Mesoporous structure regulation of activated carbons and effects on the synergistic efficacy of synchronous adsorption and bio-degradation in biological activated carbon process
Xu-Jin Gong, Yu-Qi Dong and Wei-Guang Li

ABSTRACT
Mesoporous activated carbon MCGL-4 was tailored for simultaneous enhancement of adsorption and bio-degradation by multistage depth-activation (MDA). Synergistic efficacy of synchronous adsorption and bio-degradation was evaluated in pilot-scale bio-enhanced activated carbon (BEAC) system. Results identified that MCGL-4 obtains synchronously well-developed meso- (0.7605 cm³/g), micro- (0.2655 cm³/g) and macro-porous (0.143 cm³/g) structures. Higher volume during 20.4–208.2 Å (0.6848 cm³/g) ensured higher adsorption capacities for natural organic matters (NOM). The initial immobilized biomass and stabilities on MCGL-4 were also significantly promoted. Rapid small-scale column tests system (RSSCTs) tests showed that adsorption capacities for humic-like organics were 67,725.32 mg·DOC/(kg·carbon) at 39.50 m³·H₂O/(kg·carbon). In BEAC system, MCGL-4 achieved higher removal efficiency for fulvic acid, humic acid and aromatic organic matters than commercial carbons. At 39.50 m³·H₂O/(kg·carbon), cumulative uptake of organic-pollutants achieved by MCGL-4 was 94,850.51 mg·DOC/(kg·carbon). The proportion occupied by biodegradation were 31,674.70 mg·DOC/(kg·carbon). It also confirmed that bio-degradation ability was much higher than commercial carbons after mesoporous structures regulation by MDA process.

Key words | activated carbon, adsorption, bio-degradation, bio-enhanced activated carbon (BEAC), natural organic matters, pore-structure regulation

HIGHLIGHTS
- MCGL-4 was tailored for simultaneous bio-enhancement and adsorption by multistage depth-activation.
- MCGL-4 is a promising adsorbent for effective removal of natural organic matters from water.
- MCGL-4 was more conductive to simultaneous biodegradation and adsorption of organic-pollutants.
- Mesopores (20.4 – 208.2 Å) played important role in adsorption of humic-like organics.

NOMENCLATURE

| Symbol | Description |
|--------|-------------|
| KBV    | Volume of water treated by per kilogram of activated carbon (m³·H₂O/(kg·carbon)) |
| S_BET  | BET surface area (m²/g) |
| S микр | t-Plot micropore area (m²/g) |
| V_т   | Total pore volume (cm³/g) |
| V микр | t-Plot micro-porous volume (cm³/g) |
| V мес | Calculated mesoporous volume: V мес = V_т − V микр (cm³/g) |

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Advanced water treatment using activated carbon has been applied worldwide because of the high efficiency and economic performance, such as carbon adsorption (Li et al. 2012; Gong et al. 2015), ozone-biological activated carbon (O3-BAC) (Gao et al. 2010) and bio-enhanced activated carbon (BEAC) (Zhang et al. 2011; Al-Amrani et al. 2012). Bio-enhancement in BEAC process ensured higher purification efficiency and service-life (Piai et al. 2020). The use of BEAC/BAC for removing natural organic matters and toxic xenobiotics is advisable as the final stage of water purification (Smolin et al. 2020). However, tailoring or selecting excellent carbon for BEAC process remains a challenge. The method for the assessment of the contribution of adsorption and bio-degradation in dynamic BEAC/BAC process is also extremely complex (Piai et al. 2020; Smolin et al. 2020; Ti et al. 2020; Zhiteneva et al. 2020).

High adsorption capacities for natural organic matter (NOM) and trace organic-pollutants (TrOPs) require synchronously well-developed micro- and meso-porosity distribution of carbons (Gong et al. 2020). Studies suggested that meso-pores (2–50 nm) and secondary micro-pores (1–2 nm) principally controlled adsorption of NOM from water (Velten et al. 2011). NOM suffered severely competitive adsorption with trace organic-pollutants (TrOPs) on carbon surfaces with primarily small micro-pores (<1.0 nm) (Quinlivan et al. 2005). On the other hand, synchronous adsorption and bio-degradation is the core mechanism of organic-pollutants removal in BEAC process (Velten et al. 2011; Gibert et al. 2012). And it can be significantly affected by pore structure distribution of meso- and macros-pores (Aktas & Cecen 2007).

Therefore, tailoring an efficient carbon with a perfect matching between adsorption and bio-degradation (both biomass and bio-activity levels on carbon surfaces) was a significantly important, and pore structure regulation is the promising way to improve adsorption and bio-degradation efficiency simultaneously (Sulaymon et al. 2010). Studies suggested that carbons with simultaneously well-developed meso- and micro-porous structures may achieve better matching between adsorption and bio-degradation (Singh et al. 2012). However, micro-porous carbons were still commonly employed in drinking water treatment plants (DWTPs) due to the industrialization restriction in China. Research and development of new-type mesoporous carbons was financially supported by the Ministry of Housing and Urban-Rural Development of China in the present work. A series of innovative mesoporous carbons were successfully prepared. However, it is still a challenging work to quantify the effects of pore structure regulation on synergy-effect between bio-degradation and adsorption. Therefore, quantification of adsorption and bio-degradation on new carbons in BEAC/BAC process was also conducted in present work.

**INTRODUCTION**

**MATERIALS AND METHODS**

Activated carbon preparation

Three new carbons were prepared by multi-step procedure in Figure 1, including precursor-blending, re-agglomeration, potassium hydroxide (KOH) impregnation, carbonization and multistage depth-activation (MDA) (Li et al. 2014; Gong et al. 2015a, 2015b). Take carbon MCGL-4 as an example, the detailed preparation parameters were described as the following: coal-blending (35% Taixi coal +30% Shen Fu coal) and coconut shell (30%) were first mixed and crushed to 100–200 mesh. The mixture was agglomerated using refined tar (5%) as agglomerate. The agglomerated material was crushed and screened again to 2–10 mm. Impregnation was conducted before carbonization using 10% KOH (100 rpm, 60 min). Carbonization was consequently conducted at 600 °C in N2 protection environment for 30 min. MDA was conducted in...
activation apparatus, and MDA can be divided into three stages: CO₂ activation (650 °C/30 min), steam activation (900 °C/120 min) and depth-steam activation (950 °C/20 min).

Activated carbon characterization

Nitrogen isotherms were measured by ASAP2020 Sorptometer at 77 K and the specific surface area (S_BET) was calculated by Brunauer–Emmett–Teller (BET) model (Praetorius & Voigt 2015; Spiesshofer et al. 2015; Wang 2016). Pore size distribution/pore volume distribution (PSDs/PVDs) were calculated by t-plot method (Gong et al. 2015). Especially, micro-porous volume (V_micro) was also identified by Horvath-Kawazoe (H-K) model. Mesoporous volume (BJH-V_mes) was calculated by Barrett-Joyner-Halenda (BJH) model (Choi et al. 2015; Haluszka et al. 2015). Adsorption capacities for iodine (V_IN), methylene blue (V_MB) and humic acid(V_HA) were determined according to the National Standards of China (GB/T 7702.7-2008, 7702.6-2008 and 7701.2-2008).

Commercial carbons

Three kinds of commercial carbons in Table 1 were also employed as control group, which were commonly used in a water purification plant in China.

![Figure 1](http://iwaponline.com/ws/article-pdf/21/5/2058/920081/ws021052058.pdf)

**Table 1** Parameters of commercial carbons employed in present work

| Parameters                        | Unit  | SX-10 | F400  | ZJ15  |
|-----------------------------------|-------|-------|-------|-------|
| Specific surface area (S_BET)     | m²/g  | 921   | 1,169 | 924   |
| External surface area (S_Ext)     | m²/g  | 256.3 | –     | 301.39|
| Microporous surface area (S_Micro)| m²/g  | 556.09| 939.5 | 519.17|
| Total pore volume (V_total)       | cm³/g | 0.6536| 0.8963| 0.3714|
| Microporous volume (V_micro)      | cm³/g | 0.2390| 0.4716| 0.2541|
| Mesoporous volume (V_mes)         | cm³/g | 0.2927| 0.3170| 0.042 |
| Macroporous volume (V_macr)       | cm³/g | 0.1219| 0.1077| 0.0753|
| Average pore diameter (D)         | Å     | 26.98 | 28.94 | 18.26 |

Experimental apparatus

Testing apparatus of functional bacteria immobilization

As shown in Figure 2(a), carbons (300 mL) were fixed into conical bottles after steam sterilization, and the empty bed contact time (EBCT) was 30 min. Functional bacteria were enriched from steady BEAC process, mainly contains *Acinetobacter Harbinensis* sp., three strains of *Pseudomonas* sp. and *Bacillus subtilis*. After fermenting, functional bacteria (10⁹ CFU/L) were circularly immobilized onto carbons (24 h). Biomass (phospholipid contents) on different carbons was determined at different times.
Utilization rates of dissolved oxygen (DO) during biodegradation by different carbons were determined using apparatus in Figure 2(b) in both adsorption system (column A) and bio-enhancement system (column B with functional bacteria immobilization). The influent raw water was sterilized by ultraviolet and fully aerated. Dissolved organic carbon (DOC) and NH$_4^+$-N were adjusted to 4.0 ± 0.25 mg/L and 0.50 ± 0.16 mg/L, respectively, using sodium acetate and ammonium chloride. After stable operation for a week, changes of DOC, DO and NH$_4^+$-N were determined for 5 days, using HQ30D portable DO analyzer and TOC analyzer (TOC-VCPH).

Herein, bio-degradation can be ignored in column A and the DOC and NH$_4^+$-N removal can be attributed to
adsorption, rather than bio-degradation. And DO consumption in column A can be defined as \( \Delta \text{DO}_{\text{CS}} \) (surface affinity for DO by adsorption process). Therefore, utilization efficiency of DO which was caused by surface bio-degradation in column B can be calculated using as following Equations (1)–(8):

| No. | Equations | Units | Annotation |
|-----|-----------|------|------------|
| (1) | \( \Delta \text{DO}_{\text{CS}} = \text{DO}_{A1} - \text{DO}_{A2} \) | mg/L | Surface affinity for DO by adsorption in column A |
| (2) | \( \Delta \text{DOC}_{\text{bio}} = \Delta \text{DOC} - \Delta \text{DOC}_A \) | mg/L | DOC removal by bio-degradation in column B |
| (3) | \( \Delta \text{N}_{\text{bio}} = \Delta (\text{NH}_4^+ - N)_B - \Delta (\text{NH}_4^+ - N)_A \) | mg/L | NH\(_4\)-N removal by bio-degradation in column B |
| (4) | \( \Delta \text{DO} = 2.66\text{mg} \cdot \text{O}_2/\text{mg} \cdot \text{DOC} \times \Delta \text{DOC}_{\text{bio}} \) | mg/L | Theoretical amount of DO required for DOC degradation |
| (5) | \( \Delta \text{D}O_N = 4.33\text{mg} \cdot \text{O}_2/(\text{mg} \cdot \text{NH}_4^+ - N) \times \Delta \text{N}_{\text{bio}} \) | mg/L | Theoretical amount of DO required for NH\(_4\)-N degradation |
| (6) | \( \Delta \text{DO}_{\text{TH}} = \Delta \text{DOC} + \Delta \text{DO}_N + \Delta \text{DO}_{\text{CS}} \) | mg/L | Theoretical consumption of DO in column B |
| (7) | \( \Delta \text{D}O_R = \text{DO}_{B1} - \text{DO}_{B2} \) | mg/L | Actual consumption of DO in column B |
| (8) | \( P\text{ADO} = \frac{\Delta \text{DO} + \Delta \text{DO}_N}{\Delta \text{DO}_R} \times 100\% \) | % | Actual effective utilization rate of DO by bio-degradation |

**Pilot-scale column testing system (BAC/BEAC process)**

As shown in Figure 2(c), pilot-scale BAC/BEAC system (1.0 m\(^3\)·h\(^{-1}\)) and rapid small-scale column tests system (RSSCTs) were established, treating water from Songhua River. Influent water was pre-treated by coagulation, inclined-tube sedimentation and rapid sand filtration. Pilot-scale BEAC system contains three parallel columns (φ50 mm × 2.10 m), packed with 1.20 m carbon bed and operated in up-flow mode (184 L/d). After enrichment and domestication, cyclic immobilization of the dominant functional in BEAC columns was conducted according to the methods described by Zhang et al. (2021). Ultraviolet sterilization (100 W·m\(^{-2}\)) was employed in raw water tank to minimize the bacteria interference. Difference between BAC and BEAC system was the formation of bio-degradation. Bio-degradation formed naturally during operation. Therefore, there was no ultraviolet sterilization in the raw tank. Operation parameters and influent water qualities of BEAC and BAC system are summarized in Table 2.

**Rapid small-scale column tests (RSSCTs) system**

RSSCTs system was established according to the dispersed flow pore surface diffusion model using EBCT and hydraulic loading to describe the adsorption process (Greenwald et al. 2015). RSSCTs can obtain breakthrough curves in a fraction of the time with a fraction of water (Sperlich et al. 2003). It was consequently employed to quickly quantify adsorption capacities and parameters are summarized in Table 2. Carbon samples were pre-treated as follows: (1) carbons were thoroughly washed with deionized water until all dust was removed and the pH of the wash water was steady; (2) well-washed carbons were dried at 150 °C for 4 h; (3) carbon water slurry was heated to boiling for 30 min and loaded into the column after cooling to room temperature. The feed water qualities were listed in Table 2.

**Sampling and analysis**

Removal efficiencies of DOC and UV\(_{254}\) were determined in pilot-scale and RSSCT system. Three-dimensional

*Table 2* | Operational parameters and feed water qualities of PCT and RSSCT system

| Parameters | Pilot system | RSSCT system |
|------------|--------------|--------------|
| Granule size (mm) | 0.60–2.50 (1.50) | 0.21 |
| Empty bed contact time (EBCT) (min) | 20 | 0.40 |
| Flow rate (m\(^3\)/d) | 0.185 | 0.064 |
| Filtering velocity (m/h) | 5.9 | 27.86 |
| Height (m) | 2.10 | 0.35 |
| Carbon bed depth (m) | 1.20 | 0.24 |
| Column diameter (cm) | 5 | 1.1 |
| Temperature (°C) | 15.45 ± 7.93 | 17.10 ± 3.59 |
| DOC(mg/L) | 3.28 ± 0.47 | 3.20 ± 0.15 |
| UV\(_{254}\) (cm\(^{-1}\)) | 0.078 ± 0.015 | 0.074 ± 0.012 |
| Turbidity (NTU) | 0.58 ± 0.16 | 0.35 ± 0.11 |
fluorescence spectra (3D-EEM) of water samples were scanned with 5 nm increments by a fluorescence spectrophotometer (FP-6500) (Gong et al. 2015). Gas chromatography-mass spectrometry analysis (GC-MS) was performed using chromatography-mass spectrometer (6890GC-5973/5975MSD).

**Cumulative uptake of micro-pollutants**

The concentration levels of micro-pollutants (DOC) were reported as functions of the operational time and water volume fed to carbon columns divided by mass of GAC (KBV). The KBV can be described by the following equation:

\[
KBV = \frac{V_{Treated}}{M_{AC}} = \frac{N \cdot Q_{in}}{1000 \cdot M_{AC}}
\]  
(9)

The KBV of pilot-scale system reached up to 39.50 m³·H₂O/(kg·carbon) and it was equivalent to 246 days of operation. Performance of micro-pollutants removal from water by carbons in BEAC/BAC and RSSCTs system was also represented by the cumulative uptake DOC (QC) as a function of KBV.

\[
QC = \frac{Q_{in}}{2M_{AC}} \cdot \sum_{i=1}^{n} \Delta t_i \cdot \left[ (DOC_{in})_i^{Mn} + DOC_{in}^{Mn} - (DOC_{out})_i^{Mn} + DOC_{out}^{Mn} \right]
\]  
(10)

**RESULTS**

**Pore structure distribution**

Results of N₂ adsorption/desorption isotherms suggested that MCGL-4/3 obtained remarkable type-IV isotherms with capacities of 815/733 cm³/g. However, N₂ adsorption capacities achieved by MCGL-2/1 were under 520 cm³/g. Physico-chemical properties based on N₂ adsorption/desorption isotherms are summarized in Figure 3 and Table 3. As shown in Table 3, total porous volumes (V_{total}) of MCGL-4 and MCGL-3 reached to 1.1688 and 1.0495 cm³/g, respectively, higher than MCGL-2 (0.8029 cm³/g) and MCGL-1 (0.7041 cm³/g). Mesoporous volume (V_{mes}) of MCGL-4 increased to 0.7605 cm³/g with highest mesoporosity (V_{mes}/V_{total} = 65.11%), followed by MCGL-3 (0.6740 cm³/g, 64.22%). Figure 3(b) further indicates that MCGL-4 had higher pore volume increment (>50 Å) with significant changes in peak value during 50~300 Å. V_{mes} of MCGL-4 was mainly contributed by pore structures during 20.4~52.5 Å (0.2405 cm³/g), 52.5~208.2 Å (0.4443 cm³/g) and 208.2~408 Å (0.1225 cm³/g). MCGL-3 achieved highest micro-porous volume (V_{micro} = 0.2900 cm³/g) and micro-porous surface area (S_{Micro} = 658.42 m²/g), followed by MCGL-4 (V_{micro} = 0.2655 cm³/g and S_{Micro} = 588 m²/g).

Results also suggested that MCGL-3 obtained highest iodine adsorption value (1.185 ± 5.6 mg/g), followed by MCGL-2 (1.062 ± 8.9 mg/g), MCGL-4 (1.110 ± 6.8 mg/g) and MCGL-1 (1.127 ± 7.4 mg/g). However, MCGL-4...
regulation, values of 0.797 and 0.303 mg/g, respectively. After pore structures commercial carbons SX-10, F400 and ZJ15 were 0.626, 0.9617) and 20.4
also identi-
ied than MCGL-2 (0.562 mg/g) and MCGL-1 (0.692 mg/g). It increased to 1.033 and 0.908 mg/g, respectively, higher
of mesoporous volume (MCGL-3 and MCGL-4), especially during 208.2 Å. However, the linear correlation was not significant. Well linear correlation ($R^2 > 0.96$) was observed during 408–905 Å, it suggested macro-
porous structure may also play an important role.

Immobilization properties for functional bacteria

Another goal of present work is to improve the properties of bio-enhancement on carbon surface. Studies suggested that initially immobilized biomass of functional bacteria in BEAC process can significantly shorten the biofilm formation, and consequently improve bio-degradation of organic-pollutants. As shown in Figure S2(a), biomass (phospholipid content) on carbons increased over time of cyclic loading. After 24 hours, MCGL-4 obtained 9.13 mmol-P/g of phospholipid content, higher than other 6 carbons. After surface back-
washing (5 minutes), phospholipid content on MCGL-4 decreased to 8.06 mmol-P/g. However, it was still higher than other carbons. It indicated that immobilized biomass and stabilities on MCGL-4 were significantly promoted. As shown in Figure S2(b), after 240 hours of continuous culture, MCGL-4 achieved higher phospholipid content (30.36 mmol-
P/g), with average growth rate of 2.213 mmol-P/g/d.

Water purification performance of MCGL-4

As mentioned above, it suggested that new carbon MCGL-4 has advantages in NOM adsorption, immobilization capability and biodegradability in BEAC process. Therefore,
MCGL-4 was selected as research target in subsequent studies treating source water from Songhua River.

**Changings of DOC**

Purification performances of pilot-scale systems were determined under 246 days of operation (KBV = 39.50 m³·H₂O/(kg·carbon)). Changing curves of DOC in BEAC/BAC system are shown in Figure 4(a).

In pilot-scale BAC system (Figure 4(a)), C-MCGL-4 achieved lower average effluent DOC (1.32 ± 0.70 mg/L) than C-SX-10 (1.82 ± 0.79 mg/L) and C-ZJ15 (2.50 ± 0.72 mg/L). Effluent DOC of C-ZJ15 exceed 3.0 mg/L during KBV ranges of 19.2–39.50 m³·H₂O/(kg·carbon). However, it remained stable lower level in C-MCGL-4 (2.03 ± 0.15 mg/L) and C-SX-10 (2.58 ± 0.25 mg/L).

In the pilot-scale BEAC system, it indicated that B-MCGL-4 achieved the highest DOC removal efficiency (76% ± 15%) with lowest average value (0.98 ± 0.56 mg/L). Effluent DOC reached a steady state (1.57 ± 0.15 mg/L) after 120 days of operation (19–39.50 m³·H₂O/(kg·carbon)). However, immobilization did not significantly facilitate the DOC removal in B-ZJ15 (2.34 ± 0.65 mg/L). Removal efficiency of DOC achieved by B-SX-10 increased 12% in comparison with C-SX-10.

**3D-EEM And GC-MS spectrometry**

The excitation (EX) and emission (EM) boundaries of 3D-EEM were classified into five regions by Chen and Liu et al. (Chen et al. 2003; Liu et al. 2015). Regions-I and -II (EX < 250 nm; EM < 380 nm) associates with aromatic proteins, Region-III (EX < 250 nm; EM > 380 nm) represents fulvic acid-like compounds, Region-IV (EX > 250 nm; EM < 380 nm) represents soluble microbial by-product-like compounds, and Region V (EX > 250 nm; EM > 380 nm) represents humic-like organic compounds. Results of 3D-EEM suggested that the major organic compounds in source water were humic acid-like organics, with two prominent fluorescence peaks (EX/EM = 263 nm/438 nm, EX/EM = 308 nm/423 nm) in Region V. After sand filter purification, the fluorescence intensity decreased slightly.

Figure 4(b) and 4(c) illustrate the average fluorescence intensity during KBV ranges of 5–30 m³·H₂O/(kg·carbon). The total intensity of influent water of pilot-scale system was 1.27 × 10⁵, with higher proportion in Region III (fulvic acid-like compounds, 3.5 × 10⁴, 27.56%) and V (humic-like organic compounds, 4.2 × 10⁴, 33.08%). Therefore, removal of fulvic acid- and humic acid-like organics were the core objectives. The total fluorescence intensities (removal
efficacy) of C-MCGL-4, C-SX-10 and C-ZJ15 decreased to 3.89 \times 10^4 (69.25\%), 5.51 \times 10^4 (56.44\%) and 6.88 \times 10^4 (45.62\%), respectively. C-MCGL-4 removed 75\% of humic acid-like organics (Region V), followed by 68.49\% of fulvic acid (Region IV). It indicated that fulvic acid- and humic acid-like organics can be well removed by new carbon MCGL-4 in BAC system.

In pilot-scale BEAC system, the total fluorescence intensity decreased by 34.96\% after bio-enhancement of B-MCGL-4, in comparison with C-MCGL-4. And descend ranges of fluorescence intensities achieved by B-MCGL-4 were 23.08\% (Region I), 67.69\% (II), 41.18\% (III), 23.08\% (IV) and 21.90\% (V). Therefore, B-MCGL-4 achieved highest removal efficiency for aromatic proteins (Region II and I), followed by fulvic acid-like compounds (Region III). Moreover, bio-enhancement also improved the removal of soluble microbial by-product-like compounds (Region IV) and humic-like organic compounds (Region V) in B-MCGL-4 system.

GC-MS was also used to characterize the purification performances of carbons (at 20 m^3·H_2O/(kg·carbon)). Results suggested that about 101 kinds of organic-pollutants were detected in influent water of pilot-scale system, mainly contains alkanes (30\%), benzene compounds (19.7\%), naphthalenes (11.1\%), olefins (6.2\%), and organic ester compounds (4.9\%) (Wang et al. 2012, 2018). For C-MCGL-4, about 65 kinds of organics were detected, and peak abundance and area decreased sharply during the retention time ranges of 6–12 min and 17–30 min (mainly alkanes, benzene and naphthalene compounds). In BEAC system (B-MCGL-4), peak abundance and area decreased during retention time range of 5–20 min in comparison with C-MCGL-4. The amount of alkanes, benzene and naphthalene compounds decreased by 15.26\%, 16.37\% and 8.29\%, respectively.

Biological proliferation on carbon surface in BEAC system

Biological proliferation on carbon surface in B-MCGL-4 was also determined. The biomass on B-MCGL-4, B-SX-10 and B-ZJ15 reached to 45.6, 34.5 and 28.6 mmol-P/g at 39.50 m^3·H_2O/(kg·carbon).

DISCUSSION

Pore structure regulation mechanisms

The normal distributions of pore structures of 47 kinds of commercial activated carbons (Figure S3) were summarized. New carbon MCGL-4 showed higher levels of $V_{total}$ and $V_{mes}$ than most of carbons, and it also has average level of $V_{micro}$. It identified that synchronous well-developed mesoporous and micro-porous structures are the most distinguishing characteristics of MCGL-4.

Catalytic carbonization or activation is a promising way to regulate pore structures, and KOH was usually used to promote condensation polymerization and aromatization, so as to form rich micro-porous structures. Martins (Martins et al. 2015) pointed that proper amount of KOH impregnation was beneficial for development of micro-porous structure, since KOH can promote the changings of pyrolysis, formatting of initial pore structures and crystallite graphite structures. KOH impregnation was introduced in preparation of MCGL-2, and its $V_{total}$ (0.8029 cm^3/g) and $V_{micro}$ (0.2368 cm^3/g) increased by 14.03\% and 48.56\%, respectively, compared to MCGL-1. Moreover, mesoporous volume of MCGL-2 (0.3986 cm^3/g) increased by 13.82\% in comparison with MCGL-1. That is to say, higher micro-porous volumes can be attributed to KOH impregnation process, by which mesoporous volumes increased during the collapse of micro-pores by steam activation.

CO_2 activation was employed after carbonization in MCGL-3. Compared to MCGL-2, $V_{total}$ and $V_{mes}$ of MCGL-3 increased by 0.2466 cm^3/g and 0.2754 cm^3/g, respectively. Studies suggested that (Gong et al. 2009, 2013) activating agent and time have significant effects on surface physio-chemical changes. Especially, surface activation using CO_2 as activator was proved to be more likely to form abundant micro-pores due to its linear molecular structure. The increase of micro-pores attributed by CO_2 activation may offer the potential mesoporous foundation during the subsequent activation. Moreover, pore structure distribution of the intermediate product (M1) after CO_2 activation was also determined. Results suggested that about 0.2024 cm^3/g of micro-porous volume increased in comparison with MCGL-2. It also interprets the effects of CO_2 activation.
Depth activation at 950 °C was employed in MCGL-4, and it can cause higher ablation rate of carbons. Studies also suggested micro-porous carbon can be commonly obtained with ablation rate below 50%. Mesoporous or macro-porous carbons can be obtained when ablation rate was higher than 70%. Well-developed micro-porous and mesoporous structures may be obtained during ranges of ablation rate of 50–70%. Higher ablation rate of C-GL-4 (68.5% ± 2.50%) was confirmed because of the employment of MDA. In comparison with MCGL-3 (with ablation rate of 55.7% ± 1.80%), depth activation at 980 °C causes collapse of micro-pores, by which \( V_{\text{total}} \), \( V_{\text{mes}} \) and \( V_{\text{mar}} \) of MCGL-4 increase by 0.1279 cm\(^3\)/g, 0.0789 cm\(^3\)/g and 0.0774 cm\(^3\)/g. However, \( V_{\text{micro}} \) of MCGL-4 decreased by 0.0284 cm\(^3\)/g because of the collapse of micro-pores during depth activation.

One objective of present work aims at improving adsorption kinetics and capacities for NOM by pore structure regulation. Results of 3D-EEM and V\(_{\text{HA}}\) identified that higher mesoporosity (65.11%) and BJH-\(V_{\text{mes}}\) (0.7605 cm\(^3\)/g) of MCGL-4 resulted in accelerating kinetics and capacity for humic-like organics (Kalkan et al. 2011; Lu et al. 2014; Gong et al. 2015a; Greenwald et al. 2015). Figure S4 suggested that adsorption of humic acids by MCGL-4/3 followed pseudo-second-order kinetics (\( R^2 > 0.998 \)) when average molecular weight ranged from 2,700 to 5,100 Da. It indicated that a key step of velocity control was the adsorption reaction stage, rather than pore diffusion stage. However, adsorption process achieved by MCGL-2/1 followed Weber-Morris kinetic model (\( R^2 > 0.998 \)), and it indicated that adsorption process was mainly influenced by the diffusion of adsorbents in the pores of the adsorbents. The adsorption kinetics results confirmed that mesoporous regulation during 20.4–408 Å promoted adsorption capacities and kinetics.

**Comprehensive quantitative indicators of carbons**

Selecting or tailoring an excellent carbon for bio-enhancement is a complex process, especially when the pilot-scale or production experimental data were scarce. Lots of factors can influence the carbon selection such as raw water quality, biomass, bio-activities and parameters of filtration, etc. Therefore, methods which can be used to prejudge properties of carbons based on physical and chemical characteristics are of extraordinary value. Under relatively steady operation mode, the key factors of BEAC process were biomass and bio-activities, especially the initial immobilization capacity of biomass (BI). It determined the extent and efficacy of bio-degradation in initial and stably BEAC process. In order to evaluate the BI by different carbons with different PSD/PVD distribution, ‘Comprehensive Quantitative Indicators (CQI)’ was proposed.

Figure 5(a) firstly calculated the linear correlation coefficients (\( R^2 \)) between initially immobilized biomass (BI, 24 h) and parameters of seven carbons used in present work. Linear fitting results identified that orders of correlation coefficient (\( R^2 > 0.800 \)) were as followed: \( V_{\text{mes}}(0.9827) > V_{\text{HA}}(0.9692) > D(0.948) > V_{\text{total}}(0.9323) > V_{\text{MB}}(0.8896) > \text{oxygen content} (0.8221) > V_{\text{micro}}(0.0011) \). It confirmed that functional bacteria immobilization was significantly influenced by mesoporous structures, adsorption capacities of NOM and surface oxygen content. While \( V_{\text{micro}} \) had little correlation, and it also explained the deficiency of micro-porous carbons.

An Ideal Model of Carbons for BEAC process (\( IMC_{\text{BEAC}} \)) was proposed in the present work. Parameters of \( IMC_{\text{BEAC}} \) were assigned as follows: \( S_{\text{BET}} \geq 1,400 \text{ m}^2/\text{g}, V_{\text{total}} \geq 1.90 \text{ cm}^3/\text{g}, V_{\text{micro}} \geq 0.60 \text{ cm}^3/\text{g}, V_{\text{mes}} \geq 1.00 \text{ cm}^3/\text{g}, V_{\text{mar}} \geq 0.25 \text{ cm}^3/\text{g}, D \geq 40 \text{ Å}, V_{\text{IN}} \geq 1,400 \text{ mg}/\text{g}, V_{\text{MB}} \geq 350 \text{ mg}/\text{g}, V_{\text{HA}} \geq 2.0 \text{ mg}/\text{g}, \text{strength} \geq 90\% \) and density \( \geq 500 \text{ g}/\text{L} \). Based on the \( IMC_{\text{BEAC}} \), Comprehensive Quantitative Indicators (CQI) was proposed consequently to evaluate the initial immobilization capacity of biomass (BI) by different carbons. It was identified using Equation (11).

\[
CQI = \sum_{i=1}^{n} CQI_{i} = \sum_{i=1}^{n} \left( W_{i} \times \frac{V_{i}}{V_{i-MC}} \right)
\]

Here, \( V_{i} \) was parameters of carbons used in present work (Tables 1 and 3); \( W_{i} \) was the linear correlation coefficients (\( R^2 \)) in Figure 5(a), \( V_{i-MC} \) was parameters of \( IMC_{\text{BEAC}} \) as mentioned above.

As shown in Table 4, the calculated CQI of \( IMC_{\text{BEAC}} \) was 6.97, followed by MCGL-4(5.36)>MCGL-3(4.95)>MCGL-2(4.12)>F400(3.78)=MCGL-1(3.78)>SX-10(3.53)>ZJ15(2.51). Linear correlation analysis between CQI
and BI was conducted in Figure 5(b), based on 12 tested carbons. Results suggested that initial immobilization capacity of biomass (BI) can be well reflected by CQI of carbons. According to equations (BI = 0.9231CQI + 4.0649(R² = 0.9776)) obtained from Figure 5(b), calculated BI of IMCB EAC was 10.499 mmol-P/g. This phenomenon suggested a feasible method to rapidly evaluate the surface immobilization ability of functional bacteria. CQI proved to be a promising parameter (R² = 0.9319) to prejudge BI of different carbons. Results of pilot-scale BEAC and BAC system also identified that the selected new carbon MCGL-4 obtained higher efficacy for organics removal and bio-degradation efficiency.

**DO consumption and utilization efficiency during bio-degradation**

Yapsakli et al. (Yapsakli & Cecen 2010; Yapsakli et al. 2010) and Aktas & Cecen (Aktas & Cecen 2010) suggested that bio-degradation was closely related to DO consumption and utilization efficiency. Surface affinity for DO was affected by surface oxidation degree. The amount of DO which can be available for bio-degradation decreased with the increase in surface affinity for DO. Surface oxygen content was also proved to be an important factor that can affect the immobilization of functional bacteria (R² = 0.8221). Therefore, DO consumption and...
utilization efficiency during bio-degradation were determined in Figure 5 and Table 5 according to methods described earlier.

As shown in Table 5, considerable differences were observed in surface affinity for DO during adsorption process ($\Delta$DO$_{CS}$) in column-A. And it indicated that $\Delta$DO$_{CS}$ were negatively correlated with thermal ablation rate of carbons. Fitting results also showed that linear correlation coefficient between $\Delta$DO$_{CS}$ and surface oxygen content was 0.9725. The bio-degradation efficiency of DOC and NH$_4$-N in column B increased with the decrease of $\Delta$DO$_{CS}$. The theoretical amounts of DO required in bio-degradation of DOC ($\Delta$DO$_C$) and NH$_4$-N ($\Delta$DO$_N$) in column B (MCGL-4) were 4.62 ± 0.12 mg/L and 0.64 ± 0.15 mg/L, respectively. The

| Table 4 | Comprehensive quantitative indicators (CQI, dimensionless unit) |
|---------|----------------------------------------------------------|
| i | Parameters | W$_i$ | IMC | MCGL-4 | MCGL-3 | MCGL-2 | MCGL-1 | SX-10 | ZJ15 | F400 | C-1 | C-2 | C-3 | C-4 | C-5 | C-6 |
| 1 | Strength | 0.0124 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 |
| 2 | Density | 0.0202 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 |
| 3 | Oxygen content | 0.8221 | 0.82 | 0.82 | 0.74 | 0.59 | 0.54 | 0.41 | 0.60 | 0.65 | 0.51 | 0.35 | 0.46 | 0.43 |
| 4 | $S_{BET}$ | 0.6721 | 0.67 | 0.63 | 0.57 | 0.52 | 0.44 | 0.44 | 0.56 | 0.48 | 0.51 | 0.44 | 0.58 | 0.49 |
| 5 | $V_{total}$ | 0.9323 | 0.93 | 0.58 | 0.51 | 0.39 | 0.32 | 0.18 | 0.44 | 0.41 | 0.36 | 0.27 | 0.24 | 0.33 |
| 6 | $V_{micro}$ | 0.0011 | – | – | – | – | – | – | – | – | – | – | – | – |
| 7 | $V_{mes}$ | 0.9827 | 0.98 | 0.74 | 0.66 | 0.39 | 0.35 | 0.18 | 0.44 | 0.41 | 0.36 | 0.27 | 0.24 | 0.33 |
| 8 | $V_{mar}$ | 0.1207 | 0.12 | 0.08 | 0.04 | 0.04 | 0.05 | 0.03 | 0.04 | 0.03 | 0.01 | 0.04 | 0.04 |
| 9 | D | 0.948 | 0.95 | 0.90 | 0.78 | 0.62 | 0.61 | 0.64 | 0.43 | 0.69 | 0.79 | 0.75 | 0.66 | 0.24 |
| 10 | $V_{IN}$ | 0.6043 | 0.60 | 0.48 | 0.51 | 0.49 | 0.46 | 0.42 | 0.41 | 0.48 | 0.49 | 0.44 | 0.41 | 0.48 |
| 11 | $V_{MB}$ | 0.8896 | 0.89 | 0.64 | 0.59 | 0.52 | 0.50 | 0.48 | 0.44 | 0.47 | 0.61 | 0.64 | 0.50 | 0.02 |
| 12 | $V_{HA}$ | 0.9692 | 0.97 | 0.50 | 0.44 | 0.34 | 0.27 | 0.30 | 0.15 | 0.34 | 0.42 | 0.37 | 0.29 | 0.04 |
| CQI | 6.97 | 5.36 | 4.95 | 3.78 | 4.12 | 3.53 | 2.51 | 3.78 | 4.25 | 4.14 | 3.35 | 3.05 | 3.38 |

| Table 5 | Parameters relating to DO consumption and utilization during biodegradation |
|---------|----------------------------------------------------------|
| Parameters | unit | MCGL-4 | MCGL-3 | MCGL-2 | MCGL-1 | SX-10 | ZJ15 |
| DO | mg/L | 7.76 ± 0.27 | 7.65 ± 0.34 | 7.82 ± 0.26 | 7.66 ± 0.31 | 7.69 ± 0.21 | 7.88 ± 0.13 |
| $\Delta$DO$_{CS}$ | mg/L | 0.42 ± 0.07 | 0.84 ± 0.05 | 1.56 ± 0.06 | 2.20 ± 0.06 | 2.41 ± 0.13 | 3.59 ± 0.06 |
| $\Delta$DO$_C$ | mg/L | 1.74 ± 0.06 | 1.55 ± 0.09 | 1.45 ± 0.04 | 1.37 ± 0.12 | 1.42 ± 0.03 | 1.05 ± 0.04 |
| $\Delta$DO$_N$ | mg/L | 0.15 ± 0.03 | 0.13 ± 0.03 | 0.12 ± 0.04 | 0.10 ± 0.05 | 0.10 ± 0.04 | 0.09 ± 0.03 |
| $\Delta$DO$_TH$ | mg/L | 4.62 ± 0.10 | 4.13 ± 0.06 | 3.84 ± 0.11 | 3.64 ± 0.09 | 3.77 ± 0.08 | 2.80 ± 0.11 |
| PADO | % | 91.17 ± 0.59 | 83.67 ± 2.81 | 70.65 ± 2.28 | 63.16 ± 3.11 | 62.89 ± 2.39 | 46.66 ± 3.49 |
| Ablation rate | % | 68.5 ± 2.30 | 57.70 ± 1.80 | 49.30 ± 2.70 | 43.5 ± 3.20 | 40.15 ± 3.3 | 33.63 ± 1.8 |
| Oxygen content | % | 15.96 | 9.02 | 8.45 | 7.22 | 6.57 | 4.12 |
total theoretical consumption of DO in column B (MCGL-4) ($\Delta DO_{TH} = \Delta DO_C + \Delta DO_N + \Delta DO_{CS}$) was 5.69 ± 0.18 mg/L. As shown in Figure 5(c) (in column B, MCGL-4), percentage occupied by $\Delta DO_{CS}$, $\Delta DO_C$ and $\Delta DO_N$ were 7, 81 and 11%, respectively. Actual effective utilization rate of DO ($PADO$) by bio-degradation achieved by MCGL-4 in column B reached to 91.17%. In comparison with MCGL-4, micro-porous carbon ZJ15, SX-10 and F400 obtained higher percentage which was occupied by $\Delta DO_{CS}$, rather than bio-degradation of DOC and NH$_4^+$-N. Therefore, $PADO$ was significantly influenced by $\Delta DO_{CS}$ ($R^2 = 0.9868$). Moreover, relationship between $PADO$ and $CQI$ was also determined in Figure 5(d). The fitting results showed that $CQI$ was also a promising parameter ($R^2 = 0.9319$) to prejudge $PADO$ (bio-activity) of different carbons.

**Synergistic efficacy of synchronous adsorption-biodegradation enhanced by pore regulation**

Gibert (Gibert et al. 2012), Velten (Velten et al. 2011) and Aktaş & Çeçen (Aktaş & Çeçen 2007) pointed out that simultaneous adsorption and bio-degradation were the predominant factors contributing to organic-pollutants removal in BEAC process. The synergistic efficacy of adsorption and bio-degradation can be significantly affected by pore structure regulation (Wang et al. 2007; Sulaymon et al. 2010). However, it is difficult to quantify the relative contribution rate of the two mechanisms at different operational stages due to lack of methodologies (Oleinikova et al. 2018; Schupp et al. 2018; Li et al. 2019). Cumulative uptake of DOC ($QC$) and RSSCT tests were introduced in present work to quantify synergistic efficacy between adsorption and bio-degradation.

**Cumulative uptake of DOC ($QC$)**

The changing curves of $QC$ calculated from data in Figure 4(a) are illustrated in Figure 6(a) and 6(b). It indicated that $QC$ values of pilot-scale BEAC/BAC increased with the extent of operational time/$KBV$. In BAC system (Figure 6(a)), $QC$ of C-MCGL-4 reached to 79,614.35 mg-DOC/(kg-carbon) when KBV was 39.50 m$^3$·H$_2$O/(kg-carbon) (246 days). While $QC$ values of C-SX-10 and C-ZJ15 were 56,539.40 and 28,584.34 mg-DOC/(kg-carbon), respectively. In BEAC system (Figure 6(b)), $QC$ obviously increased from the initial stage due to immobilization. $QC$ values of B-MCGL-4, B-SX-10 and B-ZJ15 increased to 94,655.50, 67,366.73 and 35,941.86 mg-DOC/(kg-carbon), respectively, at 39.50 m$^3$·H$_2$O/(kg-carbon). Well nonlinear fitting ($R^2 > 0.999$) in Figure 6(a) and 6(b) also suggested that $QC$ obtained from BAC/BEAC system can be well fitted by nonlinear equation as a function of $KBV$.

Although it is difficult to directly quantify the relationship between adsorption and bio-degradation, it is clear...
that effects of bio-degradation caused by immobilization of functional bacteria in BEAC system can be first evaluated based on data from BAC system. Variable $\alpha$ and $\beta$ were consequently employed as a function of KBV. Variable $\alpha$ is described by the following Equation (12): 

$$\alpha_{C-i} = \frac{Q_{CB}}{Q_{CC}}$$

Here, parameter $i$ represents carbon MCGL-4, SX-10 or ZJ15. Results suggests $\alpha_{C-MCGL-4}$ was always higher than 1.0 even at the initial stage of operation; however, it required 3.78 m$^3$·H$_2$O/(kg·carbon) for $\alpha_{C-SX-10}$ and 3.09 m$^3$·H$_2$O/(kg·carbon) for $\alpha_{C-ZJ15}$, respectively. It indicated that simultaneous bio-degradation and adsorption occurred in B-MCGL-4 after bacteria immobilization, while B-SX-10 and B-ZJ15 still required a short operational time to achieve effective bio-degradation. The $\alpha_{C-MCGL-4}$, $\alpha_{C-SX-10}$ and $\alpha_{C-ZJ15}$ were 1.184, 1.192 and 1.257, respectively, at 39.50 m$^3$·H$_2$O/(kg·carbon). However, increment value $\Delta Q_{C-MCGL-4}$ ($Q_{CB}/C_{MCGL-4} - Q_{RC}/C_{MCGL-4}$) reached to 15,041.16 mg·DOC/(kg·carbon), and it was obviously higher than $\Delta Q_{C-SX-10}$ ($Q_{CB}/C_{SX-10} - Q_{RC}/C_{SX-10}$) and $\Delta Q_{C-ZJ15}$ ($Q_{CB}/C_{ZJ15} - Q_{RC}/C_{ZJ15}$ = 7,357.52 mg·DOC/(kg·carbon)).

Synergy effect between bio-degradation and adsorption

RSSCTs have been widely employed as an established way to accurately predict removal of numerous trace organic chemicals via adsorption to GAC by utilizing pilot-scale columns and thus minimize removal via bio-degradation (Anumol et al. 2015). Therefore, cumulative uptake of DOC calculated from the RSSCTs system was compared to results from a BEAC/BAC filter operated in parallel to determine the relative contribution of biodegradation (illustrated in Figure 7(a)) (Zhiteneva et al. 2020).

Results suggested that RSSCT-calculated QC can be well nonlinearly represented by RSSCT-calculated KBV ($R^2 > 0.997$). R-MCGL-4 achieved highest capacity (67,725.32 mg·DOC/(kg·carbon)) at 61.40 m$^3$·H$_2$O/(kg·carbon), and 63,175.79 mg·DOC/(kg·carbon)) at 39.50 m$^3$·H$_2$O/(kg·carbon).

Under the assumption above, $\Delta R_{QC-B-MCGL-4}$, $\Delta R_{QC-B-SX-10}$ and $\Delta R_{QC-C-MCGL-4}$ were defined in Equations (13)–(15).

$$\Delta R_{QC-B-MCGL-4} = (Q_{CB-B-MCGL-4} - Q_{RC-B-MCGL-4})_{39.5 KBV}$$

(13)

$$\Delta R_{QC-B-SX-10} = (Q_{CB-B-SX-10} - Q_{RC-B-SX-10})_{39.5 KBV}$$

(14)

$$\Delta R_{QC-C-MCGL-4} = (Q_{C-C-MCGL-4} - Q_{RC-C-MCGL-4})_{39.5 KBV}$$

(15)

When RSSCT-calculated KBV were 39.50 m$^3$·H$_2$O/(kg·carbon), the calculated $\Delta R_{QC-B-MCGL-4}$, $\Delta R_{QC-B-SX-10}$ and $\Delta R_{QC-B-ZJ15}$ were defined in Equations (13)–(15).

| Figure 7 | Variation of the RSSCT-predicted parameters. (a) Variation of RSSCT-predicted QC, (b) variation of $\delta$. |

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and ΔRQC_{MCGL-4} were 31,674.72, 21,598.21 and 16,963.54 mg·DOC/(kg·carbon), respectively. It identified that B-MCGL-4 achieved highest bio-degradation abilities. Parameter \( \delta \) (100*\( \Delta RQC/QC \)) can be consequently used to represent the contributions of bio-degradation in either BEAC or BAC process for DOC removal.

\[
\begin{align*}
\delta_B-(\%) &= 100 \times \frac{\Delta RQC_B-i}{Q_{C-B-i}} \\
\delta_C-(\%) &= 100 \times \frac{\Delta RQC_C-i}{Q_{C-C-i}} \\
(i \text{ was } MCGL-4, \ SX-10 \text{ or ZJ15})
\end{align*}
\]

As shown in Figure 7(b), \( \delta_B-MCGL-4 \) was always higher than \( \delta_B-SX-10 \) and \( \delta_B-ZJ15 \) in BEAC system. The \( \delta_B-MCGL-4 \) increased from 12.83% to 33.39% with the extent of KBV, while \( \delta_B-SX-10 \) and \( \delta_B-ZJ15 \) ranged during 6.13~32.06% and 12.14~27.49%, respectively. Moreover, \( \delta_B-SX-10 \) was lower than \( \delta_B-ZJ15 \) during KBV ranges of 10~24 m\(^3\)·H\(_2\)O/(kg·carbon), it may be attributed to higher adsorption efficiency for DOC by carbon SX-10. However, biological activities were slight (\( \delta < 5\% \)) in C-SX-10 (KBV < 20 m\(^3\)·H\(_2\)O/(kg·carbon)) and C-ZJ15 (KBV < 33 m\(^3\)·H\(_2\)O/(kg·carbon)). \( \delta_C \) obtained from C-MCGL-4, C-SX-10 and C-ZJ15 increased to 18.08%, 17.05% and 8.84%, respectively, at 39.50 m\(^3\)·H\(_2\)O/(kg·carbon). Therefore, bio-degradation in B-MCGL-4 accounted for the highest percentages in DOC removal than B-SX-10, B-ZJ15 and BAC process.

**CONCLUSIONS**

New carbon MCGL-4, tailored by KOH impregnation and MDA, obtained synchronously well-developed meso- (0.7605 cm\(^3\)/g), micro- (0.2655 cm\(^3\)/g) and macro-porous (0.145 cm\(^3\)/g) structures. Mesoporous regulation of MCGL-4 resulted in the promotion of both NOM adsorption and initially immobilized biomass/bio-activity. Mesoporous structure during 20.4~208.2 Å played the most important role in the promotion of adsorption kinetics and capacity for humic-like organics, followed by 208.2~408 Å. Comprehensive Quantitative Indicators of Carbons (CQI) was proved to be a promising parameter to prejudge the initial immobilized biomass and bio-activity of different carbons. A new methodology is proposed to quantify the relative contribution rate of adsorption and bio-degradation based on cumulative uptake of DOC (QC) in RSSCTs tests system and pilot-scale BEAC system. QC achieved by B-MCGL-4 reached to 94,850.51 mg·DOC/(kg·carbon) at 39.50 m\(^3\)·H\(_2\)O/(kg·carbon). Based on the RSSCTs-calculated cumulative adsorption of DOC, bio-degradation abilities achieved by MCGL-4 in BEAC system reached up to 31,674.70 mg·DOC/(kg·carbon).

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**COMPLIANCE WITH ETHICAL STANDARDS**

The manuscript is the original work of authors and it has not been previously submitted to Water Supply or other journals for simultaneous consideration. The manuscript has not been published previously. This study is not split up into several parts to increase the number of submissions and submitted to various journals or to one journal over time. No data have been fabricated or manipulated (including images) to support conclusions. No data, text, or theories by others are presented as if they were the authors’ own. All authors mutually agree for its submission to Water Supply. The publication is approved by all authors and tacitly or explicitly by the responsible authorities where the work was carried out.

**DATA AVAILABILITY STATEMENT**

All relevant data are included in the paper or its Supplementary Information.
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