

Influence of granular activated carbon media properties on natural organic matter and disinfection by-product precursor removal from drinking water

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ABSTRACT

Operational and financial constraints challenge effective removal of natural organic matter (NOM), and specifically disinfection by-product (DBP) precursors, at remote and/or small sites. Granular activated carbon (GAC) is a widely used treatment option for such locations, due to its relatively low maintenance and process operational simplicity. However, its efficacy is highly dependent on the media capacity for the organic matter, which in turn depends on the media characteristics.

The influence of GAC media properties on NOM/DBP precursor removal has been studied using a range of established and emerging media using both batch adsorption tests and rapid small-scale column tests. DBP formation propensity (DBPFP) was measured with reference to trihalomethanes (THMs) and haloacetic acids (HAAs). All GAC media showed no selectivity for specific removal of precursors of regulated DBPs; DBP formation was a simple function of residual dissolved organic carbon (DOC) levels.

UV₂₅₄ was found to be a good surrogate measurement of DBPFP for an untreated water source having a high DOC. Due to the much-reduced concentration of DBP precursors, the correlation was significantly poorer for the coagulation/flocculation-pretreated water source.

Breakthrough curves generated from the microcolumn trials revealed DOC removal and consequent DBP reduction to correlate reasonably well with the prevalence pores in the 5–10 nm range. A 3–6 fold increase in capacity was recorded for a 0.005–0.045 cm³/g change in 5–10 nm-sized pore volume density. No corresponding correlation was evident with other media pore size ranges.

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1. Introduction

Granular activated carbon (GAC) is used extensively in drinking water treatment in various roles, including removal of pesticides, heavy metals and other micro-pollutants, and more recently in wastewater reuse (de Almeida Alves et al., 2019; Hoslett et al., 2018; Sun et al., 2018). The process is also frequently applied downstream of conventional coagulation/clarification for supplementary removal of natural organic matter (NOM) and to improve the bio-stability of the water, through removal of assimilable dissolved organic carbon (DOC) (Bhatnagar and Sillanpää, 2017; Graf et al., 2014; Velten et al., 2011; Liao et al., 2019). It may also be

employed at the beginning of the water treatment works (WTWs) as a “roughing” filter to aid with NOM and pesticide removal (Ratnayaka et al., 2008; Reckhow and Singer, 2010; Zeng et al., 2019).

One of the key drivers for NOM removal is the reduction of disinfection by-product (DBP) forming compounds following chemical disinfection (Ndiweni et al., 2019), expressed as the formation propensity (hence DBPFP). The trihalomethanes (THMs) and haloacetic acids (HAAs) have been the most extensively studied DBPs since they are usually present at the highest mass concentration (Gibert et al., 2013; Golea et al., 2017). In the EU, currently only THMs are regulated, with the maximum permissible combined concentration being 100 µg/L. Limits of 80 µg/L or 60 µg/L for 9 or 5 HAAs respectively are currently under consideration in the EU, in alignment with US regulations (USEPA, 2010).

NOM is substantially removed by coagulation/clarification in

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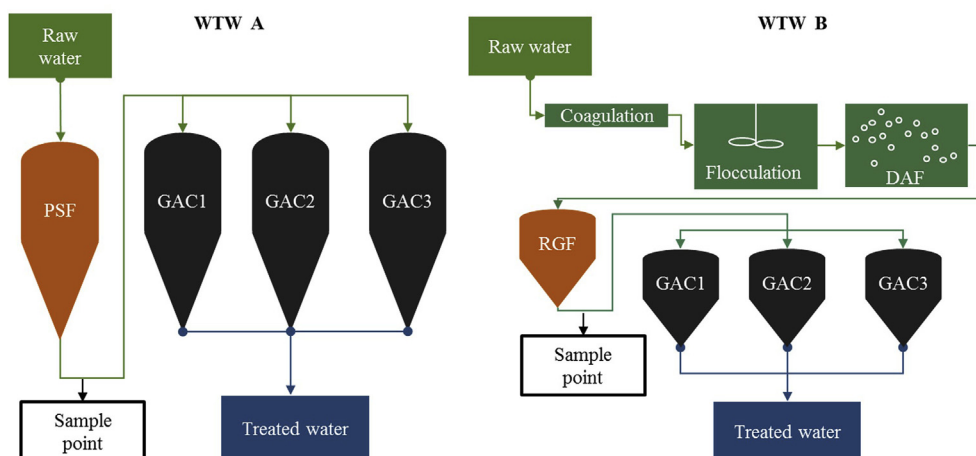


Fig. 1. Water treatment flow sheet at the 2 WTWs featuring rudimentary and advanced pretreatment respectively. WTW A: Pressure sand filtration; WTW B: Coagulation/flocculation, dissolved air flotation and rapid gravity filtration.

large-scale potable WTWs, provided rigorous monitoring and control is applied. However, this process is not always appropriate at small scale in remotely located sites where low-maintenance processes are preferred to reduce labour costs. These include membrane and adsorption technologies, with GAC sometimes favoured on the basis of cost effectiveness and versatility (Bhatnagar and Sillanpää, 2017; Iriarte-Velasco et al., 2008). It is known that the high molecular weight (MW) hydrophobic (HPO) NOM fraction is readily removed by conventional coagulation, such that the influent NOM to GAC processes in secondary potable treatment stages is usually dominated by the low MW and relatively hydrophilic (HPI) fractions (Matilainen et al., 2006). The HPO fraction is generally more reactive with chlorine, with thus a high DBPFP (Golea et al., 2017). When GAC is used as a roughing filter, the main loading of NOM is from HPO and high MW organic compounds. In this case, high MW NOM can block the pores of the adsorbent, preventing other compounds from accessing the adsorbent. The NOM characteristics and the corresponding required GAC media properties are thus influenced by the position of the adsorption process in the treatment scheme (Valdivia-García et al., 2016).

One of the most significant GAC media properties is pore size (d_p) distribution; the useful pore size range for NOM has been shown to be the secondary micropores (1–2 nm) and the mesopores (2–50 nm), with pores smaller than 1 nm offering negligible adsorption (Dastgheib et al., 2004; Velten et al., 2011). High MW (1–10 kDa) NOM such as humic substances with molecular diameters above 2 nm are adsorbed largely within the mesopores. However, adsorption is not solely governed by bulk physical properties, since physicochemical properties – and specifically surface charge and hydrophobicity – also impact on adsorption; HPO NOM is preferentially removed over hydrophilic material. It thus follows that the low MW hydrophilic fraction, whilst less reactive with chlorine, poses the greatest challenge to removal by GAC and may still have a sufficiently high DBPFP to be problematic (Golea et al., 2017).

Given the above challenge presented by NOM removal by GAC it is of interest to determine (a) the most effective GAC media for DBP precursor removal from different water sources and (b) the most effective position of the GAC process in the treatment train. Previous studies of GAC adsorption of NOM have tended to focus on physicochemical characteristics of the NOM, rather than those of the GAC (Aschermann et al., 2018; Shimabuku et al., 2017; Velten et al., 2011), with this work including the key area of competitive adsorption/desorption of NOM and micro-pollutants (Aschermann

Table 1
Physicochemical characteristics of the two different water sources.

Parameter	Water A	Water B
pH	6.8	8.1
DOC (mg/L)	5.98	3.12
UV ₂₅₄ (L/cm)	0.254	0.068
SUVA (mg/L/m)	4.25	2.18
tTHM (μg/L)	676.3	282
THMFP (μg/L per mg DOC)	113.1	90.4
tHAA (μg/L)	1006.4	126
HAA ₅ FP (μg/L per mg DOC)	168.3	40.4
Colour (mg/L Pt/Co)	33	4.47
Turbidity (NTU)	0.37	0.1
Conductivity (μS/cm)	166	569
HPO (mg/L)	3.44	1
TPI (mg/L)	1.25	0.71
HPI (mg/L)	0.37	1.05

et al., 2018; Piai et al., 2019). However, there have thus far been few studies quantitatively correlating NOM or DBPFP adsorption with media characteristics. Those studies that have encompassed GAC media with a range of pore sizes (Gui et al., 2018) have not quantitatively correlated media capacity with pore-related parameters.

The current study correlates GAC properties, specifically the media pore size distribution, with NOM and DBPFP removal from two water sources having differing NOM chemistry with reference to DBPFP. Tests encompassed both batch adsorption measurements and small-scale media column tests for determining adsorption capacity, and DBPFP both as trihalomethanes (THMFP) and haloacetic acids (HAAFP). Outcomes can then be expected to (i) inform decisions regarding GAC media selection for NOM removal, and (ii) direct developments on novel adsorptive media for maximum NOM capacity.

2. Methods and materials

2.1. Sampling

Source water was taken from two WTWs of differing process configuration (Fig. 1). WTW A employs simple media filtration via a pressurised sand filter (PSF) followed by GAC adsorption. WTW B uses clarification by conventional coagulation-flocculation followed by dissolved air flotation (DAF), rapid gravity filtration (RGF) and GAC adsorption. The water used in the current study was

Table 2

The physicochemical properties of the media used for removal of NOM from two different water sources.

GAC media	V_{total}^a cm ³ /g	d_p nm	$V_{micropores}^b$ cm ³ /g	$V_{meso-pores}^c$ cm ³ /g	DFT area (m ² /g) ^d			Granulation ^e mm	$S_{BET,s}^e$ m ² /g	S_{BET}^e m ² /g	IN ^{e,f} mg/g	Precursor ^e
					0.7–1.7	1–2	>2					
COL-L900	0.460	≤26.1	0.347	0.112	444	506	72	0.425–1.70	900–1000	977 ± 5	900	Bituminous coal
F400	0.442	≤26.1	0.271	0.073	431	416	49	0.425–1.70	1050	1032 ± 5	1050	Bituminous coal
208EA	0.517	≤16.1	0.301	0.120	424	465	67	0.6–1.7	1000	1078 ± 6	1000	Coal
XC30	0.511	≤26.1	0.205	0.156	325	340	66	0.6–2.36	1000	986 ± 6	950	Coal
DEO	0.331	≤27.3	0.174	0.013	274	285	8	0.6–1.70	800	809 ± 11	825	Coconut shell
HT5	0.581	≤27.3	0.401	0.029	621	652	14	0.42–1.70	1400	1419 ± 12	1300	Coconut shell
FY5	0.400	≤16.1	0.288	0.004	452	471	3	1.40–3.35	1150	1043 ± 11	1100	Coconut shell
Brimac	0.430	≤25	0.246	0.131	334	373	62	0.7–2.38	200	841 ± 3	700	Bovine bones

^a According to DFT (density functional theory), determined to <30 nm.^b 1–2 nm pore size range.^c >2 nm pore size.^d With reference to pore size range indicated.^e Data sourced from supplier technical sheets.^f Iodine number.

sampled from the filtrate, i.e. downstream of the PSF stage at the WTW A site (Water A) and the RGFs at WTW B (Water B).

2.2. GAC media

GAC media sourced from four different precursor materials were used, selected to encompass a range of specific surface areas and d_p values, and comprised:

- Bituminous coal: COL-L900 (Carbon-Activated LTD, Bristol, UK); Filtrasorb F400 (Chemviron, Tipton, UK).
- Coal: 208EA (Chemviron); Hydriffin XC30 (Donau Carbon, Frankfurt, Germany).
- Coconut shell: DEO, HT5 (Eurocarb, Bristol, UK); FY5 (CPL Carbon Link, Wigan, UK)
- Bovine bones: Brimac (Inverclyde, UK).

2.3. GAC preparation

For the batch adsorption isotherm tests, the GAC media was crushed and fractionated by sieving to generate a 38–90 µm size fraction. The media were then washed thoroughly in ultrapure water, dried overnight at 105 °C and kept in a desiccator until use for the adsorption capacity batch tests. For the rapid small-scale column test (RSSCT), the GAC was crushed using a hammer mill, and then sieved to between 212 and 300 µm, yielding a column diameter:grain size ratio of >30:1 and so avoid channelling effects. The media were then rinsed and dried as with the isotherm tests (Philippe et al., 2010), then re-wetted prior to testing by boiling in DI water for 10 min. Media preparation in this manner has been shown to have no significant impact on the internal structural pore features (Ando et al., 2010).

2.4. GAC characterisation using N₂ pore size distribution

The total pore volume V_{total} of the dried media was measured as the adsorbed volume of N₂ gas near the saturation volume ($P/P_0 = 0.98$) (Iriarte-Velasco et al., 2008), and the surface area calculated from Brunauer–Emmett–Teller (BET) theory (Brunauer et al., 1938). The d_p distribution was determined using density functional theory (DFT) for pores sizes quantified between 0.7 and 36 nm (Velten et al., 2011). The DFT model was employed to provide a more accurate interpretation of the isotherm data for non-homogenous liquids on microporous materials (Lastoskie et al., 1993). Calculations assumed a graphite structure with slit-like

pore geometry (Iriarte-Velasco et al., 2008; Moore et al., 2001) using an ASAP 2010 (Micrometrics, St Andrews, UK) physisorption apparatus. GAC were primarily characterised by the volume of the secondary micropores (1–2 nm) and mesopores (2–50 nm), since smaller pores have been shown to exhibit negligible adsorption of NOM (Velten et al., 2011). Further analysis of the d_p distribution was undertaken to correlate specific pore size ranges with removal of NOM, with a maximum measured pore size of 30 nm.

2.5. Adsorption capacity batch tests

The prepared media were dosed at 0–0.1 g/L, with dose modulated based on the DOC of the source water, and agitated continuously in an orbital shaker at 200 rpm for 24 h at 20 °C, which preliminary trials established was a sufficient period for equilibration. The water samples were then 0.45 µm-filtered prior to analysis. The equilibrium adsorption capacity (q_e , mg DOC/g adsorbent) was calculated as the change in solution DOC concentration $C_i - C_e$, C_i being the initial and C_e the equilibrium concentration, divided by the adsorbent concentration D_0 . Base D_0 values of 150 and 50 mg/L for Water A and B respectively were established as being appropriate for removing significant organic matter whilst still leaving a sufficient (>1 mg/L) residual DOC concentration to permit subsequent THMFP and HAAFP analysis. All tests were carried out in duplicate.

2.6. Rapid small-scale column tests

1000 L samples of water were taken from WTW A and B and were passed through media beds of 15 mm diameter and 140 mm height for 14 days. The RSSCT columns were undertaken according to the recommendations of Crittenden et al. (2012), following the proportional intra-particle diffusivity (PD) model:

$$\frac{EBCT_{SC}}{EBCT_{LC}} = \frac{d_{G,SC}}{d_{G,LC}} = \frac{t_{SC}}{t_{LC}} \quad (1)$$

$$M_{SC} = EBCT_{LC} \times \frac{d_{p,SC}}{d_{p,LC}} \times Q_{SC} \times \rho_{LC} \quad (2)$$

where $EBCT_{LC}$ = empty bed contact time in full-scale adsorber; $EBCT_{SC}$ = empty bed contact time for small experimental columns; $d_{G,SC}$ = diameter of GAC particles in small column; $d_{G,LC}$ = diameter of GAC particles in full scale column; t_{SC}/t_{FS} = time required to conduct a small-scale test (t_{SC}) relative to the time necessary to conduct a large-scale test (t_{FS}); M_{SC} = the mass of media in the small

Table 3

Volumetric pore size distribution, determined from DFT for pores sizes <30 nm.

Media/pore size:	<0.7 nm	0.7–5 nm	5–10 nm	10–15 nm	15–20 nm	20–25 nm	25–30 nm	Total
Col-L900	0.001	0.440	0.011	0.006	0.002	0.001	0	0.460
F400	0.055	0.375	0.010	0.002	0	0	0	0.442
208EA	0.096	0.386	0.027	0.008	0.001	0	0	0.517
XC30	0.115	0.314	0.042	0.018	0.012	0.009	0.001	0.511
DEO	0.144	0.183	0.001	0.002	0.000	0	0	0.331
HT5	0.151	0.417	0.005	0.004	0.003	0.002	0	0.581
FY5	0.108	0.291	0	0.001	0	0	0	0.400
Brimac	0.053	0.316	0.029	0.016	0.010	0.007	0	0.430

column; Q_{SC} = the flow in the small column; ρ_{LC} = density of the GAC media in the large column. Equation (2) was used to ensure that the different GAC media densities were accounted for.

For NOM removal, the PD approach has proven to work well since the relatively high MW organic matter diffuses significantly faster into the pores of the GAC when compared to micropollutants (Summers et al., 1995). Scaled from an operational empty bed contact time of 20 min for full scale adsorbers as typically used in Scottish Water (EBCT_{LC}), this translated to an EBCT in the experimental columns (EBCT_{SC}) of 4.24 min for a 25 mL bed volume.

2.7. Sample chlorination and DBP formation potential determination

250 mL water samples were diluted to a concentration of 1 mg C/L and buffered to pH 7 and dosed with NaOCl at a Cl₂:DOC weight ratio of 5:1. Samples were then sealed and stored in the dark at a temperature of 25 °C for seven days. The chlorine was then quenched with excess sodium thiosulphate and the THM and HAA concentrations measured. The total THM concentration (tTHM) was measured using gas chromatography spectrometry with headspace

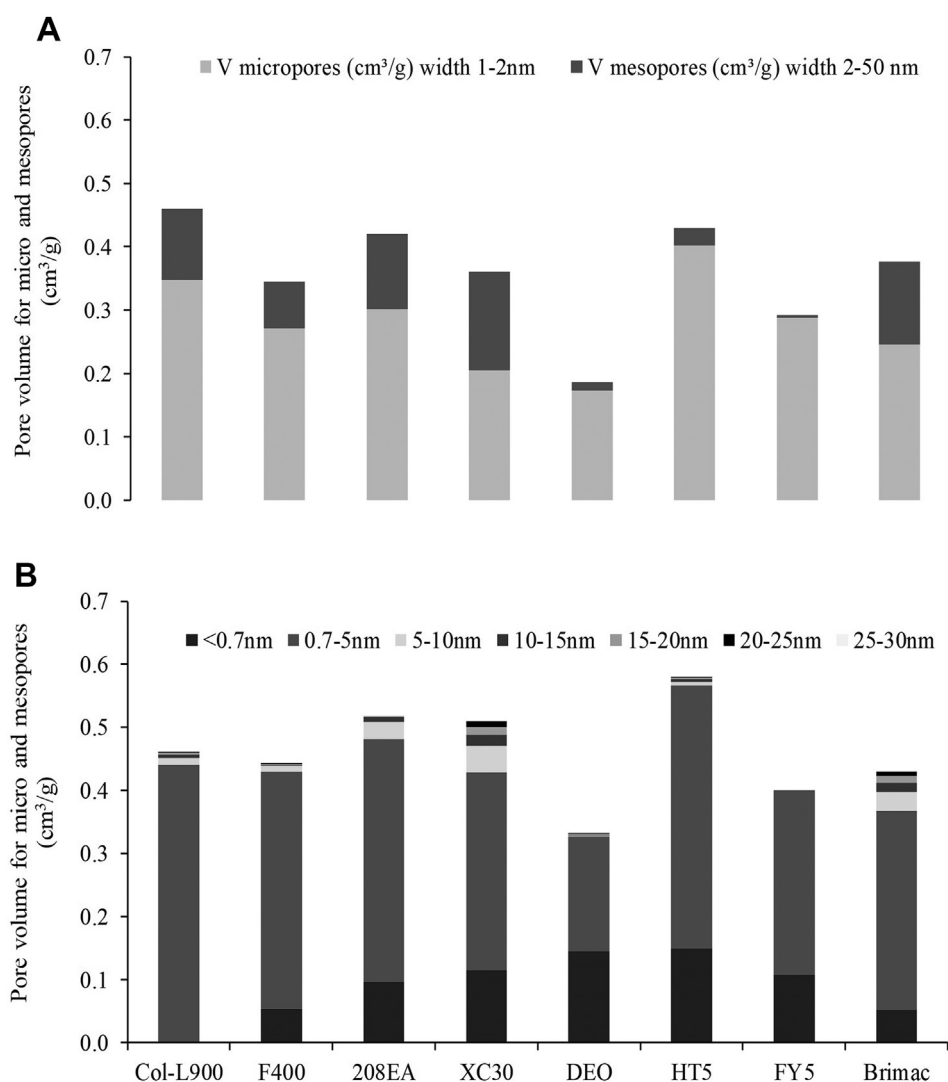


Fig. 2. GAC pore volumes for (a) the micro (1–2 nm) and mesopores (2–50 nm) pore size, and (b) the full distribution of pore sizes.

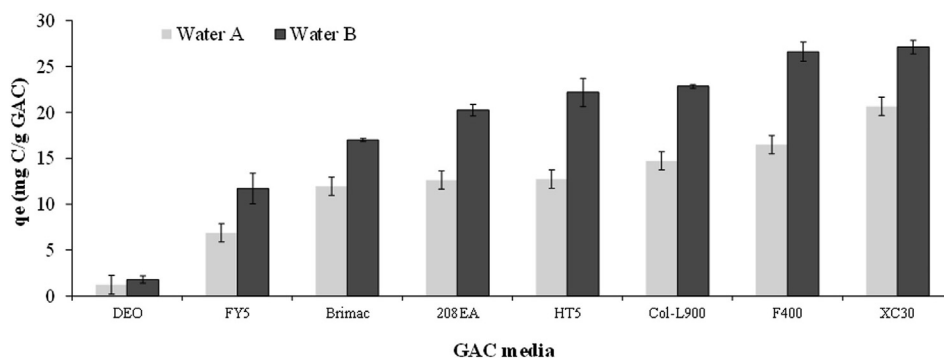


Fig. 3. Organic carbon capacity (q_e) of the 8 media.

injection using the standard USEPA 551 method (USEPA, 1998). The total concentration of the five most predominant HAAs (tHAA₅) was measured using liquid-liquid separation and analysis by gas chromatography with mass spectrometric detection following the USEPA method 552.3 (APHA, 2012), with at least seven injections undertaken for each measurement.

3. Results and discussion

3.1. Source water characterisation

Sample filtrate water quality varied significantly between the two sites (Table 1) due to the differences in pre-treatment, *Water B* samples receiving full clarification cf. *Water A* which was treated only by sand filtration (Fig. 1). Whilst the pH and conductivity values were both lower for the *Water A* samples (6.8 and 166 μ S/cm, cf. 8.1 and 569 μ S/cm for *Water B*), reflecting the reduced chemical addition, the DOC of *Water A* was double that of *Water B* and the UV₂₅₄ absorption 3.8 times higher. UV₂₅₄ absorption is recognised as broadly reflecting the HPO content of the water (Bhatnagar and Sillanpää, 2017), which was commensurately 3.4 times higher for *Water A*. Conversely, the HPI content was 2.8 times lower. The elevated DOC and HPO concentrations of *Water A* were reflected in THMFP and HAA₅FP values, respectively 1.25 and 4.2 times higher on average for *Water A* cf. *Water B*. These factors increased to 2.4 and 8 respectively under worst-case conditions. No significant change in the distribution of individual DBP species was observed between the two samples, with trichloromethane being the predominant THM (85–90% by weight) and the dichloroacetic and trichloroacetic acids making up 80–85% of the tHAA₅ concentration in both cases.

3.2. Physical media characteristics

Total pore volumes ranged from 0.331 (*DEO*) up to 0.581 cm³/g (*HT5*) for the GAC media investigated. Mesopore volumes measured for the GAC media studied ranged from as low as 0.004 cm³/g (*FY5*) up to 0.156 cm³/g (*XC30*). The secondary micropores were between 0.174 cm³/g (*DEO*) and 0.401 cm³/g (*HT5*) (Table 2). None of the media had d_p values above 27.3 nm. The media with the highest total pore volume (*HT5*) had pores that were predominantly in the 1–2 nm pore size range (0.401 cm³/g). The media with the most evenly distributed pore sizes was the coal media *XC30* with 0.205 (57%) and 0.156 (43%) cm³/g distributed between micro and mesopores respectively (Fig. 2). *F400* had a 78:22 distribution of pore volume between the micropore and mesopore size range. Further examination revealed pore size to be predominantly below 5 nm, contributing 84.0–99.9% of the total pore volume (Fig. 2b, Table 3).

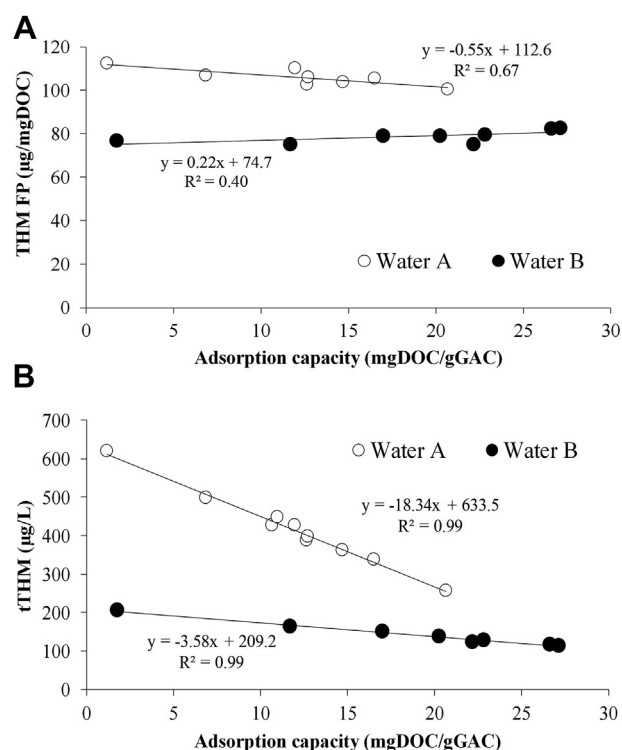


Fig. 4. (a) Normalised THMFP and (b) tTHMs for Waters A and B. Each datum corresponds to a single GAC media.

The media with the highest proportion of small pores (<5) nm were the coconut shell media (*FY5* and *DEO*) at 99.8 and 99.9%. Conversely, the GAC with the smallest proportion of small pores were the coal-based *XC30* and the bone char media *Brimac*, at 83.9 and 85.7% respectively.

There was good agreement between the specific surface area values measured in the current study (S_{BET}) and those reported by the supplier ($S_{BET,s}$) and other researchers (Table 2). The exception was the S_{BET} for *Brimac* (bone char). For *Brimac*, S_{BET} has been previously reported as being 130–283 m²/g, with a V_{total} of 0.287 cm³/g (Moreno et al., 2010; Nili-Ahmadabadi, 2011), compared to the much higher values of 841 m²/g and 0.430 cm³/g respectively recorded in the current study. For *F400*, there was a small difference in the $V_{micropores}$ measured in the current study (0.271 cm³/g), a value which was 20–33% lower than the 0.30–0.41 cm³/g range previously reported (Summers et al., 2010; Dastgheib et al., 2004, and Gibert et al., 2013, Table 2). Differences are likely to reflect the

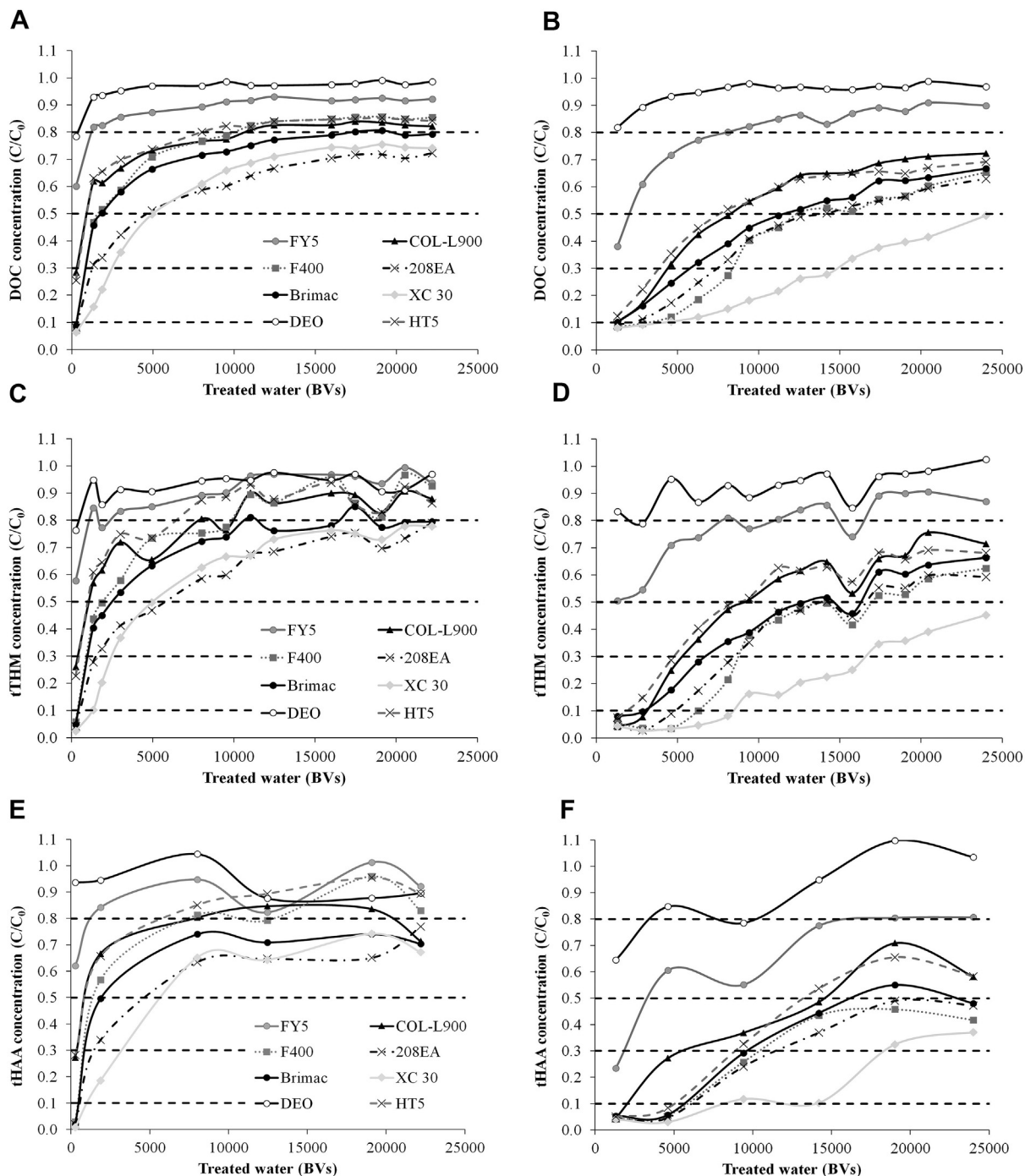


Fig. 5. Removal of (a–b) DOC and precursors of (c–d) tTHM and (e–f) tHAA for waters A (a, c, e) and B (b, d, f), for up to 24,000 bed volumes (BVs) of treated water.

media sample heterogeneity, a point noted by other researchers (Ando et al., 2010) and differences in the range of pore sizes quantified during the analysis. The surface area of the *Brimac* media was nonetheless the lowest measured of all those investigated.

3.3. Batch adsorption isotherms

Batch adsorption isotherms revealed significant differences in DOC capacity across the different media (Fig. 3), with *DEO* having the lowest capacity (1.19 and 1.76 mg/g for Waters A and B respectively) and *XC30* the largest (20.7 and 27.1 mg/g respectively).

The higher capacity for the *Water B* organic matter reflects the impact of the coagulation pre-treatment on the DOC characteristics, which similarly accounts for the difference in THMFP. Increased GAC capacity following coagulation has been noted by Karanfil et al. (1999), and was attributed to the removal of high MW HPO NOM which otherwise cause pore blockage and so reduce media capacity. Two-fold changes in THMFP between raw and treated waters have been previously reported for predominantly upland water samples (Golea et al., 2017).

No selective removal of THM precursors was observed for any of the media, the THMFP values all lying between 100 and 113 μg

Table 4

Throughput to a filtrate DOC of 30%, 50% and 80% of the feed concentration (BV₃₀, BV₅₀ and BV₈₀ respectively) for the GAC media studied by RSSCT, waters A and B, EBCT_{LC} = 20 min.

GAC media	WTW A			WTW B		
	BV ₃₀	BV ₅₀	BV ₈₀	BV ₃₀	BV ₅₀	BV ₈₀
COL-L900	355	946	10,710	4,467	8,284	≥ 23,980
F400	858	1,775	10,030	8,402	12,308	≥ 23,980
208EA	1,301	4,704	≥ 22,194	7,455	13,728	≥ 23,980
XC30	2,514	5,059	≥ 22,194	14,911	23,964	≥ 23,980
DEO	≤ 267	≤ 267	503	≤ 1,302	≤ 1,302	1,302
HT5	355	946	8,047	3,875	7,633	≥ 23,980
FY5	≤ 267	≤ 267	1,242	≤ 1,302	2,041	8,284
Brimac	858	1,775	17,101	5,798	11,657	≥ 23,980

THM/mg DOC for Water A and 75–83 for Water B (Fig. 4a), despite a >10 times change in capacity. THMFP tended to decrease with increasing media capacity regardless of the media characteristics, a trend more readily recognisable from the non-normalised THM concentration data (Fig. 4b). However, no other trend in THM concentration vs bulk media characteristics, specifically *IN* and *S_{BET}*, was evident.

3.4. Rapid small-scale column tests

The breakthrough curves for the individual media inferred relative capacities which generally followed the trends recorded for the batch tests (Fig. 5). Breakthrough curves were steeper for Water A due to the higher organic loading for this source water and the impact of the larger and HPO organic carbon fraction exhausting the GAC surface area.

Overall, the two coal-based media (208EA and XC30) offered the highest capacities, reflected in shallower breakthrough curves. For Water A, the DOC removal efficiency for these media progressively decreased from 92–94% to 25–27% after 22,000 BVs (Fig. 5a), the maximum volume reached for this campaign. For Water B, XC30 provided the shallowest curve, from 92% DOC removal initially to an end value of 50%, with two other coal-based media (F400 and 208EA) removing 90–91% DOC initially and progressively declining to 36–38%.

Differences in performance between Waters A and B again reflect the impact of clarification pre-treatment, which both decreases the DOC concentration and the proportion of the high MW organic compounds which otherwise block the media pores. The lower MW NOM fraction, reported to be in the 0.5–5 nm size range (Dastgheib et al., 2004; Karanfil et al., 1999; Moore et al., 2001; Velten et al., 2011) can then access the media pores (Graf et al., 2014; Iriarte-Velasco et al., 2008) with the 2–50 nm mesopores expected to provide the most accessible adsorption sites for such NOM macromolecules. This was consistent with the two media having the lowest mesopore volumes (FY5 and DEO, derived from coconut shell, with mesopore volumes of 0.004–0.013 cm³/g) offering the lowest DOC removal (Fig. 5b) despite their relatively high surface area (*S_{BET}* values). Conversely, the mesopore volume of the 208EA and XC30 media were amongst the highest of those tested. The Brimac media performed comparatively well for both water sources despite its low *S_{BET}* value due to its high mesopore volume.

The reduction in THMFP (Fig. 5c–d) and HAAs (Fig. 4e–f) generally followed the removal profile of the DOC. There was no indication of selective removal of DBP precursors from either water by any of the GAC media, a result consistent with that observed from the batch experiments.

The throughput to 30, 50 and 80% breakthrough (BV₃₀, BV₅₀ and BV₈₀) of DOC (Table 4) confirm XC30 as achieving the highest BV₃₀

for both water sources. For Water A, XC30 treated almost double the amount of water (2514 BVs) than the next best GAC (208EA), and respectively three and seven times more water than Brimac and the best coconut shell-based media HT5. The Brimac GAC performed at a similar level to the F400 media. Both FY5 and DEO failed to achieve a quantifiable BV₃₀ due to rapid exhaustion at <267 BVs, the point when the first sample was taken. The same order of removal was seen when the BV₅₀ was considered, although the differences were less pronounced, with the best performing media being XC30 with a BV₅₀ of 5059 compared with only 946 BVs for HT5. The BV₈₀ indicated more significant differences between the media, with no BV₈₀ value obtained after 23,980 BVs for two of the media (XC30 and 208EA) for Water A indicating removal was always >20%. This compares with a BV₈₀ of only 503 for DEO. For the other GAC, Brimac treated 40% more water than F400, while COL-L900 treated the same number of BVs as HT5 (946).

For Water B, XC30 was again the best performing media with a BV₃₀ of 14,911, a value substantially higher than the next best GAC F400, having a BV₃₀ of 8,402. No BV₃₀ value was recorded for DEO and FY5 since the 30% target was exceeded before the first sample taken at 1,302 BVs. This was also the case for the BV₅₀ value for DEO, whereas the corresponding value for FY5 was 2,041. This value was less than 10% of the BV₅₀ values recorded for XC30. All media other than FY5 and DEO removal achieved removal exceeding 20% throughout the run, thus providing no measurable BV₈₀, with XC30 maintaining ≥50% removal.

3.5. UV₂₅₄ for monitoring of DBP formation propensity breakthrough

It is of practical significance to correlate DBP breakthrough with a more readily monitored water quality determinant, such as UV₂₅₄ absorbance. UV₂₅₄ is widely acknowledged as being a reasonable analogue measurement for DBPFP due to its association with the more labile HPO organic content of the NOM (Bougeard et al., 2010; Karapinar et al., 2014). Breakthrough data based on number of BVs passed recorded for 10, 30 and 50% breakthrough (BV₁₀, BV₃₀, and BV₅₀ respectively) for Waters A and B (Fig. 6) indicate a consistently better correlation for the former. R² values range from 0.98 to 1.00 for Water A data, compared with 0.75–0.99 for Water B. This is a consequence of the increased HPO content of the DOC in Water A compared with Water B, which was subject to pre-clarification. Similar increases in DBPFP data scatter for residual DOC following clarification have been reported by Golea et al. (2017).

However, the slope for these correlations varies significantly across the different data sets, from 0.99 to 1.36 for Water A and 0.52–1.09 for Water B with no pattern evident. This may reflect the vagarious nature of the reactivity of the organic carbon, as noted by previous authors (de la Rubia et al., 2008; Golea et al., 2017). Thus, whilst UV₂₅₄ provides a reasonable representation of DBPFP for both raw and treated waters, and is apparently unaffected by the GAC media characteristics, the coefficient is dependent on the DOC characteristics.

3.6. Correlation of DOC removal with GAC characteristics

A consideration of the impact of media characteristics on the removal of DOC and THMFP from the RSSCTs (Fig. 7) indicates a reasonable correlation of the BV₃₀ and BV₅₀ data for both DOC and tTHM concentration with the absolute pore volume density for the 5–10 nm pore size range *V_{p,5-10}* (Fig. 7a–b). The tHAA breakthrough data also correlated reasonably with this pore size range (Fig. 7c). Across these 12 data sets R² values ranged from 0.59 to 0.83 for all but the BV₃₀ data set for tTHM breakthrough, for which there was no evident correlation (R² = 0.20). Against this, all correlations

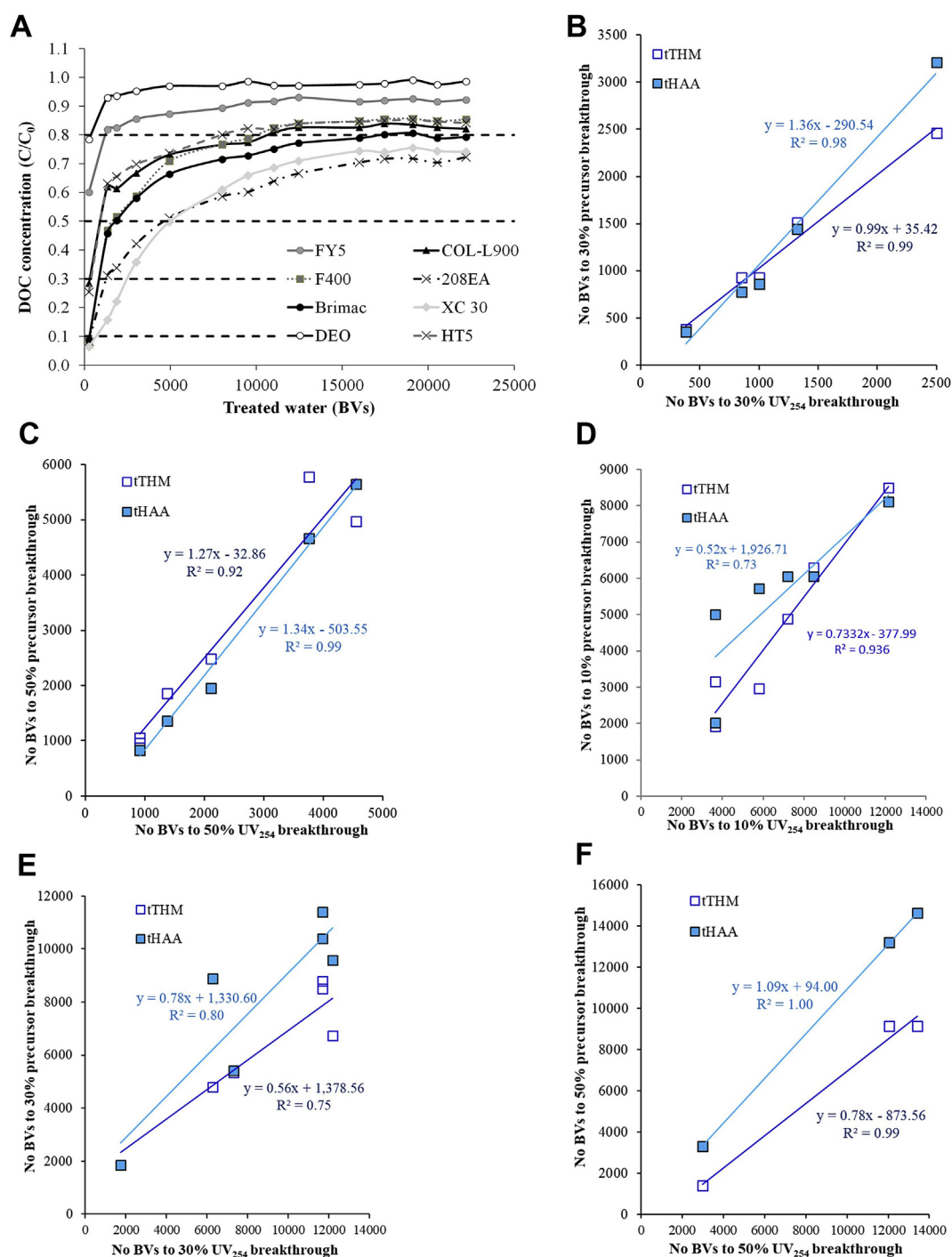


Fig. 6. Correlation of bed volumes passed until target percentage breakthrough is reached, DBP precursor concentration vs. UV_{254} for waters A (a–c) and B (d–f) at 10% (a, d), 30% (b, e) and 50% (c, f) breakthrough. For a single correlation each individual datum relates to a single GAC media.

between the breakthrough BV and pore volume density produced for the other pore size ranges generated R^2 values below 0.27 (Supplementary Information, Table S1). Evidence therefore suggests that removal of NOM-derived DOC, and subsequently the THM and HAA byproducts generated from the residual DOC in the treated water, is primarily a function of the density of 5–10 nm-sized pores in the GAC media. This is a result consistent with that of Velten et al. (2011), who advocated selection of 1–50 nm pore-sized GAC media for NOM removal. The present research suggests that the key pore size range to be 5–10 nm.

The values of the slopes depicted in Fig. 7, i.e. $\Delta BV_{\text{breakthrough}} / \Delta V_{p,5-10}$, provide an indication of the extent to which the practical adsorption capacity of the media is influenced by the 5–10 nm pore volume. Accordingly, in the case of Water A (Fig. 8), the volume treated to 50% breakthrough increases by 105–125 BVs per cm^3/kg 5–10 nm pore volume density based on either DOC or DBPFP concentration. The corresponding range for Water B, for an organic carbon concentration around half that of Water A, is 500–670 BVs per cm^3/kg – the difference being attributable to the pore-blocking effect of the HPO in Water A. In both cases, the tHAA data forms the

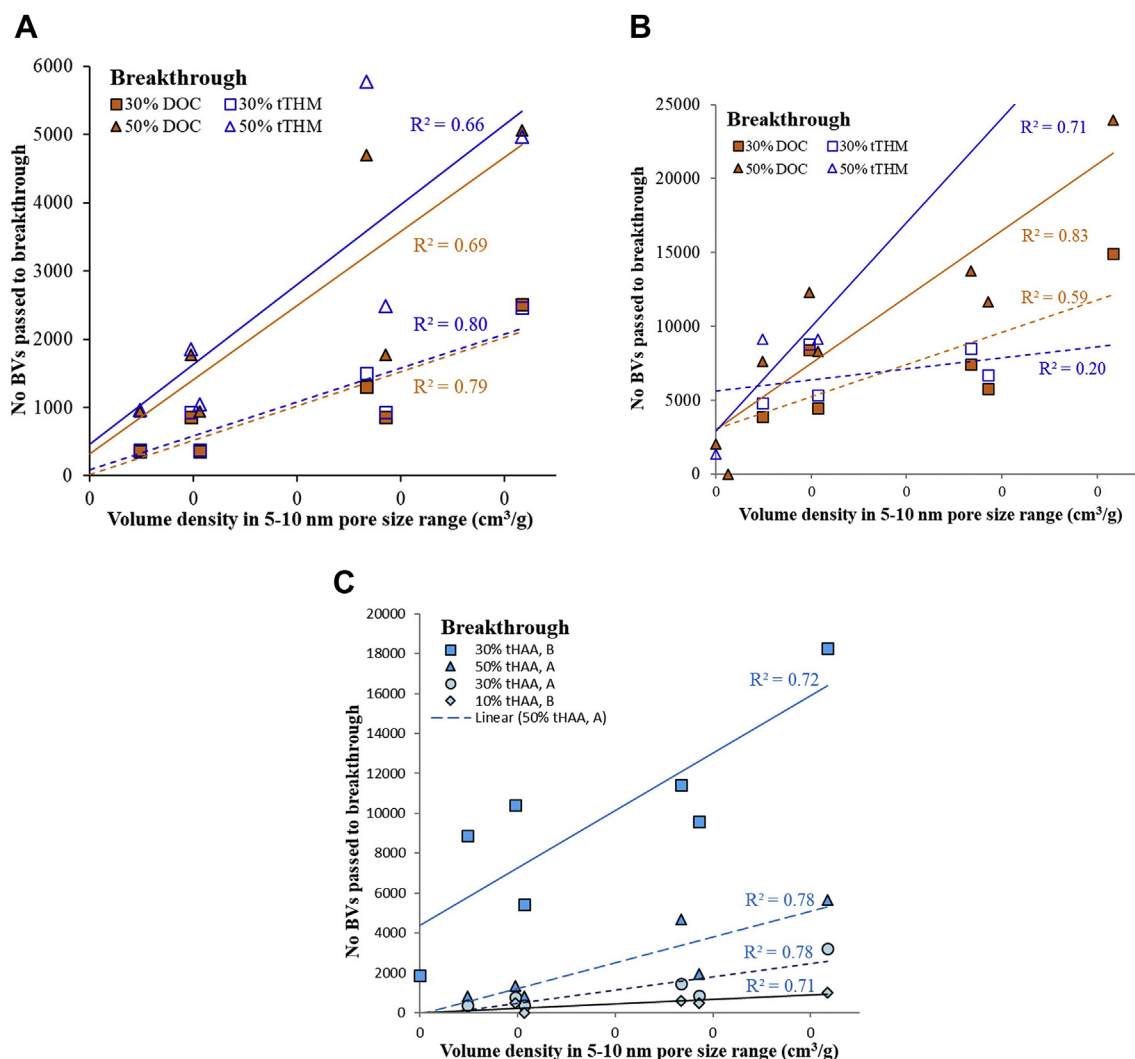


Fig. 7. No. BVs passed to 30% and 50% breakthrough of DOC and tTHMs vs. total volume of pores within 5–10 nm size range for waters (a) A, and (b) B, and for (c) 10–50% breakthrough of THAAs.

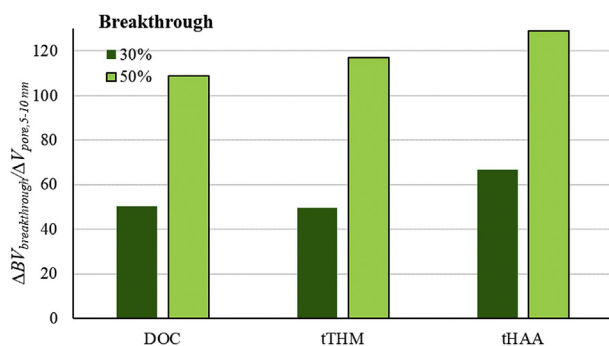


Fig. 8. Values of slopes in Fig. 7a and c, i.e. the change in treated volume to breakthrough as a function of the volume of pores in the 5–10 nm size range ($\Delta BV_{\text{breakthrough}}/\Delta V_{p,5-10}$) in units of BV per cm³/kg, for Water A.

top of the range.

There is evidently a significant influence of the total 5–10 nm pore volume per kg material on the media capacity; 3–6 fold capacity changes arise, the precise value depending on the % breakthrough value, as $V_{p,5-10}$ changes from 0.005 to 0.042 cm³/g. Whilst

previous authors have qualitatively identified the importance of pores above 3 nm in size, specifically for removing humic and fulvic acid-like substances (Gui et al., 2018), the quantification of practical capacity in terms of breakthrough volume against the total volume provided by pores within a specific size range has not previously been reported.

Results are comparable with previous work on NOM removal by GAC, with relatively low water volumes treated prior to significant breakthrough e.g. 50% DOC breakthrough at 5–10,000 BVs for the treatment of water containing ~1 mg/L of DOC (Li et al., 2007; Velten et al., 2011). In comparison, removal of micropollutants normally provides higher removal levels for more sustained periods (e.g. 80% removal of the antibiotic sulfamethoxazole after ~68,000 BVs, Greiner et al., 2018). In the current study most of the media removed 20–30% DOC after extended run times for both water sources, with the most effective media removing >50% DOC after >20,000 BVs for water pre-treated by coagulation. This shows potential for continuous precursor removal, particularly for the two coal-based media and the bone char GAC, provided 20–30% removal is acceptable. However, the relatively fast breakthrough to 50% DOC and tTHM/tHAA for the higher-DOC, substantially untreated water source (Water A) indicated limited capacity for long-

term bulk removal of NOM for source waters having a high DBP-FP. Against this, GAC was found to be an effective polishing process for pre-clarified water (*Water B*), where longer term reduction in DOC and DBP precursors was recorded.

4. Conclusions

Granular activated carbon (GAC) media of various origins (coal, coconut shell and bovine bone), and providing a range of physical characteristics with reference to pore size, have been appraised with reference to their capacity for natural organic matter (NOM). Experiments comprised (a) batch adsorption experiments for determination of equilibrium capacity, and (b) tests on micro-columns to represent capacity under normal operating conditions. Two different water sources were tested, a raw water with rudimentary pretreatment (pressure sand filtration) and one pre-treated by full clarification. The media capacity both for organic carbon and for chlorinated disinfection byproduct formation propensity (DBPFP), with reference to both trihalomethane (THM) and haloacetic acid (HAA) formation, was determined. The applicability of UV₂₅₄ absorption as a surrogate for was also assessed.

Results revealed:

- The 8 media tested were found to have a wide range of pore size distributions and pore volume densities (V_p in cm³/g), specifically within the key range of 5–10 nm ($V_{p,5-10}$).
- There was no evidence of any selectivity for DBPFP removal by any of the media tested: the ratio of THM and HAA concentrations generated from DOC in treated waters did not change significantly between the different media.
- In view of (b) above, UV₂₅₄ provided a reasonable surrogate measurement of both DOC and DBPFP.
- Batch adsorption tests provided a good indicator of media performance in terms of NOM removal: ranking of media capacities from batch testing generated the same sequence as that from microcolumn testing.
- The media capacity, quantified in terms of bed volumes treated to breakthrough, was found to correlate with the pore volume density of the 5–10 nm pores ($V_{p,5-10}$), in terms of pore volume provided per unit mass of media. A 3–6 fold increase in capacity was recorded for a change in $V_{p,5-10}$ from 0.005 to 0.042 cm³/g.
- Correlations were stronger for the water with rudimentary treatment than for the preclarified water due to both its increased organic carbon concentration and the hydrophobic content, the latter having a higher reactivity.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.watres.2020.115613>.

References

- Ando, N., Matsui, Y., Kurotobi, R., Nakano, Y., Matsushita, T., Ohno, K., 2010. Comparison of natural organic matter adsorption capacities of super-powdered activated carbon and powdered activated carbon. *Water Res.* 44 (14), 4127–4136.
- Apha, 2012. *Standard Methods for the Examination of Water and Wastewater*, twenty-second ed. American Water Works Association, American Public Works Association, Water Environment Federation, Washington, DC.
- Aschermann, G., Zietzschmann, F., Jekel, M., 2018. Influence of dissolved organic matter and activated carbon pore characteristics on organic micropollutant desorption. *Water Res.* 133, 123–131.
- Bhatnagar, A., Sillanpää, M., 2017. Removal of natural organic matter (NOM) and its constituents from water by adsorption - a review. *Chemosphere* 166, 497–210.
- Bougeard, C.M.M., Goslan, E.H., Jefferson, B., Parsons, S.A., 2010. Comparison of the disinfection by-product formation potential of treated waters exposed to chlorine and monochloramine. *Water Res.* 44 (3), 729–740.
- Brunauer, S., Emmett, P.H., Teller, E., 1938. Adsorption of gases in multimolecular layers. *J. Am. Chem. Soc.* 60 (2), 309–319.
- Crittenden, J.C., Trussell, R.R., Hand, D.W., Howe, K.J., Tchobanoglous, G., Borchardt, J.H., 2012. *MWH Water Treatment Principles and Design*, third ed. Wiley, New Jersey.
- Dastgheib, S.A., Karanfil, T., Cheng, W., 2004. Tailoring activated carbons for enhanced removal of natural organic matter from natural waters. *Carbon* 42 (3), 547–557.
- de Almeida Alves, A.A., de Oliveira Ruiz, G.L., Campos Martins Nonato, T.C., Müller, L.C., Sens, M.L., 2019. Performance of the fixed-bed of granular activated carbon for the removal of pesticides from water supply. *Environ. Technol.* 40 (15), 1977–1987.
- de la Rubia, A., Rodríguez, M., León, V., Prats, D., 2008. Removal of natural organic matter and THM formation potential by ultra- and nanofiltration of surface water. *Water Res.* 42 (3), 714–722, 2008.
- Gibert, O., Lefèvre, B., Fernández, M., Bernat, X., Paraira, M., Pons, M., 2013. Fractionation and removal of dissolved organic carbon in a full-scale granular activated carbon filter used for drinking water production. *Water Res.* 47 (8), 2821–2829.
- Golea, D.M., Upton, A., Jarvis, P., Moore, G., Sutherland, S.T., Parsons, S.A., Judd, S.J., 2017. THM and HAA formation from NOM in raw and treated surface waters. *Water Res.* 112, 226–235.
- Graf, K.C., Cornwell, D.A., Boyer, T.H., 2014. Removal of dissolved organic carbon from surface water by anion exchange and adsorption: bench-scale testing to simulate a two-stage countercurrent process. *Separ. Purif. Technol.* 122, 523–532.
- Greiner, B.G., Shimabuku, K.K., Summers, R.S., 2018. Influence of Biochar Thermal Regeneration on Sulfamethoxazole and Dissolved Organic Matter Adsorption', *Environmental Science Water Research & Technology*, vol. 4. Royal Society of Chemistry, pp. 169–174.
- Gui, H.J., Li, F.S., Wei, Y.F., Yamada, T., 2018. Adsorption characteristics of natural organic matter on activated carbons with different pore size distribution. *Int. J. Environ. Sci. Technol.* 15 (8), 1619–1628.
- Hoslett, J., Massara, T.M., Malamis, S., Ahmad, D., van den Boogaert, I., Katsou, E., Ahmad, B., Ghazal, H., Simons, S., Wrobel, L., Jouhara, H., 2018. 'Surface water filtration using granular media and membranes : a review'. *Sci. Total Environ.* 639, 1268–1282.
- Iriarte-Velasco, U., Álvarez-Urriarte, J.I., Chimenó-Alanís, N., González-Velasco, J.R., 2008. Natural organic matter adsorption onto granular activated carbons: implications in the molecular weight and disinfection byproducts formation. *Ind. Eng. Chem. Res.* 47 (20), 7868–7876.
- Karanfil, T., Kitis, M., Kilduff, J.E., Wington, A., 1999. Role of granular activated carbon surface chemistry on the adsorption of organic compounds . 2 . natural organic matter. *Environ. Sci. Technol.* 33 (18), 3225–3233.
- Karapinar, N., Uyak, V., Soylu, S., Topal, T., 2014. Seasonal variations of NOM composition and their reactivity in a low humic water. *Environ. Prog. Sustain. Energy* 33 (3), 962–971.
- Lastoskie, C., Gubbins, K.E., Quirke, N., 1993. Pore size distribution analysis of microporous carbons: a density functional theory approach. *J. Phys. Chem.* 97 (18), 4786–4796.
- Li, F., Yuasa, A., Katamine, Y., Tanaka, H., 2007. Breakthrough of natural organic matter from fixed bed adsorbers: investigations based on size-exclusion HPLC. *Adsorption* 13 (5–6), 569–577.
- Liao, X.B., Cheng, Y.S., Liu, Z.H., Shen, L.L., Zhao, L., Chen, C., Li, F., Zhang, X.J., 2019. Performance of BAC for DBPs Precursors' Removal for One Year with Micro-polluted Lake Water in East-China. *Environmental Technology*.
- Matilainen, A., Vieno, N., Tuhkanen, T., 2006. Efficiency of the activated carbon filtration in the natural organic matter removal. *Environ. Int.* 32 (3), 324–331.
- Moore, B.C., Cannon, F.S., Westrick, J.A., Metz, D.H., Shrive, C.A., DeMarco, J., Hartman, D.J., 2001. Changes in GAC pore structure during full-scale water treatment at Cincinnati: a comparison between virgin and thermally reactivated GAC. *Carbon* 39 (6), 789–807.
- Moreno, J.C., Gómez, R., Giraldo, L., 2010. Removal of Mn, Fe, Ni and Cu ions from wastewater using cow bone charcoal. *Materials* 3, 452–466.
- Ndiweni, S.N., Chys, M., Chaukura, N., Van Hulle, S.W.H., Nkambule, T.T.I., 2019. Assessing the impact of environmental activities on natural organic matter in South Africa and Belgium. *Environ. Technol.* 40 (13), 1756–1768.

- Rezaee, A., Ramin, M., Ghanizadeh, G., Nili-Ahmadabadi, A., 2011. Adsorption of *Escherichia coli* using bone char. *J. Appl. Sci. Environ. Manag.* 15 (1), 57–62.
- Philippe, K.K., Hans, C., MacAdam, J., Jefferson, B., Hart, J., Parsons, S.A., 2010. Photocatalytic oxidation, GAC and biotreatment combinations: an alternative to the coagulation of hydrophilic rich waters? *Environ. Technol.* 31 (13), 1423–1434.
- Piai, L., Dykstra, J.E., Adishakti, M.G., Blokland, M., Langenhoff, A.A.M., van der Wal, A., 2019. Diffusion of hydrophilic organic micropollutants in granular activated carbon with different pore sizes. *Water Res.* 162, 518–527.
- Ratnayaka, D.D., Brandt, M.J., Johnson, K.M., 2008. TWORT's Water Supply, sixth ed. Reckhow, D.A., Singer, P.C., 2010. Formation and control of disinfection by-products. In: Edzwald, J.K. (Ed.), *Water Quality & Treatment : A Handbook on Drinking Water: A Handbook on Drinking Water*, sixth ed. McGraw-Hill Publishing, New York. 1–60.
- Shimabuku, K.K., Paige, J.M., Luna-Aguero, M., Summers, R.S., 2017. Simplified modeling of organic contaminant adsorption by activated carbon and biochar in the presence of dissolved organic matter and other competing adsorbates. *Environ. Sci. Technol.* 51 (17), 10031–10040.
- Summers, R.S., Hooper, S.M., Solarik, G., Owen, D.M., Hong, S., 1995. Bench-scale evaluation of GAC for NOM control. *J. AWWA (Am. Water Works Assoc.)* 87 (8), 69–80.
- Summers, R.S., Ph, D., Knappe, D.R.U., Carolina, N., States, U., 2010. Adsorption of organic compounds by activated carbon. In: Edzwald, J.K. (Ed.), *Water Quality & Treatment : A Handbook on Drinking Water: A Handbook on Drinking Water*, sixth ed. McGraw-Hill Publishing, New York, pp. 1–106.
- Sun, Y., Angelotti, B., Brooks, M., Dowbiggin, B., Evans, P.J., Devins, B., Wang, Z., 2018. A pilot-scale investigation of disinfection by-product precursors and trace organic removal mechanisms in ozone-biologically activated carbon treatment for potable reuse. *Chemosphere* 210, 539–549.
- USEPA, 1998. National primary drinking water regulations: disinfectants and disinfection byproducts. U.S. Environmental protection agency. Fed. Regist. 63 (241), 69390–69476.
- USEPA, 2010. Stage 2 Disinfectants and Disinfection Byproducts Rule. Consecutive Systems Guidance Manual. EPA 815-R-09-017.
- Valdivia-Garcia, M., Weir, P., Frogbrook, Z., Graham, D.W., Werner, D., 2016. Climatic, geographic and operational determinants of trihalomethanes (THMs) in drinking water systems. *Sci. Rep.* 6, 35027.
- Velten, S., Knappe, D.R.U., Traber, J., Kaiser, H.-P., von Gunten, U., Boller, M., Meylan, S., 2011. Characterization of natural organic matter adsorption in granular activated carbon adsorbents. *Water Res.* 45 (13), 3951–3959.
- Zeng, J., Chen, S., Wan, K., Li, J., Hu, D., Zhang, S., Yu, X., 2019. Study of Biological Up-Flow Roughing Filters Designed for Drinking Water Pretreatment in Rural Areas: Using Ceramic Media as Filter Material. *Environmental Technology* (in press).