations, BC and GAC had similar adsorption capacities for  $COD_T$ ,  $PO_4$ , and  $NH_4$ . For each  $COD_T$  concentration, BC had an average TSS removal rate of 90% compared to GAC with an average of 75%. For  $COD_D$  (no TSS), the GAC material showed similar or even higher adsorption capacities for  $COD_D$  and nutrients compared to BC regardless of the initial concentration, presumably due to the higher specific surface area.

Both physical and chemical characteristics of the carbon materials play a dual and often complex role in their adsorption performance (Bansal and Goyal, 2005). From the batch adsorption data it can be seen that at high  $COD_T$  and TSS concentrations the BC material has a significantly higher adsorption capacity. However, when the TSS is filtered from the wastewater solution the two

materials have similar adsorption capacities regardless of the initial concentration. Due to the high surface area and adsorption capacity of TSS, both materials have an affinity to accumulate a significant amount of COD (Mulligan et al., 2009). This effect can be seen with the increased  $COD_T$  and nutrient adsorption capacity for each material in the presence of TSS compared with the filtered adsorption tests. The ability of BC to remove a higher percentage of TSS compared to GAC contributes to the increased adsorption capacity at higher  $COD_T$  and nutrient concentrations with the macroporous structure. This argument is further validated by the similar adsorption capacity of each material for  $COD_D$  when the TSS are filtered from solution. However, at lower  $COD_T$  and TSS concentrations, the added advantage of TSS adsorption is diminished and the two materials have similar adsorption capacity for  $COD_T$ ,  $COD_D$ , and nutrients.

### 3.3. Removal of organics using BC and GAC materials in a packed bed column

The wastewater treatment performance for each material was evaluated in packed bed column filters. Repeated batch studies with recirculation were conducted using real brewery wastewater until a COD concentration lower than  $100 \text{ mg L}^{-1}$  was achieved to determine average removal rate and efficiency and allow for the comparison with conventional treatment systems. The  $COD_T$  concentration was measured every day with final phosphate and ammonium concentrations in order to calculate removal rates (Fig. 4). From our measurements it can be seen that the BC material had a significantly higher average  $COD_T$  removal rate of  $0.41 \pm 0.08 \text{ kg m}^{-3} \text{ d}^{-1}$  compared to GAC with  $0.28 \pm 0.08 \text{ kg m}^{-3} \text{ d}^{-1}$  during the initial stages of treatment where  $COD_T$  concentrations were above  $500 \text{ mg L}^{-1}$ . Towards the latter part of the treatment where  $COD_T$  is below  $500 \text{ mg L}^{-1}$ , GAC had a slightly higher average  $COD_T$  removal rate of  $0.12 \pm 0.05 \text{ kg m}^{-3} \text{ d}^{-1}$  compared to BC with  $0.091 \pm 0.04 \text{ kg m}^{-3} \text{ d}^{-1}$ . Averaging the  $COD_T$  removal rate over the entirety of the treatment process shows a

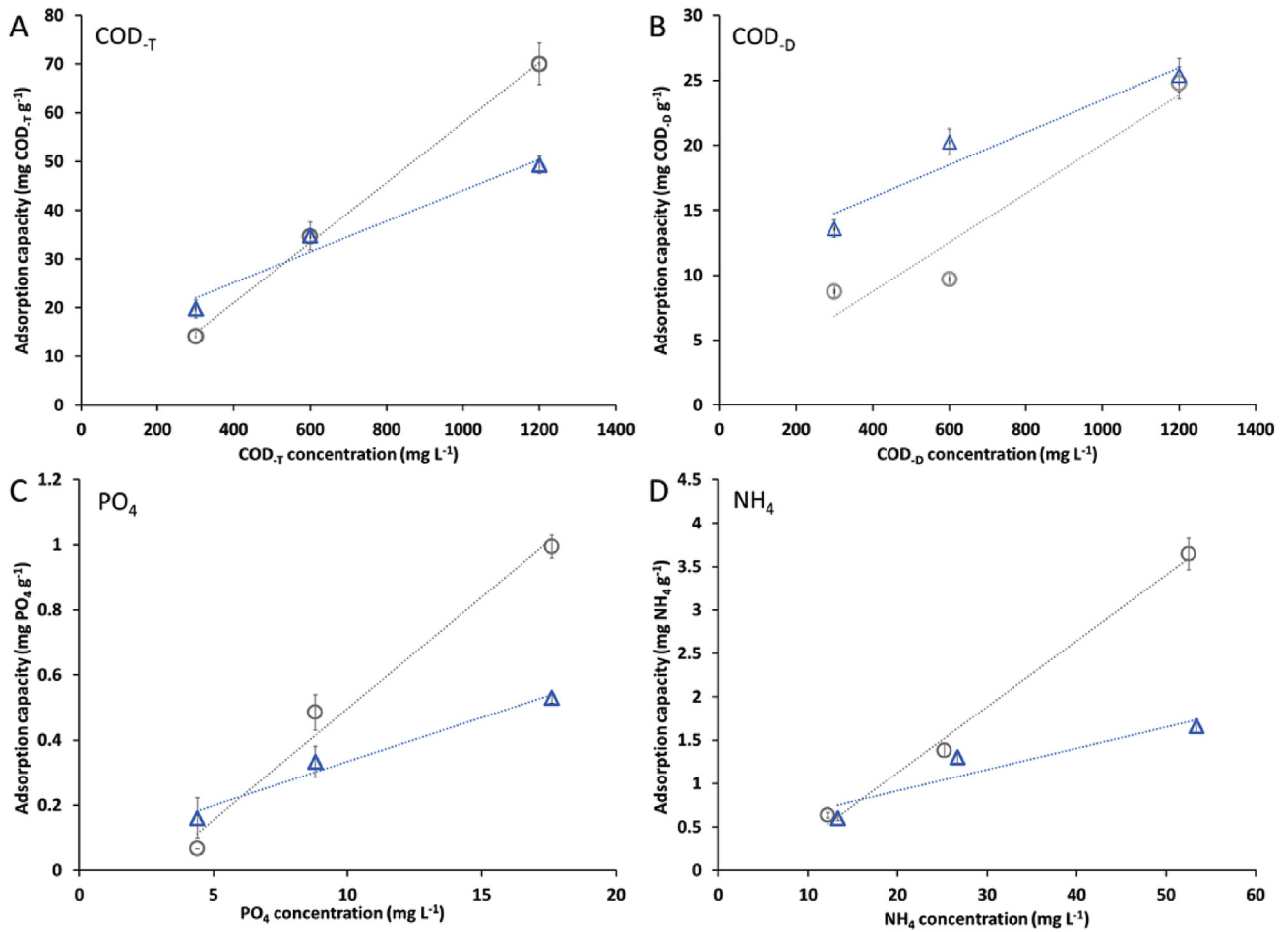


Fig. 3. Adsorption capacity of COD<sub>T</sub> (A), COD<sub>D</sub> (B), PO<sub>4</sub> (C), and NH<sub>4</sub> (D) for BC (○) and GAC (△) materials using real wastewater.

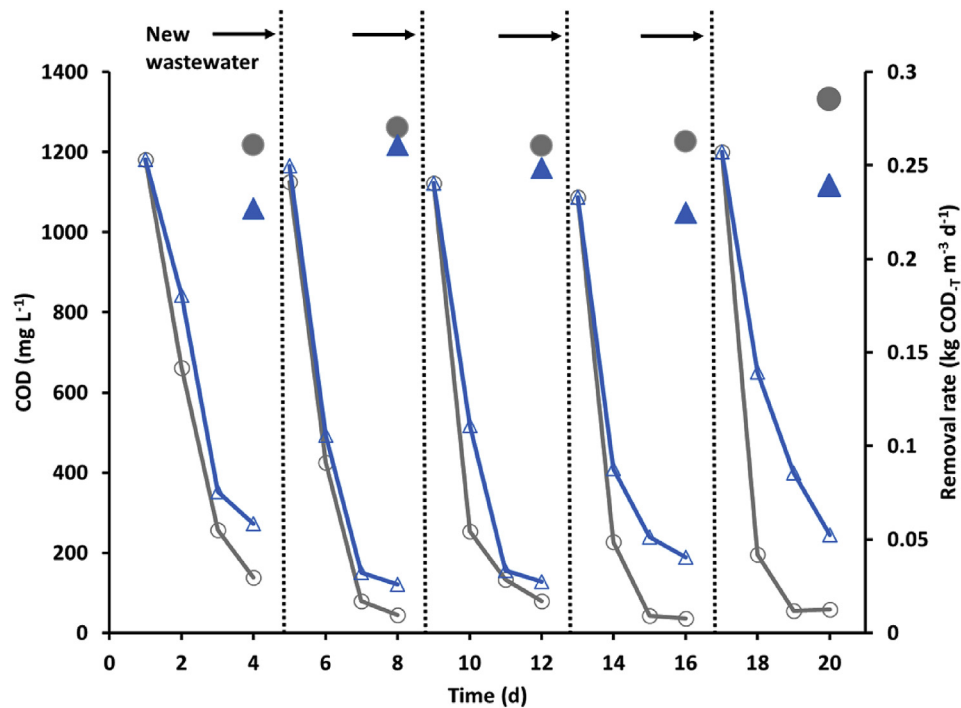


Fig. 4. COD<sub>T</sub> concentration of packed bed column filter using BC (○) or GAC (△) materials and COD<sub>T</sub> removal rate for packed bed column filter using BC (●) or GAC (▲) materials treating real wastewater.

**Table 3**  
Wastewater treatment characteristics for BC and GAC materials.

Material	BC	GAC
COD <sub>T</sub> removal rate (kg m <sup>-3</sup> d <sup>-1</sup> )	0.27 ± 0.01	0.24 ± 0.01
COD <sub>T</sub> removal (%)	94% ± 3%	83% ± 5%
NH <sub>4</sub> removal rate (g m <sup>-3</sup> d <sup>-1</sup> )	5.4 ± 0.51	4.1 ± 0.40
NH <sub>4</sub> removal (%)	90% ± 4%	67% ± 6%
PO <sub>4</sub> removal rate (g m <sup>-3</sup> d <sup>-1</sup> )	3.8 ± 0.01	3.5 ± 0.01
PO <sub>4</sub> removal	87% ± 2%	79% ± 4%
TSS removal rate (mg TSS L <sup>-1</sup> )	66 ± 5	53 ± 6
TSS removal (%)	82% ± 4%	67% ± 7%

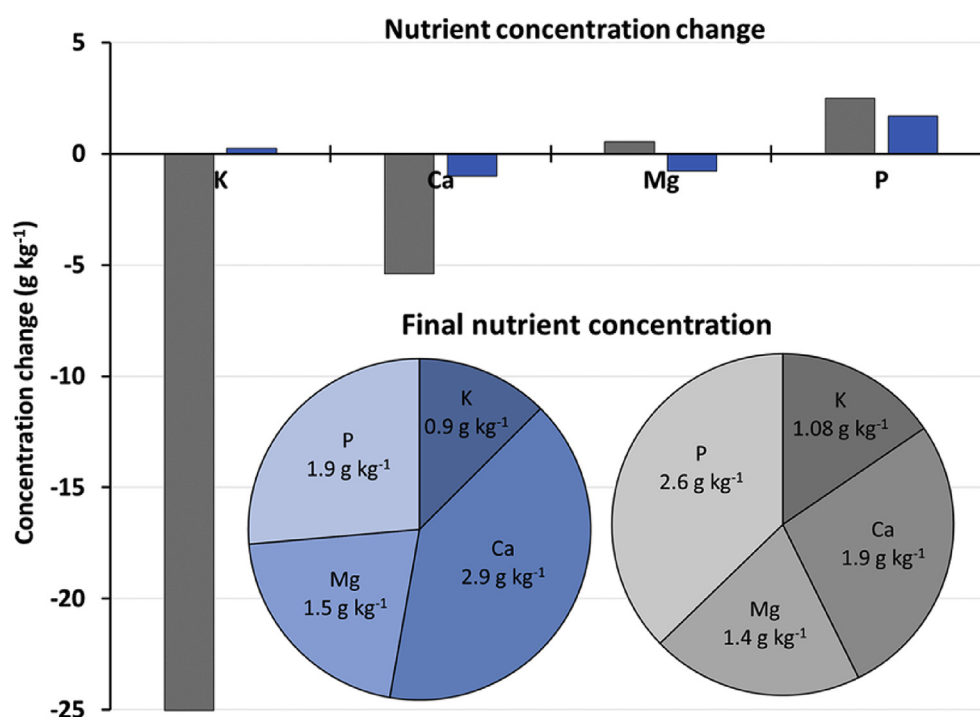
similar COD<sub>T</sub> removal rate of  $0.27 \pm 0.01 \text{ kg m}^{-3} \text{ d}^{-1}$  and  $0.24 \pm 0.01 \text{ kg m}^{-3} \text{ d}^{-1}$  for BC and GAC, respectively (Table 3). We also observed an increase in removal rate for each material over the course of the study, with an 8.5% increase and 4.9% increase from over the 20-day period for the BC and GAC material, respectively. The increase in removal rate is thought to be attributed to the development of a robust bacterial biofilm as seen in other column studies (Simpson, 2008). Nutrient removal data showed that the materials had similar removal rates of  $3.8 \pm 0.01 \text{ mg PO}_4 \text{ m}^{-3} \text{ d}^{-1}$  for BC and  $3.5 \pm 0.01 \text{ mg PO}_4 \text{ m}^{-3} \text{ d}^{-1}$  and BC had a slightly higher NH<sub>4</sub> removal rate of  $5.4 \pm 0.51 \text{ mg m}^{-3} \text{ d}^{-1}$  compared to GAC with  $4.1 \pm 0.40 \text{ mg m}^{-3} \text{ d}^{-1}$ . Measuring TSS before and after treatment also revealed that BC had a higher capacity to remove TSS at  $66 \pm 5 \text{ mg m}^{-3} \text{ d}^{-1}$  compared to GAC at  $53 \pm 6 \text{ mg m}^{-3} \text{ d}^{-1}$ .

Treatment data and characteristics gathered from this experiment highlight the increased capacity for BC to treat high strength wastewaters with COD<sub>T</sub> concentrations above  $500 \text{ mg L}^{-1}$  compared to GAC. Additionally, the BC material had an overall higher TSS removal rate than GAC. This data is supported by the higher adsorption capacities for all contaminants at the highest concentrations measured. The physical analysis of each material showed that this is primarily due to the larger pore sizes of the BC material compared to that of the microporous GAC. Since GAC is

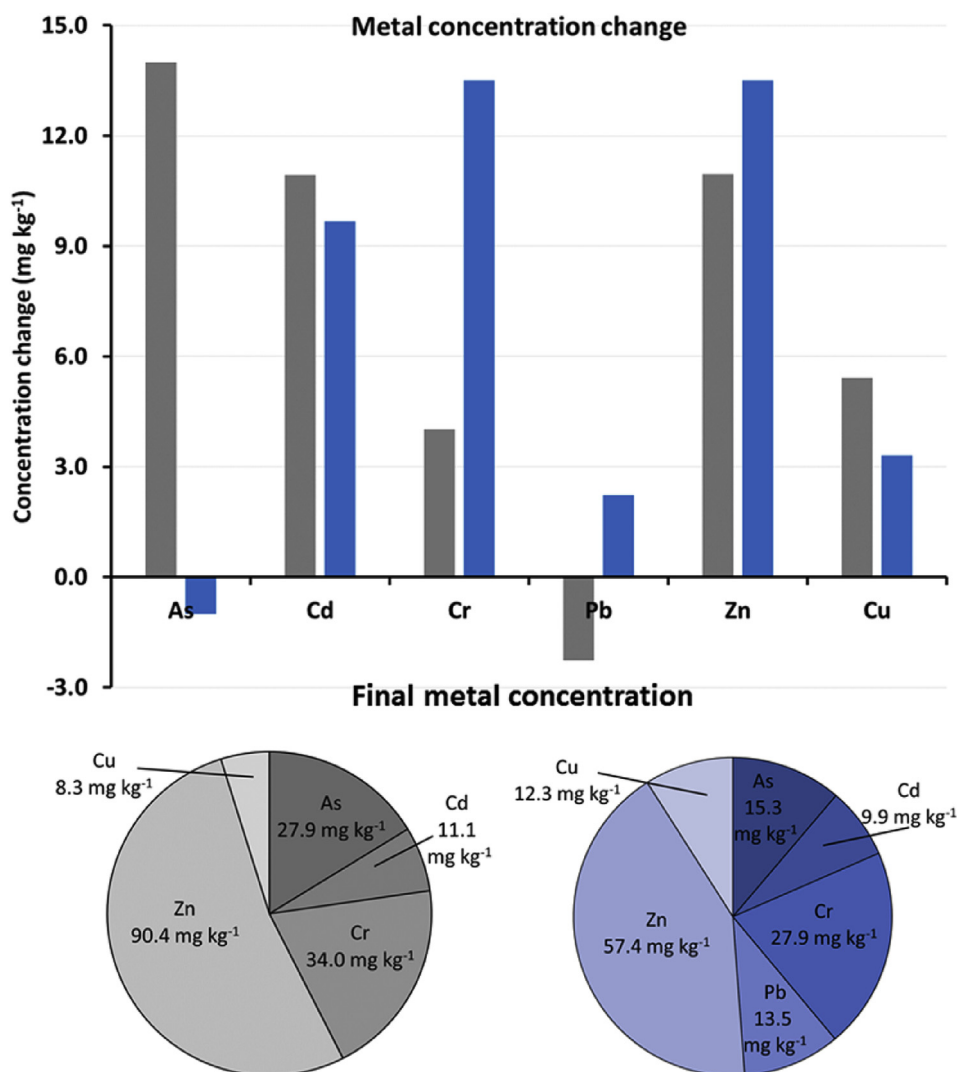
primarily used as a polishing media during the tertiary treatment of wastewater, it is designed for the adsorption of dilute and fully dissolved contaminants. The information gathered for the BC materials from this study will help expand the use of packed bed column filters for other treatment applications, especially for highly complex wastewaters. It must be clarified however, that further analysis is needed to determine the effect of prolong use and steady state conditions of BC in a BAC filter, often achieved after several months of operation.

### 3.4. Nutrient recovery and retention during wastewater treatment

To determine the potential for nutrient recovery through adsorption and retention on the carbon surface, the elemental composition, including macronutrients (P, K, Ca, and Mg) and metals (As, Cd, Cr, Pb, Zn, and Pb), contained on each material, were measured before and after wastewater treatment and these data are shown in Figs. 5 and 6. For the macro nutrients, it was revealed that K was released from the BC material at nearly  $25 \text{ g kg}^{-1}$  and Ca at  $5 \text{ g kg}^{-1}$  due to their initial high content in the virgin BC (Table 1). Similarly, higher release of Mg was observed from GAC. Although there was some loss in these nutrients, the final concentrations were still satisfactory for land application. Interestingly, both materials accumulated P after treatment, with  $2.6 \text{ g kg}^{-1}$  and  $1.9 \text{ g kg}^{-1}$  for BC and GAC, respectively, which demonstrates good potential in nutrient recovery. In total, each material had a balanced concentration of macronutrients opening up its use in land applications. However, the land application of spent GAC material is often not considered given its high replacement cost and would be the greatest advantage for using BC. Traditionally spent GAC materials are reactivated through thermal treatment which would also be applicable for BC as well. This process however carries additional life-cycle cost. Given that BC is less expensive than GAC by ~90% and has been thoroughly studied for its use as an agricultural amendment, it will be more advantageous to land apply the spent BC and



**Fig. 5.** Nutrient concentration change (bar) for BC (gray) and GAC (blue) and final nutrient concentration (pie) for BC (gray) and GAC (blue) after wastewater treatment. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



**Fig. 6.** Metal concentration change (bar) for BC (gray) and GAC (blue) and final metal concentration (pie) for BC (gray) and GAC (blue) after wastewater treatment. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

further expand its life-cycle benefits.

Given concerns over the accumulation of heavy metals in areas with repeated biosolids applications, metal concentrations were also measured for each material. Based on our measurements neither of the materials had metal concentrations exceeding those that the EPA regulates for biosolids land application (Iranpour et al., 2004). However, similar to the leaching of macronutrients, some metals present in the original material were also lost during treatment. Most noticeably, As and Pb were leached from both materials. Although this should be taken into consideration in scaled systems, both metals were leached from the system at very low concentrations, below 3 mg kg<sup>-1</sup>. It should be noted that this experiment was carried out for a total of 20 d with each material treating 95 L of wastewater.

#### 4. Conclusion

In this study we compared macroporous BC to microporous GAC for capacity and efficiency of contaminant removal and nutrient recovery during wastewater treatment. GAC is widely used as an adsorbent material for dissolved contaminants removal from aqueous solution and its superior performance can be attributed to

its high surface area and micro-porosity. However, in a complex wastewater environment micropores can become blocked by larger organic matter or biofilm, quickly losing its advantage if contaminants cannot reach the internal pore structure. Data from batch adsorption studies showed that BC has a significantly higher adsorption capacity for COD<sub>T</sub>, PO<sub>4</sub>, and NH<sub>4</sub> at high concentrations. The superior performance of BC for the treatment of high COD<sub>T</sub> wastewater (>500 mg L<sup>-1</sup>) was also observed during column treatment studies. These data strengthen the concept that macroporosity avoids clogging and the blocking of smaller micropores thereby can result in higher overall adsorption capacities, especially in the case of complex wastewaters with high COD<sub>T</sub> and TSS. In addition, each material showed similar and high retention capacities for macronutrients. Given BC's lower cost and history of land application, it is more likely to be used as a soil amendment than GAC. As engineers and scientist look into using carbon based adsorbents in more complex environments, larger pore sizes should be considered to avoid clogging.

#### Competing financial interests

Authors declare no competing financial interests.



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