Enhanced removal of organic matter and typical disinfection byproduct precursors in combined iron–carbon micro electrolysis-UBAF process for drinking water pre-treatment

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ABSTRACT
The organic matter and two types of disinfection byproduct (DBP) precursors in micro-polluted source water were removed using an iron–carbon micro-electrolysis (ICME) combined with up-flow biological aerated filter (UBAF) process. Two pilot-scale experiments (ICME-UBAF and UBAF alone) were used to investigate the effect of the ICME system on the removal of organic matter and DBP precursors. The results showed that ICME pretreatment removed 15.6% of dissolved organic matter (DOM) and significantly improved the removal rate in the subsequent UBAF process. The ICME system removed 31% of trichloromethane (TCM) precursors and 20% of dichloroacetonitrile (DCAN) precursors. The results of measurements of the molecular weight distribution and hydrophilic fractions of DOM and DBP precursors showed that ICME pretreatment played a key role in breaking large-molecular-weight organic matter into low-molecular-weight components, and the hydrophobic fraction into hydrophilic compounds, which was favorable for subsequent biodegradation by UBAF. Three-dimensional fluorescence spectroscopy (3D-EEM) further indicated that the ICME system improved the removal of TCM and DCAN precursors. The biomass analysis indicated the presence of a larger and more diverse microbial community in the ICME-UBAF system than for the UBAF alone. The high-throughput sequencing results revealed that domination of the genera Sphingomonas, Brevundimonas and Sphingorhabdus contributed to the better removal of organic matter and two types of DBP precursors. Also, Nitrosomonas and Pseudomonas were beneficial for ammonia removal.

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Introduction

In China, the development of industry and agriculture has caused many problems that endanger the safety of drinking water quality due to excessive discharge of wastewater without the necessary treatment. The resulting micro-polluted surface water, mainly containing high contents of organics and ammonia nitrogen, is often used as source water for water supply (Chu et al., 2010; Xu et al., 2007). However, conventional drinking water treatment has a poor removal efficiency for organic matter and ammonia nitrogen. Ammonia may be a threat to the bio-stability of drinking water by providing nutrients for nitrifying bacteria. Meanwhile, ammonia may react with organics and chlorine to form nitrogenous disinfection by-products (N-DBPs) (Charrois and Hrudey, 2007; Han et al., 2013). Organic matter makes the main contribution to disinfection by-products (DBPs) during chlorination, causing damage to the health of human beings (Lavonen et al., 2013; Tan et al., 2017). DBPs have been due to the increasing needs for drinking water quality safety. In recent years, N-DBPs have been of concern widely due to their higher cyto- and geno-toxicity compared to carbonaceous DBPs (C-DBPs) (Tan et al., 2017). For the reduction of DBPs, it is more effective and practical to remove their precursors than to change the disinfection conditions or remove the already formed DBPs by other technologies (Bond et al., 2012).

This issue is especially serious and tough when it appears in rural areas. Inadequate supervision and non-point source pollution in rural areas has caused more contaminated water resources (Huang et al., 2013a). The less-advanced water treatment technology used in rural areas has difficulty removing high contents of organics and ammonia. Pretreatment of micro-polluted surface water is necessary, and there is an urgent need to develop a new treatment technology for high-quality drinking water production from micro-polluted surface water in rural areas.

To handle this problem, biological treatment in the drinking water process is considered to be an appropriate technical method. As an advanced purification process in drinking water treatment plants, the integrated process of ozonation and biological activated carbon filtration (BAC) was confirmed to show good removal performance for normal organic matter and DBP precursors (Chu et al., 2012; Yan et al., 2010). The membrane bioreactor (MBR), used as a pretreatment in traditional water treatment, was shown to be capable of decreasing the bulk organic content and specific fractional components when used for micro-polluted surface water (Zhang et al., 2015). Chu et al. (2010) investigated the treatment of micro-polluted surface water with a bio-diatomite dynamic membrane reactor (BDDMR), indicating that it is an effective approach for removing organics and THM formation potential (FP). However, the above technologies are complicated and difficult for operation and management, especially in rural areas, in spite of their good removal efficiency. Recently, the biological aerated filter (BAF) has been considered to be a feasible technology for treating micro-polluted source water in rural areas due to its small volume, high flexibility toward fluctuating loading rates and low investment (Mendoza-Espinosa and Stephenson, 1999). It has been reported that the BAF shows a high ammonia removal rate of around 80%–90% (Han et al., 2012; Liu et al., 2017). However, the removal efficiency for organic matter was found to be unsatisfactory when the micro-polluted source water contained high contents of refractory organics with limited biodegradability (Han et al., 2013). Therefore, promotion of the organic removal efficiency in the BAF is urgently needed. Iron–carbon (Fe–C) micro-electrolysis (ICME) has been considered to be a promising advanced oxidation process for organics removal in water treatment due to its great efficiency, low cost, simple operation and innocuous nature (Yang et al., 2017). The ICME system is based on the electrochemical reactions of numerous microscopic galvanic cells between the electrode materials iron (anode) and carbon (cathode) (Yang et al., 2017). Its electrochemical oxidation may remove or transform refractory organic compounds and improve the biodegradability for the subsequent biodegradation step. It has been proved that ICME shows good performance in treating different refractory waters (Huang et al., 2013b; Wang et al., 2009; Yang et al., 2017; Zhang et al., 2017; Zhou et al., 2013). Notwithstanding, ICME suffers from some shortcomings that constrain its wide application, such as blockage of the reaction bed and the need for disposal of iron-containing sludge. In our study, raw water was used for drinking water treatment and was much clearer than industry or medical wastewater, which means less blockage and less iron-containing sludge production. The up-flow configuration can also reduce the extent of blockage, as the produced ferrous and ferric hydroxides can be excluded from the bed by the flow. In addition, application of a modified micro-electrolysis filter can also reduce blockage and passivation. It has a porous structure, a large surface area and uniform flow channels to reduce the resistance of the original cell reaction and blockage of the reaction bed (Zhang et al., 2014). In addition, regular backwash with high aeration is also helpful. The iron-containing sludge can be collected together with the sludge in the sedimentation tank. The mixture can be used for building materials after sludge disposal in the waterworks.

The UBAF configured with a pre-ICME system may be an innovative pretreatment for organic matter and DBP precursors removal in drinking water treatment. Previous studies on removal of organics by ICME have mainly focused on wastewater with high contents of organics (Li et al., 2009; Zhang et al., 2018), whose characteristics were significantly different from the raw water used in drinking water treatment. Few studies are available concerning the performance of ICME combined with a subsequent biological treatment process in removal of organic matter and DBP precursors in drinking water pretreatment. In this study, an investigation was carried out to evaluate the enhancement of organic matter and DBP precursor removal obtained by the modified UBAF system configured with iron–carbon micro-electrolysis, and to better illustrate the evolution of the microbial community during the degradation of organic matter and DBP precursors in UBAF. One typical carbonaceous DBP, trichloromethane (TCM), and one typical nitrogenous DBP, dichloroacetanilide (DCAN), were selected as the representative DBPs due to their high health risk concerns and widespread presence (Yan et al., 2010; Yu et al., 2015).
1. Materials and methods

1.1. Pilot-scale systems

The pilot-scale ICME-UBAF coupled system and UBAF-only system were continuously operated in this study. A schematic diagram is presented in Fig. 1. The UBAF-only system had the same UBAF column as used in ICME-UBAF. The iron-carbon particles purchased from domestic manufacturers were depressed globose and the iron-carbon ratio (Fe/C) was around 7.5:2. The material was made from iron and activated carbon as the main raw materials, and bentonite as a caking agent, sintered together under oxygen-free conditions. The modified iron–carbon filter had a porous structure, large surface area and uniform flow channels to reduce the resistance of the original cell reaction and the blockage of reaction bed (Zhang et al., 2014). Nano-crystalline ceramsite purchased from domestic manufacturers was used for the UBAF. The physical characteristics including diameter, bulk density, specific surface area, and porosity for Fe–C particles, and nano-crystalline ceramic particles are 25–35 mm, 4–6 mm; 1.323 g/cm³, 0.892 g/cm³; 1.6 m²/g, 8.65 m²/g; and 65%, 46%, respectively.

The raw water was adjusted to pH 4 using 0.1 mol/L H₂SO₄ and then pumped into the ICME column in an up-flow manner. The ICME effluent was of neutral pH and directly pumped into the bottom of the UBAF system. The UBAF was initially inoculated with ceramsite from a biological aerated filter of a rural waterworks. The two systems were started up for 20 days and operated for 60 days under the optimum operation conditions. The hydraulic retention time (HRT), up-flow velocity and ratio of air to water (A/L) of the ICME system were 35 min, 2.6 m/hr and 1:3, respectively. The HRT of 40 min, up-flow velocity of 4.0 m/hr and air–water ratio of 1:1.5 was utilized in the UBAF system. The optimization of operational conditions is detailed in Appendix A Text S1.

The UBAF-only and combined ICME-UBAF systems were backwashed according to the water head loss and effluent turbidity, at around per 8 days for the UBAF-only and 9 days for the combined ICME-UBAF system, respectively. The backwashing of the UBAF was conducted in three steps. The first step was air flushing at 12 L/ (m² sec) for 3 min. The second step included combined air and water flushing at 12 L/ (m² sec) and 4 L/ (m² sec) for 5 min, respectively. The third stage involved water flushing at 4 L/ (m² sec) for 8 min.

1.2. Characteristics of feed water

The feed water was collected from a rural waterworks receiving source water from a reservoir in Chongqing, Southeast China. The reservoir was a micro-polluted water source. The feed water contained high contents of organics and ammonia nitrogen. During the operation, the DOC concentration in raw water was 8.1–12.5 mg/L, ammonia 1.12–1.86 mg/L and UV₂₅₄ 0.17–0.38 cm⁻¹. The detailed water quality is listed in Appendix A Table S1.

1.3. Chemicals

Standard solutions of trichloromethane (TCM) and dichloroacetonitrile (DCAN) (99%) were obtained from
Sigma–Aldrich (St Louis, USA). Methyl tert-butyl ether and acetonitrile of HPLC grade were obtained from Merck (Darmstadt, Germany). Other chemicals of analytical grade were purchased from Sinopharm (Shanghai, China). The ultrapure water used was obtained using a Millipore Milli-Q gradient purification equipment (Billerica, USA).

1.4. Analytical methods

1.4.1. Basic water quality parameters

Turbidity was measured using a turbidimeter (2100N, HACH, USA). Color degree was measured using a Colorimeter (XinRui, China). The dissolved oxygen (DO) was detected by a DO analyzer (SC100, HACH, USA). Chemical oxygen demand (COD) was analyzed using a COD quick-analysis apparatus (Lianhua Tech., China). BOD$_5$ was measured by a BOD rapid monitor (Lianhua Tech., China), with samples in accordance with the required volume incubated at constant temperature 20°C for 5 days. Dissolved organic carbon (DOC) contents were measured using a TOC analyzer (1030W, OI, USA). Ammonia was determined using Nessler’s reagent colorimetry with a spectrophotometer (U-3900H, HITACHI, Japan). UV$_{254}$ absorbance was measured with a UV/Vis spectrophotometer (U-3900H, HITACHI, Japan) SUVA was calculated as the ratio of UV$_{254}$ to DOC. The water samples for analysis of regular indicators were collected in pre-cleaned glass bottles every two days and then measured with the specific analyzers on the same day. Samples for DOC, ammonia and UV$_{254}$ were filtered through a microporous filter membrane (0.45 μm, Millipore, USA) for pretreatment. All the samples were analyzed in triplicate to ensure the accuracy of results.

1.4.2. Measurement of DBPs

The DBP FP test was performed according to the description of Krasner et al. (2006). A sodium hypochlorite stock solution (available chlorine 20,000 mg/L as Cl$_2$) was used as the disinfectant. The chlorine dosage was calculated according to Eq. (1)

$$\text{Cl}_2 \text{ dosage (mg/L)} = 3 \times \text{DOC (mg C/L)} + 7.6 \times \text{NH}_3\text{(mg N/L)} + 10$$

(1)

Chlorine residual was determined using the N,N-diethyl-p-phenylenediamine colorimetric titration method (Gilcrease, 1966). Water samples were firstly adjusted to pH 7 and then chlorinated at 25°C in 100-mL sealed amber glass bottles in the dark for 48 hr. Disinfectant residuals were then quenched by ascorbic acid.

The concentration of bromide in raw water was low, so only chlorinated disinfection by-products were measured. TCM and DCAN were analyzed according to USEPA Method 551.1 (USEPA, 1995) and a report by Tan et al. (2017), with modifications. The water samples were firstly extracted by liquid-liquid extraction using methyl tert-butyl ether followed by injection into a gas chromatograph (7890B, Agilent, USA) equipped with a micro-electron capture detector (HP-5 column, 30 m × 0.25 mm × 0.1 μm, Agilent, USA). Samples were collected every three days in pre-cleaned glass bottles. Once collected, the water samples were immediately filtered through a 0.7 μm microporous membrane (GF/F, Whatman, UK) and then preserved in 1 L amber glass bottles at 4°C in the dark until use. All the samples were analyzed in triplicate to ensure the accuracy of results. Details about the determination of DBPs are provided in Appendix A Text S2.

1.4.3. Molecular weight (MW) fraction

After the same pretreatment as DOC samples, organic matter was fractionated by ultra-filtration through Millipore membranes (Millipore, USA) with MW cut-offs of 1, 3 and 10 kDa, using a sealed ultrafilter cup (Amicon, Millipore) with nitrogen gas pressure of 0.15 MPa. The filtrate passing through the 10 kDa membrane was considered to contain organic matter of MW < 10 kDa, with the fraction >10 kDa absorbed on the Millipore membrane. Similarly, the filtrates of the 1 and 3 kDa membranes contained organic matter of MW <1 kDa and <3 kDa, respectively. The content of each fraction was calculated by subtraction. The sampling time was on the 55th day and the experiments were conducted in triplicate.

1.4.4. Hydrophilic and hydrophobic fraction

After the same pretreatment as DOC samples, organic matter was also fractionated into three types using XAD-8 and XAD-4 resins. The fraction that passed through both the XAD-8 and XAD-4 columns was defined as hydrophilic (HPI). The fraction retained by XAD-8 was defined as hydrophobic (HPO), while the fraction absorbed by XAD-4 was defined as transphilic (TPI). Those two resins were activated as described by Leenheer (1981). Prior to use, the resins were washed with methanol and deionized water. The pH of samples was adjusted to 2.0 before they were fed into the XAD-8 absorption column (at 5 mL/min) and the XAD-4 resin (at 15 mL/min). The sampling was carried out on the 55th day and the experiments were conducted in triplicate.

1.4.5. EEM spectra measurement

EEM spectra were obtained using a HITACHI F-7000 fluorescence spectrophotometer (Japan) equipped with a xenon lamp. The excitation and emission wavelengths were both scanned from 200 to 600 nm with an interval of 2 nm and the scanning speed was adjusted to 3600 nm/min. Samples used for EEM scanning was collected on the 55th day and filtered through a microporous filter membrane (0.45 μm, Millipore, USA) for pretreatment.

1.4.6. Biomass, biological activity and high-throughput sequencing

According to the method reported by Findlay et al. (1989), biomass can be represented by the lipid-bound phosphate content. 10–20 g ceramsite was extracted and collected in a 200-ml cone bottle. The lips of the biomass were recovered after some experimental procedures. Phosphate was liberated from the recovered lipids by potassium persulfate digestion. Detailed experimental procedures are shown in Appendix A Text S3. The phosphate concentration was determined by ammonium molybdate spectrophotometry. Results were represented as nmol P for unit mass of ceramsite. Biological activity was characterized by the biomass respiration potential. Detailed procedures were based on the research of Urfer and Huck (2001).

DNA samples were extracted from the biofilm of ceramsite using the E.Z.N.A Mag-Bind Soil DNA Kit (Omega, USA) according to the manufacturer’s instructions. Gene sequencing was conducted using the Illumina Miseq™ PE300 platform.
Sequences were processed using the Quantitative Insights into Microbial Ecology software. Detailed experimental procedures are shown in Appendix A Text S4.

The ceramsite samples used for biomass analysis and high-throughput sequencing were both collected on the 56th day. The ceramsite samples were collected at 40 cm height above the gravel layer (lower layer in UBAF), 110 cm height (middle layer in UBAF) and 180 cm height (upper layer in UBAF), respectively, to investigate the differences in the biomass and microbial communities at different heights.

2. Results and discussion

2.1. Performance of the two systems

In order to investigate the performance of the ICME-UBAF coupled system, parallel experiments were conducted using the micro-polluted source water as the feed water, which was pretreated with or without ICME.

2.1.1. Removal of regular indicators in the two systems

The performance of organic matter removal in the UBAF and coupled system is shown in Fig. 2. The variations of turbidity, color degree and ammonia in two systems are shown in Appendix A Fig. S3. It can be observed that the removal rates of turbidity, color and ammonia in two systems are around 14.4% and 26.0%; due to the digestion of impurities (such as iron filings and particulate carbon), Fe$^{2+}$ and Fe$^{3+}$ generated from the microscopic galvanic cells in the ICME system. However, the Fe$^{2+}$ and Fe$^{3+}$ produced ferrous and ferric hydroxides through the combined contribution of co-precipitation, enmeshment, interparticle bridging to strengthen the coagulation and adsorption, contributing to the removal of turbidity (Cheng et al., 2007; Ma et al., 2017). The variations in ammonia did not show any significant difference in the two systems since the ICME had no contribution to its removal. The high removal rate (90%) was owing to the great multiplication of the nitrifying bacteria in the UBAF.

UBAF alone removed 16.6% of DOC, mainly through its adsorption, filtration and limited biodegradation, failing to ensure the safety of the water supply. The coupled system showed enhanced DOC removal (average value of 53.7%) compared to the UBAF alone. The ICME contributed 15.6% of DOC removal. The initial Fe$^{2+}$ generated at the anode and [H] and O· generated at the cathode have strong chemical activities to destroy the carbon chains of organic contaminants effectively by electron transfer and electrochemical oxidation (Yang et al., 2017). These species may destroy macromolecular organic groups and generate biodegradable small-molecule organic matter (Matheson and Tratnyek, 1994). The reactions are shown as follows.

Iron anode: Fe $\rightarrow$ Fe$^{2+} + 2e^{-} E^0 = -0.44$ V.
Carbon cathode: O$_2 + 4H^+ + 4e^{-} \rightarrow 2O^- + 4[H] \rightarrow 2H_2O E^0 = 1.23$ V.

When the conditions are acidic and oxygen-rich, H$_2$O$_2$ may be generated to produce Fenton’s reagent to oxidize DOC (Ying et al., 2012). Furthermore, the dissolved Fe$^{2+}$ and Fe$^{3+}$ can form ferrous and ferric hydroxide flocs to improve the coagulation and adsorption, eliminating DOC (Cheng et al., 2007; Tang and Stumm, 1987; Zhang et al., 2018). Previous studies have shown that ICME had a good removal effect on polychlorinated organic compounds, nitrobenzene organic compounds and azo organic compounds (Gregory D. Sayles et al., 1997; Novak et al., 1998; Xu et al., 2016). The subsequent UBAF in the combined system removed 38% of DOC due to the changes in the physicochemical properties of the feed water caused by ICME pretreatment.

2.1.2. Removal of DBP precursors in the two systems

Fig. 3 shows the variations in the TCM and DCAN precursors in the two systems. The TCM FP and DCAN FP in raw water were 287.4–439.6 μg/L and 13.7–21.0 μg/L, respectively, which were both much higher than those reported in other source waters (Tan et al., 2017; Yan et al., 2010). The higher DBP FP implies high risk during the subsequent disinfection. Generally, the UBAF-only treatment had poor removal of both TCM and DCAN precursors, with average removal rates of 20% and 17%, respectively. The unsatisfactory elimination of DBP precursors may be attributed to their high contents and limited biodegradability by the UBAF. The coupled system exhibited obviously enhanced removal of both TCM and DCAN precursors, with average removal rates of 66% and 57%, respectively. ICME alone removed 31% TCM of precursors and 20% of DCAN precursors. The electrochemical oxidation in ICME may change the initial DBP precursors into those with lower yield or no yield. In addition, the ferrous and ferric hydroxide flocs generated from the galvanic cells could also contribute to the removal of DBP precursors. Due to the significant influence on DBP precursors’ properties by ICME, the subsequent UBAF achieved better removal of TCM and DCAN precursors (35% and 37%, respectively), indicating an effective level of control of the potential risk of DBPs.

2.2. The mechanisms of pollutant removal

This part focuses on the reason for the differences in removal efficiency and the mechanisms of organic matter and the DBP precursor removal in the two systems.
2.2.1. Variations of UV\textsubscript{254} and SUVA

UV absorbance at 254 nm indicates the existence of unsaturated carbon bonds, including aromatic compounds (Nishijima and Jr, 2004). As shown in Fig. 4, the UBAF-only treatment removed 12.2% of UV\textsubscript{254} while the ICME removed 39.8% of UV\textsubscript{254} due to the oxidative cleavage of unsaturated carbon bonds. The combined UBAF also removed 25.8% of UV\textsubscript{254}, higher than the UBAF alone. UV\textsubscript{254} had a positive correlation with TCM FP during chlorination, which was found in previous studies (White et al., 2003; Zhou et al., 2015).

The SUVA value is a quantitative indicator associated with the organic compounds’ aromaticity and hydrophobicity (Kikuchi et al., 2017), which generally correlate to being recalcitrant for biodegradation. The ICME removed 27.1% of SUVA, indicating a decrease in the organic compounds’ aromaticity. There was slight increase in SUVA after UBAF treatment. That may be because the compounds with low UV\textsubscript{254} absorbance were consumed by microorganisms, leaving behind other UV\textsubscript{254}-absorbing aromatic compounds. Meanwhile, the BOD\textsubscript{5}/COD\textsubscript{Mn} was measured to evaluate the improvement in the biodegradability of feed water treated by ICME. The results showed that a significant increase in the ratio was achieved, from 0.21 to 0.56, which implied that the organic matter and DBP precursors had become more prone to biodegradation.

2.2.2. Molecular weight distribution of DOC and DBP precursors

Fig. 5 shows the MW distribution of DOC and DBP precursors in the parallel experiments. As can be seen, the UBAF-only treatment mainly removed low-MW DOC, where the fractions <1 and 1–3 kDa were decreased by 26.0% and 20.2%, respectively. This may be attributed to their better biodegradability, as they had smaller molecular mass and simpler molecular structures. The organic fraction >10 kDa was removed at the efficiency of 12%, mainly due to the filtration and adsorption functions of the biological aerated filter. The lower removal rate of this fraction may be because the high-MW organic matter is more likely to have complex structures and to be less biodegradable. In the coupled system, the fates of low-MW and high-MW DOC were different in the ICME system, which showed removal of 28.9% (>10 kDa), 22.2% (10–3 kDa), 6.4% (3–1 kDa) and 4.3% (<1 kDa), respectively. It can be concluded that the ICME played a key role in breaking large-molecular-weight compounds into low-molecular-weight ones, due to the great chemical activity of Fe\textsuperscript{2+} and [H] generated by galvanic interaction (Yang et al., 2017; Zhang et al., 2018). The subsequent UBAF in the combined system greatly removed DOC compared to the UBAF alone.

The precursors of TCM in feed water were characterized by dominance in the high-MW fraction (>10 kDa), which accounted for 60.1% of TCM FP. This was similar to the results
of a previous study (Yan et al., 2010). The UBAF-only treatment mainly removed the low-MW (<3 kDa) fraction of TCM precursors, leading to unsatisfactory removal of TCM precursors. In contrast, the ICME mainly removed the MW fraction >3 kDa of TCM precursors rather than those <3 kDa. The oxidation performed by ICME as mentioned above may destroy the carbon chains of TCM precursors and change them into lower DBP yield compounds in the smaller MW fraction. It was worth noting that the increased TCM FP of the MW fraction (1–3 kDa) in the ICME effluent seemed to be caused by the transformation of TCM precursors in the high MW fraction. After ICME, the subsequent UBAF could greatly remove the TCM precursors with MW fraction <3 kDa.

The main precursors of DCAN in feed water were in the low-MW fraction <1 kDa and high-MW fraction >10 kDa, accounting for 38.6% and 45.4% of DCAN FP respectively. The UBAF-only treatment removed relatively more of the low-MW fraction (< 10 kDa) DCAN precursors than the high-MW ones (>10 kDa). The ICME mainly removed the MW fraction of DCAN precursors >10 kDa, at the removal efficiency of 35.8%. The oxidation performed by ICME may transform DCAN precursors in the high MW fraction into lower yield ones. The subsequent UBAF mainly removed DCAN precursors in the MW fractions <10 kDa.

2.2.3. Hydrophilic and hydrophobic fractions of DOC and DBP precursors

The fates of the hydrophilic and hydrophobic components of organic matter are shown in Fig. 6. The results show that the DOC in raw water consisted mainly of HPO components (40.5%) and HPI components (45.1%). The UBAF-only treatment removed relatively more of the low-MW fraction (< 10 kDa) TCM precursors than the high-MW ones (>10 kDa). The ICME mainly removed the MW fraction of TCM precursors >10 kDa, at the removal efficiency of 35.8%. The oxidation performed by ICME may transform TCM precursors in the high MW fraction into lower yield ones. The subsequent UBAF mainly removed TCM precursors in the MW fractions <10 kDa.

2.2.4. The fluorescence EEM spectra of DOM fractions in water samples

The fluorescence spectra were divided into five regions: Regions I–V represent aromatic protein-like type I, aromatic protein (AP)-like type II, fulvic acid (FA)-like, soluble microbial products (SMP)-like and humic acid (HA)-like substances, respectively. In the raw water, the organic matter was composed of compounds in regions II, III, IV and V, indicating an important role in transforming the functional groups of hydrophobic organic compounds into hydrophilic groups, which is similar to the effect of ozonation on organics (Yu et al., 2016). As a consequence of oxidation caused by ICME, the removal rate in the subsequent UBAF was 61.2% for the HPI and 56.1% for TPI. The combined system removed 53.1% of HPO components, which was better than that of UBAF alone.

Most of the precursors of TCM in feed water were in the HPO component, which had the maximum contribution to both the TCM FP (51.7%) and its yield (45.0 μg/mg DOC). The UBAF-only treatment removed 31.1% of HPI, 23.2% TPI and 15.8% HPO for the TCM precursors, leading to unsatisfactory removal performance. In the combined system, the ICME removed HPO TCM precursors well, at the rate of 38.6%, and the subsequent UBAF showed good removal of the HPI and TPI precursors, at 53.1% and 50.7%.

The main precursors of DCAN in feed water were in the HPI component, which had the highest contribution to DCAN FP (60.6%) and highest DCAN yield (2.25 μg/mg DOC). The UBAF-only treatment removed 23.6% of HPI, 18.8% TPI and 5.9% HPO in terms of DCAN precursors. In the combined system, the ICME mainly removed HPO DCAN precursors (42.6%). That may be because the HPO component was oxidized directly by the ICME into byproducts with less DCAN yield. The subsequent UBAF showed good removal of HPI (56.5%) and TPI precursors (38.6%).

Fig. 5 – Molecular weight distribution of DOC and DBP precursors in UBAF-only and ICME-UBAF coupled (C-UBAF) systems.
that the physicochemical properties of the raw water were complex.

Results showed that the UBAF-only treatment removed part of the SMP-like and HA-like substances due to its adsorption and limited biodegradation, which was consistent with its poor removal of DOC and DBP precursors. The HA-like and FA-like substances are usually large molecules with aromatic structures, which are recalcitrant to biodegradation in BAF systems (Han et al., 2013). Part of the high-MW SMP-like substances could also be refractory (Barker and Stuckey, 1999). As shown in Fig. 7a and c, it was obvious that the fluorescence intensity was greatly weakened by the ICME pretreatment, especially in regions IV and V. The fluorescence variations may be partly attributed to physical coagulation and adsorption by ferrous and ferric hydroxides (Cheng et al., 2007; Lefebvre and Legube, 1990). Considering the incongruity of the observed fluorescence intensity decrease and the limited DOC removal in the ICME system, chemical oxidation may play the key role, leading to the cleavage of unsaturated carbon bonds or carbon chains and a decrease in color and fluorescence. The HA-like substances are considered to be large-molecular-weight and hydrophobic organics (De Melo et al., 2016) and reported to be important precursors of TCM (Abouleish and Wells, 2012). The weakened fluorescence intensity of HA-like substances accounts for the decrease of TCM FP brought about by ICME. Chu et al. (2011) have reported that the nitrogen-rich AP-like and SMP-like substances are important precursors of N-DBPs. The removal of SMP-like substances by ICME may contribute to the removal of DCAN precursors.

2.3. Microbial community analysis

To further clarify the cause for the differences in pollutant removal in the two systems, we next focused on the growth, activities and diversity of microbes attached to the ceramsite.

2.3.1. Biomass, biological activity and diversity of microbial communities

The biomass can be represented by its lipid-bound phosphate content (Findlay et al., 1989). Oxygen uptake rate (OUR) refers to the oxygen consumption by microbes in a biofilm within a unit volume and time. In this study, OUR was selected to characterize the biological activities of the biofilm attached to the ceramsite.

As shown in Fig. 8, the biomass and OURs of the microbial community attached to ceramsite in ICME–UBAF were both higher than that in the UBAF-only system. The greater amount of microbes and higher biological activities utilized more organic matter through their assimilation and metabolism, which accounted for the higher removal of organic matter and DBP precursors in ICME–UBAF. The biomass and OURs degraded along the height of the column because the microenvironment (substrate, nutrient concentration and dissolved oxygen) changed along the flow direction.

16S rRNA sequencing was employed in order to determine the richness and diversity of bacterial communities in the two
systems. These sequences were subsequently clustered into operational taxonomic units (OTUs). OTUs refer to clusters of (uncultivated or unknown) organisms, grouped by DNA sequence similarity of a specific taxonomic marker gene such as 16S rRNA (Revetta et al., 2010). Results suggested that the OTUs captured around 98% of species of all the samples, and therefore they were representative enough for the analysis. The ACE index and Chao1 index are quantitatively estimated to reflect the richness of microbial species: larger ACE and Chao1 indexes correspond to higher richness of species in a bacterial community. The Shannon index, as well as the Simpson index, is a quantitative measure reflecting the diversity of microbial species: higher Shannon index and lower Simpson index mean higher community diversity (Zhao et al., 2016). According to Table 1, the Shannon index of ICME-UBAF was higher and the Simpson index was lower than that of the UBAF alone, indicating the higher diversity of microbial species in ICME-UBAF. The higher Chao 1 index and higher ACE index indicated that the ICME-UBAF had higher richness of microbial species. The above results showed that the richness and diversity of the microbial community increased in the combined ICME-UBAF due to

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<tr>
<th>Samples</th>
<th>OTU</th>
<th>Shannon</th>
<th>Simpson</th>
<th>ACE</th>
<th>Chao1</th>
<th>Coverage</th>
</tr>
</thead>
<tbody>
<tr>
<td>UBAF</td>
<td>1327</td>
<td>4.74</td>
<td>0.037</td>
<td>2106.6</td>
<td>1903.1</td>
<td>0.98</td>
</tr>
<tr>
<td>ICME-UBAF</td>
<td>1641</td>
<td>5.29</td>
<td>0.017</td>
<td>2356.0</td>
<td>2243.4</td>
<td>0.98</td>
</tr>
</tbody>
</table>

Fig. 7 – EEM spectra of DOC in raw water (a), UBAF effluent (b), ICME effluent (c) and combined ICME-UBAF effluent (d).

Fig. 8 – Biomass and biological activities of microbes in UBAF-only and ICME-UBAF coupled (C-UBAF) systems.
the changes in the physicochemical properties of the feed water.

2.3.2. Composition and analysis of microbial communities

The relative abundance of each microbial class at different UBAF heights in the two systems is described in Fig. 9. In total, 43 bacterial classes were identified and the dominant bacteria classes were *Alphaproteobacteria*, *Betaproteobacteria*, *Gammaproteobacteria* and *Bacilli*. The relative abundance of these four bacteria classes in the two systems showed obvious differences, indicating the effect of ICME pretreatment on the microbial communities. The abundance of *Alphaproteobacteria* (43%–47%) in ICME–UBAF was much higher than that in the UBAF-only system (23%–26%). *Gammaproteobacteria* showed similar variation to *Alphaproteobacteria* in the two systems. In contrast, the relative abundance of *Betaproteobacteria* (9%–21%) was lower than that in UBAF alone (16%–36%). It was noted that the abundance of *Betaproteobacteria* gradually decreased along the flow direction. *Betaproteobacteria* are closely associated with nitrification (Liu et al., 2017), and the process of nitrification requires oxygen.

To further reveal the taxonomic composition and functional population of the two systems, the heatmap of the most-abundant species at the genus level is visualized in Fig. 10. It can be seen that the overall abundance in ICME–UBAF was higher than that in the UBAF-only system. The hierarchical cluster analysis showed three main groups of rows in the two systems. The first group was featured with higher abundance in the UBAF-only system than in ICME–UBAF. The second group showed the opposite effect, and the third one was featured by no obvious differences between the two systems.

In the first group, *Nitrosomonas* belonging to *Betaproteobacteria* are considered to be important ammonia-oxidizing bacteria (Siripong and Rittmann, 2007), and the high abundance of *Nitrosomonas* in UBAF accounted for the satisfactory ammonia removal (Liu et al., 2017). The reason for its higher abundance in the UBAF-only treatment may be because the UBAF mainly removed the ammonia and *Nitrosomonas* dominated the bacterial genera, while the ICME system had more population with other functions. The genera *Exiguobacterium* consists of facultative anaerobes (Yoon et al., 2005) that can metabolize refractory organics such as azo dyes, agricultural chemicals and petroleum (Dhanve et al., 2008; López et al., 2005; Mohanty and Mukherji, 2008). Its abundance was therefore higher in UBAF than that in ICME–UBAF due to the higher concentration of influent refractory organics in the UBAF-only system. The genera *Massilia* is aerobic and associated with nitrification (Cheng et al., 2016). Thus, the variation of *Massilia* was similar to that of *Nitrosomonas* due to having the same function and same aerobic characteristics.

In the second group, bacteria from the genera *Pseudomonas* are capable of performing heterotrophic nitrification and have a phenomenal ability to denitrify their nitrification products under aerobic conditions (Jin et al., 2015; Su et al., 2001). They can utilize not only nitrate and nitrite, but also ammonium under aerobic conditions (Zhang et al., 2011). *Pseudomonas* in the two systems contributed to the removal of ammonia. The genera *Sphingomonas*, *Brevundimonas* and *Sphingorhabdus* are all belonged to the class *Alphaproteobacteria*, accounting for the domination of *Alphaproteobacteria* in ICME–UBAF. The genera *Brevundimonas*, *Sphingorhabdus* and *Sphingomonas* are reported to be heterotrophic and metabolize organics (Jeong et al., 2016; Sartory et al., 2008). *Brevundimonas* were reported to degrade numerous organic compounds (Huang et al., 2012; Wu et al., 2018) and *Sphingorhabdus* were capable of degrading both aromatic and aliphatic hydrocarbons (Jeong et al., 2016). The increase of the two genera in ICME–UBAF illustrated the better removal of organic matter and the DBP precursors. The genera *Sphingomonas* were reported to be present in BAF systems in

Fig. 9 – Relative abundance of dominant microbial classes at different heights in the two systems, A: ICME–UBAF, B: UBAF-only.

Fig. 10 – Heatmap of most-abundant bacterial genera at different heights in the two systems, A: ICME–UBAF, B: UBAF-only. The classes to which the bacterial genera belong are shown in parentheses. Dendrograms of hierarchical cluster analysis grouping the genera and systems are shown at left and top.
previous studies (Han et al., 2013; Liu et al., 2017) and were able to degrade different kinds of pollutants as a common kind of heterotrophic bacteria, including micro-pollutants (Chanika et al., 2011). Sphingomonas could also function as traditional extracellular polysaccharide-producing bacteria (Fialho et al., 2008; Meneghine et al., 2017). The resulting rich extracellular polysaccharides increased the microbial richness and diversity, as other bacteria could feed on it. The higher abundance of Sphingomonas may also be associated with the effluent containing Fe(OH)3 flocs of the ICME system due to its Fe(III) reducing characteristics (Peng et al., 2016).

The analysis of microbial communities implied that the higher abundance of three heterotrophic bacteria, which could metalize aromatic compounds and other organics, contributed to the better removal of organic matter and DBP precursors.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jes.2018.11.010.

R E F E R E N C E S


Huang, L., Sun, G., Yang, T., Zhang, B., He, Y., Wang, X., 2013b. A preliminary study of anaerobic treatment coupled with micro-


