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Removal of Soluble Microbial Products as the Precursors of Disinfection Byproducts in Drinking Water Supplies

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Abstract

Water pollution worsens the problem of disinfection byproducts (DBPs) in drinking water supply. Biodegradation of wastewater organics produces soluble microbial products (SMPs), which can be important DBP precursors. In this laboratory study, a number of enhanced water treatment methods for DBP control, including enhanced coagulation, ozonation, and activated carbon adsorption, were evaluated for their effectiveness in treating SMP-containing water for the DBP reduction purpose. The results show that enhanced coagulation with alum could remove SMPs only marginally and decrease the DBP formation potential (DBPFP) of the water by less than 20%. Although ozone could cause destruction of SMPs in water, the overall DBPFP of the water did not decrease but increased after ozonation. In contrast, adsorption by granular activated carbon (GAC) could remove the SMP organics

from water by more than 60% and reduce the DBPFP by more than 70%. It is apparent that enhanced coagulation and ozonation are not suitable for the removal of SMPs as DBP precursors from polluted water, although enhanced coagulation has been commonly used to reduce the DBP formation caused by natural organic matter (NOM). In comparison, activated carbon adsorption is shown as a more effective means to remove the SMP content from water and hence to control the wastewater-derived DBP problem in water supply.

Key words: Disinfection byproducts (DBPs); Soluble microbial products (SMPs); Enhanced coagulation; Ozonation; Activated carbon adsorption

1. Introduction

Disinfection is a vital step in water treatment to eliminate pathogens and prevent the transmission of waterborne diseases. However, use of chemical disinfectants such as chlorine often results in the formation of disinfection byproducts (DBPs) in water with a potential health risk. Trihalomethanes (THMs) and haloacetic acids (HAAs) are the two most prevalent groups of organic DBPs formed during chlorination [1]. Because of an increasing health concern, the U.S. Environmental Protection Agency (EPA) has set more stringent regulatory limits in recent years for four THM and five HAA compounds in drinking water [2]. To comply with the regulation, a great deal of effort has been made to improve the water treatment process and hence to lower the DBP level in the finished water.

Natural organic matter (NOM) in freshwater supply has been considered as the major precursor of DBPs [3,4]. However, the DBP problem can also be attributed to water pollution caused by human activities. Water pollution has become one of the most serious global environmental problems, especially in developing countries that are experiencing rapid population and economic growth. Many surface water bodies, such as rivers and lakes, are

used for both wastewater disposal and fresh water withdrawal for municipal use. Researchers have found that organic pollutants in wastewater could become DBP precursors in the receiving water, leading to more DBP formation in water supply [5-7].

Soluble microbial products (SMPs) are organic compounds that are released by microorganisms into water during substrate metabolism and microbial decay [8]. SMPs are the majority of effluent organic matter (EfOM) in biologically treated wastewater [9-11]. Meanwhile, organics in the less treated wastewater effluent would also undergo biodegradation in the receiving water, and SMPs are the final products of the natural biodegradation process [12,13]. Thus, wastewater-based SMPs may become important DBP precursors in natural water that would worsen the DBP problem in water supply [14-16]. Our previous study indicates that SMPs have different properties from NOM as DBP precursors [13]. SMPs contain more biomolecules, e.g. proteins and polysaccharides, and less aromatic structures, in comparison to NOM that is dominated by humic substances. Moreover, and SMPs consist of a large fraction of small molecules lower than 1k Da. Although SMPs are less reactive than NOM with chlorine disinfectants, they can form more harmful DBPs such as N-containing DBPs. However, there are few studies focusing on the removal of SMPs in water treatment for the DBP control purpose. Granular activated carbon adsorption has been considered to be a promising method for organic removal [8]. Certain SMP molecules could be biologically degraded, although a long acclimation time and a long biodegradation period are required [17]. It was also reported more than 50% of SMPs could be removed or retained by the treatment with a membrane bioreactor [18]. However, these experimental studies did not evaluate the effectiveness of the treatment on reduction of DBP formation potentials in relation to the SMP removal.

To address the wastewater-derived DBP issue for polluted water resources, there is a need to evaluate the effectiveness of common DBP reduction technologies for SMP removal and

DBP reduction. The present study was designed to focus on SMPs as a group of DBP precursors in polluted surface waters. SMPs were produced purposely by organic biodegradation to form a "pure SMP solution" for the experimental study. Laboratory tests were conducted to treat the SMP water using the common DBP control processes, including enhanced coagulation, ozonation, and activated carbon adsorption. The efficiency of each method for SMP removal was determined, and the related change in DBP formation potential of the water after treatment was also evaluated.

2. Materials and methods

2.1 SMP solutions

Biological organic degradation was conducted in batch reactors to produce SMPs in water. Glucose was used as the main substrate that can be completely degraded, leaving only SMPs as soluble organics in the solution. The biodegradation experiments were carried out in 10-L bioreactors placed in a temperature-controlled biochemical oxygen demand (BOD) incubator at 20 °C (Velp Scientifica). Glucose (Unichem) was dissolved in Milli-Q water (Millipore) to have a dissolved organic carbon (DOC) concentration of about 200 mg L^{-1}. Seed biomass was activated sludge collected from a domestic sewage treatment works (Stanley STW) in Hong Kong. The seed sludge was dosed into the bioreactors as the seed biomass at a suspended solid (SS) concentration of 10 mg L^{-1}. NH_4Cl, $FeCl_3$, $CaCl_2$, and $MgSO_4$ were added as nutrients according to the guidelines for running the BOD tests [19]. The water pH was maintained at around 7 with a phosphate buffer solution consisting of 8.5 mg L^{-1} KH_2PO_4, 33.4 mg L^{-1} $Na_2HPO_4 \cdot 7H_2O$, and 21.7 mg L^{-1} K_2HPO_4. During the biodegradation, the solution in the bioreactors was aerated by an air pump at an air flow rate of 4 L min^{-1} to provide oxygen. After incubation for 5 d, the suspension was filtered through 0.45 μm mixed cellulose esters membranes (Millipore) to remove the sludge and all suspended solids. It was

found that glucose could be completely degraded in the bioreactors after no more than 3 days, and the organic substances dissolved in the filtrate were SMPs. The SMP solutions had a DOC of around 20 mg L^{-1}, which were used as the water samples for the subsequent studies on SMP removal and DBP formation potentials (DBPFPs).

2.2 Enhanced coagulation

Standard jar tests were conducted to determine the efficiency of SMP removal by enhanced coagulation. For each jar test, the SMP solution was placed into 6 beakers (200 mL each) that were situated on a jar test apparatus (ZR4-6, Zhongrun). Alum ($Al_2(SO_4)_3 \cdot 18H_2O$, Riedel-de Haen) was added as the coagulant into the SMP solutions at doses of 0, 20, 40, 60, 80, and 100 mg L^{-1}. The doses were chosen according to the enhanced coagulation guidance by U.S. EPA [20]. Immediately after dosing of the coagulant, pH of the water was adjusted to 6.5 with 1 N $NaHCO_3$ (BDH) and 0.1 N Na_2CO_3 (BDH) solutions. The jar test procedure consisted of rapid mixing at 200 rpm for 2 min, slow mixing at 20 rpm for 25 min, followed by sedimentation for 20 min. After the jar test coagulation and sedimentation, the supernatants were collected and filtered, and the solutions were then analyzed for the DOC concentration and the UV absorbance at 254 nm (UV_{254}) and tested for the DBPFP values.

2.3 Ozonation

Ozone was produced by an oxygen-fed ozone generator (Enaly) at an oxygen supply rate of 1 L min^{-1}. The ozone stock solution was obtained by aeration for 3 min to dissolve ozone into ultrapure water. The water was prior purged with N_2 gas for 2 min and chilled to 4 °C to increase the ozone solubility. The ozone stock solution was then dissolved into ultrapure water to have a series of ozone concentrations of 14, 10, 6, 2, and 1 mg L^{-1}. The ozone solutions were then mixed with the SMP solutions at a ratio of 1:1 (v:v) to result in final

ozone dosing concentrations of 7, 5, 3, 1, and 0.5 mg L^{-1}. The doses were chosen according to Alternative Disinfectants and Oxidants Guidance Manual by U.S. EPA for DBP precursor control [21]. The mixtures were sealed and left overnight in dark for reaction. After the ozonation overnight, the ozone concentration in water was measured and no residual ozone was detected. The ozonated SMP solutions were filtered and then analyzed for the organic contents and tested for DBPFPs.

The ozone concentration in a solution was determined following the ultraviolet adsorption method. The solution with ozone was measured by a UV-visible spectrophotometer (UV/VIS Lambda 25, Perkin Elmer) with a 1-cm cuvette cell for its UV absorbance at 258 nm (UV_{258}). The ozone concentration (mg L^{-1}) in water was calculated from its linear relationship with UV_{258} using $O_3 = UV_{258}/(2950 \times 48000)$ [22].

2.4 Activated carbon adsorption

Adsorption experiments were conducted using granular activated carbon (GAC) for the removal of SMPs and related DBPFPs. Before use, the GAC (Merck) was washed with ultrapure water for several times to remove impurities and then dried completely at 105 °C. The batch adsorption isotherm experiments were performed following the standard procedures [23]. In brief, for an adsorption test, the SMP solution was placed into a series of 250-mL flasks (100 mL each), and GAC was added into the flasks at different doses, i.e. 0.05, 0.1, 0.2, 0.4, 0.8, 1.6, 3.2, 6.4, 12.8, and 25.6 g L^{-1}. The similar dosage range of activated carbon has been used in other studies for treatment of polluted source water [24-26]. The solution pH was controlled at around 7 with the phosphate buffer during the adsorption tests. The flasks were sealed and placed on a shaker (S150, Stuart) at 25 °C with a rotation speed of 100 rpm, and all batch adsorption tests lasted for 12 hr. Preliminary tests showed that the SMP organic adsorption by GAC could reach equilibrium within 6 hr. After the GAC

adsorption, the SMP solution from each flask was filtered, followed by organic analysis and the DBPFP test.

The amount of SMPs adsorbed by the unit amount of GAC, Q_e, can be calculated by

$$Q_e = \frac{(C_o - C_e)V}{W} \quad (1)$$

where C_o and C_e are the initial and final DOC concentrations in the SMP solution, respectively, V is the volume of solution (100 mL), and W is the weight of GAC dosed for adsorption.

The GAC adsorption of main SMP components, including polysaccharides (PSs), proteins (PNs), and humic-like substances (HSs), were also investigated. A higher initial DOC concentration (1000 mg L^{-1}) of feeding glucose solution was used for the high detection limits (2 mg L^{-1}) of these SMP components. The GAC doses were 8, 16, 32, 64, 128, and 256 g L^{-1}. The polysaccharide concentration was determined according to the phenol-sulfuric acid method using glucose as the standard [27], and the protein and humic substance contents were analyzed by a UV/VIS spectrophotometer (UV/VIS Lambda 25, Perkin Elmer) following the modified Lowry method using bovine serum albumin (Sigma) and humic acid (Fluka) as the standards, respectively [27].

The effects of the solution pH and the particle size of GAC on the SMP adsorption result were further characterized. The pH values tested included 3, 5, 7, 9, and 11, which were adjusted with either HCl (Sigma) or NaOH (BDH) solutions, while the same GAC dose of 3.2 g L^{-1} was applied for adsorption. No obvious pH change was found after the adsorption tests. For the GAC size effect, the following five different size ranges were tested: >2.0, 1.2-2.0, 0.4-1.2, 0.2-0.4, and <0.2 mm. GAC was separated into the different size ranges by a series of sieves. The specific surface area of activated carbon granules was determined following the Brunauer-Emmett-Teller (BET) method using an adsorption analyzer (Flow

Sorb II-2300, Micromeritics). The activated carbon dose used for adsorption was also at 3.2 g L^{-1}, while the pH was controlled at around 7.

2.5 Determination of the DBPFP

DBPFP tests were conducted to evaluate the quantity and reactivity of the organics as DBP precursors in the water samples. The DBP formation tests were carried out by chlorinating the filtered water samples in accordance with the Standard Methods [28]. For each DBPFP test, a 100-mL water sample was chlorinated with NaOCl (Unichem), and the resulting solution was incubated in dark for 7 days at pH 7.0±0.2 with a 0.5 N phosphate buffer. To ensure the presence of free chlorine residual after the incubation, chlorine demand tests were conducted, i.e., the water samples were dosed with 100 mg L^{-1} Cl_2, incubated for 12 h, and the amount of free chlorine residual was measured. The NaOCl dose for the DBPFP test that would result in a free chlorine residual of between 3 and 5 mg L^{-1} was then determined. The actual free chlorine residual in the chlorinated water after 7 d of incubation was also measured, and only the samples that had a residual chlorine concentration ranging 3-5 mg L^{-1} were used for DBP determination. Immediately after the incubation, excessive chlorine in the water samples was quenched with NH_4Cl (BDH), and the DBP compounds formed in the chlorinated water were extracted.

The water samples were analyzed for the following main groups of DBPs: THMs and HAAs (the most predominant and commonly regulated DBP groups), trihaloacetaldehydes (the third largest group of organic DBPs in chlorinated water), halopropanones (commonly detected in chlorinated water after the previous three groups), and nitrogenous DBPs (N-DBPs) including haloacetonitriles and trihalonitromethanes (at lower concentrations but imposing a higher health risk). EPA Method 551.1 was adopted for liquid-liquid extraction and the subsequent chemical analysis for THMs, trihaloacetaldehydes, halopropanones, and

N-DBPs [29]. Methyl tert-butyl ether (MTBE, BDH) was used as the solvent for the liquid-liquid extraction. For HAA measurement, EPA Method 552.3 was used [30]. HAAs in water were extracted by liquid-liquid extraction with MTBE. Derivatization was then performed on the extract by adding acidic methanol at a 1:1 (v/v) ratio.

The DBP species in the extracts were analyzed using an HP 6890 gas chromatograph (GC) coupled with an HP electron capture detector (ECD) (Agilent). The GC system was equipped with a DB-35MS capillary column (Agilent) having a configuration of 30 m × 0.32 mm and a film thickness of 0.25 µm. An HP 6890 Series automatic liquid sampler was used for the sample injection, and an HP GC ChemStation was used for data processing. More details about the sample extraction procedures and GC analysis conditions can be found in previous studies [13,31].

2.6 Analytical methods

The DOC and UV_{254} of the organic content were measured for each water sample after filtration. UV_{254} indicates the UV absorbance at 254 nm of the organics in a water sample that is believed to be closely related to the DBPFP of the water [1]. A UV-visible spectrophotometer (UV/VIS Lambda 25, Perkin Elmer) with a 1-cm cuvette cell was used to determine the UV_{254}. The DOC was measured by a total organic carbon (TOC) analyzer (IL550, Lachat) based on the catalytic combustion-infrared method. The specific UV absorbance (SUVA) of the organic matter in water was calculated from the UV_{254} value divided by the DOC concentration, i.e. UV_{254}/DOC. Similarly, the DBPFP yield of the organic matter in water was determined from the DBPFP of the water sample divided by the DOC value, i.e. DBPFP/DOC.

2.7 Quality assurance (QA) & quality control (QC)

The SMP solutions were produced by organic degradation under the same incubation conditions as described in Section 2.1. The resulting SMP solutions for different tests had similar DOC, UV_{254}, and DBPFP values, indicting the reproducibility of the biodegradation incubation and SMP production. All of the experiments and tests were repeated for at least three times, and the average results were reported. For measurement of DOC and UV_{254}, the sample was measured in triplicate to ensure the accuracy of the results. For DBP analysis by the GC, a calibration curve was used for each batch of samples to ensure the reliability and accuracy of the DBP quantification. One procedure blank was also placed with each batch of samples to verify the background level of the GC detection. An internal standard, 1,2,3-trichloropropane (Sigma), was also used to check the stability of the GC measurement. Data were analyzed statistically using SPSS 18.0 for Windows, and data comparison was made using two-independent *t*-test.

3. Results and discussion

3.1 SMP solutions

SMP-containing solutions were prepared from organic biodegradation for the experiments on enhanced coagulation, ozonation, and activated carbon adsorption. The model SMP solutions had a DOC concentration of 21±5 mg L^{-1}, with a UV_{254} value of 4.3±0.9 m^{-1} and SUVA of 0.21±0.02 L mg^{-1} m^{-1} (Table 1). Chlorination of the SMP solutions resulted in DBP formation in water, and the DBPs detected included chloroform (CF) for THMs, dichloroacetic acid (DCAA) and trichloroacetic acid (TCAA) for HAAs, chloral hydrate (CH) for trihaloacetaldehydes, trichloropropanone (TCP) for halopropanones, dichloroacetonitrile (DCAN) for haloacetonitriles, and trichloronitromethane (TCNM) for trihalonitromethanes. The total DBPFP of the SMP solutions was 1036±41 μg L^{-1}, and the DBPFP yield of the SMPs in water was 51±14 μg mg^{-1}-DOC [1] (Table 1). Chloroform was the most abundant

DBP species formed, followed by DCAA, TCAA, and CH, while TCP, DCAN, and TCNM were found at trace levels.

3.2 Enhanced coagulation

Alum was dosed into the SMP water from 20 to 100 mg L^{-1} for enhanced coagulation. At the elevated alum doses, floc formation during the jar test followed by sedimentation was well observed. Enhanced coagulation at the alum dose of 100 mg L^{-1} could significantly (p<0.05) reduce the UV_{254} of the SMP solution from the initial value of 4.6 to 3.6 m^{-1}. DOC concentration also showed significant (p<0.05) decrease from 21 to 18 mg L^{-1} after the enhanced coagulation and sedimentation (Fig. 1(a)). The SUVA value decreased only slightly from 0.22 to 0.20 L mg^{-1} m^{-1} at the alum dose of 100 mg L^{-1}.

Enhanced chemical coagulation could result in certain reductions of the DBPFPs of the SMP solutions, as the DBPFP value (841 µg L^{-1}) of the treated water was significantly lower (p<0.05) than the original DBPFP of the SMP water (1053 µg L^{-1}). However, a 20% DBPFP reduction may not be sufficient for the DBP control purpose, and the DBPFP yield decreased slightly from 49 to 46 µg mg^{-1}-DOC (Fig. 1(b)). More specifically, the CF and CH formation potentials decreased from the initial values of 282 and 325 µg L^{-1} to 242 and 297 µg L^{-1}, respectively (Fig. 1(c)). A higher level of reduction in HAA formation was observed, as the DCAA and TCAA formation potentials decreased from 285 and 155 µg L^{-1} to 218 and 79 µg L^{-1}, respectively. Chemical coagulation is believed to be more effective for removing more hydrophobic substances [32]. Compared to THM precursors, HAA precursors are supposed to be more hydrophobic [4], which would therefore be removed more effectively by enhanced coagulation. However, generally speaking, enhanced coagulation does not appear to be an effective means to remove wastewater organic-derived SMPs as DBP precursors from water.

Enhanced coagulation has been suggested and used as a practical and effective method for NOM removal and DBP control in water supply [33]. Chang *et al.* found that an alum dose of 20 mg L^{-1} could reduce the NOM content by 25%, the THMFP by 69%, and the HAAFP by 69%, and as the alum dose increased to 100 mg L^{-1}, the NOM removal increased to 66% [34]. Freese *et al.* also reported reductions of up to 50% for THMFP and between 40 and 70% for the organic carbon and color using enhanced coagulation [35]. Coagulation is more effective and selective in removing hydrophobic and/or large organic compounds than hydrophilic and/or small organic chemicals [33,36,37]. Compared to NOM, SMPs are mainly composed of small and hydrophilic molecules [11,16,38]. Thus, as shown by the alum coagulation results, the effect of enhanced coagulation on SMP removal is largely limited. While enhanced coagulation is effective to remove NOM for DBP control, it is apparent that chemical coagulation is not efficient for the removal of SMP-based DBP precursors from polluted water.

3.3 Ozonation

For the ozone doses applied into the SMP water, from 0.5 to 7.0 mg L^{-1} (0.03 to 0.43 mg-O_3/mg-DOC), the resulted DOC reduction was not significant (p<0.05). However, the UV_{254} value was reduced significantly (p<0.05) from 3.3 to 0.8 m^{-1} at a high ozone dose (Fig. 2(a)). Although ozonation could not mineralize SMP substances, it might lead to the destruction of organic molecules, resulting in lower UV_{254} and SUVA values. However, despite of the reduction in UV absorbance, the overall DBPFP of the SMP solutions did not decrease but increased significantly (p<0.05) from 1035 to 1252 μg L^{-1} after ozonation. The DBPFP yield of the ozonated SMPs also increased accordingly (Fig. 2(b)). More specifically, the CF and CH formation potentials increased considerably after ozonation, as the average values increased from 313 to 375 μg L^{-1} for CF and from 335 to 577 μg L^{-1} for CH (Fig. 2(c)). The

nitrogenous DBP, TCNM, also increased from 1 to 11 μg L^{-1}. The HAA formation potentials however became lower after ozonation, as DCAA and TCAA decreased from 228 and 157 μg L^{-1} to 178 and 110 μg L^{-1}, respectively.

Ozone was expected to destruct organic substances, which would lead a shift of the organics to smaller and more hydrophilic molecules or a change of the organics from a polyaromatic nature to a more polysaccharidal and proteinaecous nature [39]. The resulting functional groups after ozonation, such as carboxyl and hydroxyl, can be more reactive in chlorination to give rise to more CF and CH formations [40,41]. However, the destruction of aromatic structures might lead to a decrease in HAA formation. Nonetheless, the increase in other DBP species, especially CH, exceeded the reduction of HAA formation. For NOM, there were also reports that organic removal could not be achieved by ozonation at the ozone doses between 0.5 and 1.5 mg mg^{-1} DOC [42]. Bekboleta *et al.* found that ozone did not decrease but increased the THMFPs of the NOM-containing water from 44.2 to 45.6 μg mg^{-1} C, likely due to the formation of more reactive sites on NOM in forming THMs upon chlorination [39]. Thus, it can be concluded that ozonation alone is not a proper method to remove SMPs and other organics for DBP control in water treatment.

3.4 Activated carbon adsorption

Adsorption by activated carbon was shown to be highly efficient to remove both DOC and UV_{254} from the SMP water. At a GAC dosing content of 25.6 g L^{-1}, DOC was reduced from 26 to 9 mg L^{-1} (Fig. 3(a)). As a result of SMP removal by GAC adsorption, the DBPFP of the SMP solutions decreased significantly (p<0.05). For the four main DBP species, GAC at a dosage of 25.6 g L^{-1} decreased the CF formation potential from 335 to 106 μg L^{-1}, DCAA from 242 to a trace level of 16 μg L^{-1}, TCAA from 201 to 92 μg L^{-1}, and CH from 204 to 75

μg L^{-1} (Fig. 3(c)). The highest reduction was achieved for DCAA in comparison to other DBPs, indicating a preferential removal of DCAA precursors by GAC adsorption.

Activated carbon was highly capable of removing SMPs from water and hence reducing its DBP formation during chlorination (Fig. 3(b)). The total DBPFP of the SMP solution was reduced from 988 to 294 μg L^{-1} by GAC adsorption at a dose of 25.6 g L^{-1}. The DBPFP yield also decreased as the GAC dose increased (Fig. 3(b)). Other research has indicated that activated carbon preferentially adsorbs nonpolar organic compounds that are considered to be typical precursors of THMs and HAAs [3]. The present results suggest that GAC would adsorb preferentially the SMPs with a high DBPFP yield, leaving the SMPs in the solutions with a lower DBP formation reactivity. The linear adsorption isotherms for DOC and DBPFP of SMP solutions also indicated the efficient organic removal by activated carbon (Fig. 4(a) & (b)).

GAC has been reported to be highly effective to remove NOM and related DBP formation potentials in water [34,43,44]. Kristiana *et al.* reported that GAC could remove NOM by 70% and its DBP formation by 80-95% [43]. Another study on NOM found that GAC dosed at 2.4 g L^{-1} could reduce the DOC, THMFP, and HAAFP of the water by 96%, 92%, and 96%, respectively [34]. Although the removal of SMPs by GAC appeared to be less efficient than that reported for NOM, the present study shows that GAC adsorption is an effective method for decreasing SMP-based DBP formation in water.

The GAC adsorption of the three main SMP components, including polysaccharides, proteins, and humic-like substances, were also specified (Fig. 5). The raw SMP solution had a concentrated DOC of 123 mg L^{-1} with 36.2 mg L^{-1} polysaccharides, 4.9 mg L^{-1} proteins, and 12.6 mg L^{-1} humic-like substances. After GAC adsorption at a high dose of 256 g L^{-1}, the concentrations decreased to 12.6 mg L^{-1} for polysaccharides, 1.8 mg L^{-1} for proteins, and 5.1 mg L^{-1} for humic-like substances (Fig. 5(a)). GAC displayed a greater adsorption capability

for humic-like substances than for polysaccharides and proteins as shown by their adsorption isotherms (Fig. 5(b)). Adsorption by GAC is more effective for the removal of humic-like substances that are considered as the predominant DBP precursors in water. The lab result is consistent with the finding of other studies on activated carbon adsorption for the removal of typical DBP precursors such as NOM [3].

In general, activated carbon adsorption is shown to be much more effective than enhanced coagulation and ozonation for removing SMPs from water. SMPs are known to contain more biomolecules and less aromatic structures compared to NOM, with a large fraction of small molecules lower than 1k Da [13]. As discussed previously, enhanced coagulation is not an effective means for the removal of SMPs from water because of the small size and hydrophilic nature of SMP molecules. In comparison, GAC is supposed to be more efficient to remove small SMP molecules by adsorption, Although activated carbon prefers to adsorb humic-type materials, it can also perform well in the adsorption of hydrophilic and small organic molecules [34], leading to a much reduced DBPFP of the water as observed in the present study.

The efficiency of SMP removal by GAC adsorption would be affected by not only the SMP properties but also other factors, such as the particle size of GAC and pH of the solution [45,46]. In this study, the effects of pH and GAC size on SMP adsorption were evaluated at a GAC dose of 3.2 g L^{-1}. When the initial pH of the SMP solutions changed from 3 to 11, the resulting DOC after GAC adsorption tests decreased slightly, while the UV_{254} value showed little change (Table 2). It is apparent that the GAC adsorption of SMP-based DBP precursors is not sensitive to the change in solution pH. In comparison, when the size of GAC became smaller, the removals of both DOC and UV_{254} by adsorption increased considerably (Table 2). Hence, a smaller GAC size is more favorable to the adsorption of SMPs. The final DBPFP of the SMP solution after the adsorption by smaller GAC (< 0.2 mm) was 348 μg L^{-1}, which was

much lower than that of 477 μg L^{-1} after the adsorption by larger GAC (>2.0 mm). This may be explained by the different specific surface area of GAC of different size groups. It is known that an increase in specific surface area benefits adsorption [47]. The change of the specific surface area of GAC with the granule size was determined during the study. It was found that as the GAC size decreased from >2.0 to <0.2 mm, its specific surface area increased from 762.2 to 871.5 m^2 g^{-1}. Such an increase of the specific surface area apparently contributed to the additional SMP removal by the adsorption of smaller GAC in comparison to the test by larger GAC.

4. Conclusions

- SMPs resulted from biological organic degradation can be important DBP precursors in water. Enhanced coagulation with alum could reduce DOC and UV_{254} of the SMP solution only marginally, and the reduction in DBP formation by enhanced coagulation was less than 20%. Although ozone could cause destruction of SMPs in water and reduce its UV absorbance, the overall DBPFP of the SMP solution would not decrease but increase after ozonation. Upon ozonation of the SMPs, more active sites for chlorination were apparently formed, leading to more formation of THMs and CH. Thus, both enhanced coagulation and ozonation are not suitable for removing SMPs from polluted water for the DBP control purpose.
- Adsorption by activated carbon can effectively remove both the SMP organics and UV absorbance, with the respective removal efficiencies of 64% and 59%. The DBP formation potential of the SMP water can be reduced by more than 70% after GAC adsorption. While GAC is highly efficient for the removal of larger and humic-like molecules, it is also effective for the removal of smaller and hydrophilic molecules from water. Hence, activated carbon adsorption is shown as an effective treatment method to

remove SMPs for DBP reduction in water supply. Nonetheless, more effective treatment technologies still need to be developed for the control of wastewater-derived DBP problems in polluted water supplies.

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Figure captions:

Fig. 1. Treatment results for the SMP water after enhanced coagulation and sedimentation as a function of the alum dosage: (a) DOC and UV_{254}; (b) overall DBPFP sum and DBPFP yield; (c) the formation potentials of different DBP species.

Fig. 2. Treatment results of the SMP water after ozonation as a function of the ozone dosage: (a) DOC and UV_{254}; (b) overall DBPFP sum and DBPFP yield; (c) the formation potentials of different DBP species.

Fig. 3. Treatment results of the SMP water after GAC adsorption as a function of the GAC dosage: (a) DOC and UV_{254}; (b) overall DBPFP sum and DBPFP yield; (c) the formation potentials of different DBP species.

Fig. 4. Adsorption isotherms for (a) DOC and (b) DBPFP of the SMP solution by GAC adsorption.

Fig. 5. GAC adsorption of main SMP components (polysaccharides, proteins and humic-like substances): (a) changes of the equilibrium concentrations after adsorption as a function of the GAC dosage; (b) adsorption isotherms for the SMP components by GAC adsorption.

Table 1. Characteristics of the model SMP water prepared for the DBP control tests by enhanced coagulation, ozonation and activated carbon adsorption.

		Coagulation	**Ozonation**	**Adsorption**	**Mean**
DOC (mg L^{-1})		21	16	26	21
UV_{254} (m^{-1})		4.6	3.3	4.9	4.3
SUVA (L mg^{-1} m^{-1})		0.22	0.20	0.19	0.21
DBPFP (µg L^{-1})	CF	282	340	335	319
	DCAA	285	228	242	252
	TCAA	155	157	201	171
	CH	325	335	204	288
	TCP	2	2	3	3
	DCAN	1	1	1	1
	TCNM	2	2	3	2
DBPFP sum (µg L^{-1})		1053	1065	990	1036
DBPFP yield (µg mg^{-1}-DOC)		51	66	38	52

Table 2. Effects of the solution pH and the GAC particle size on the treatment results of the SMP water by GAC adsorption (GAC dose = 3.2 g L^{-1}, and results are presented as the mean±standard derivation of three tests).

	pH				
	3	5	7	9	11
DOC (mg L^{-1})	14±2	13±2	13±1	13±1	12±2
UV_{254} (m^{-1})	3.1±0.1	3.3±0.1	3.2±0.1	3.2±0.2	3.5±0.1
DBPFP (μg L^{-1})	420±63	418±8	454±15	397±41	434±38
	GAC size (mm)				
	>2.0	1.2-2.0	0.4-1.2	0.2-0.4	<0.2
DOC (mg L^{-1})	16±1	16±1	13±2	10±1	8±1
UV_{254} (m^{-1})	3.4±0.2	3.6±0.2	2.7±0.1	2.8±0.1	2.2±0.1
DBPFP (μg L^{-1})	477±21	465±39	414±22	385±13	348±35

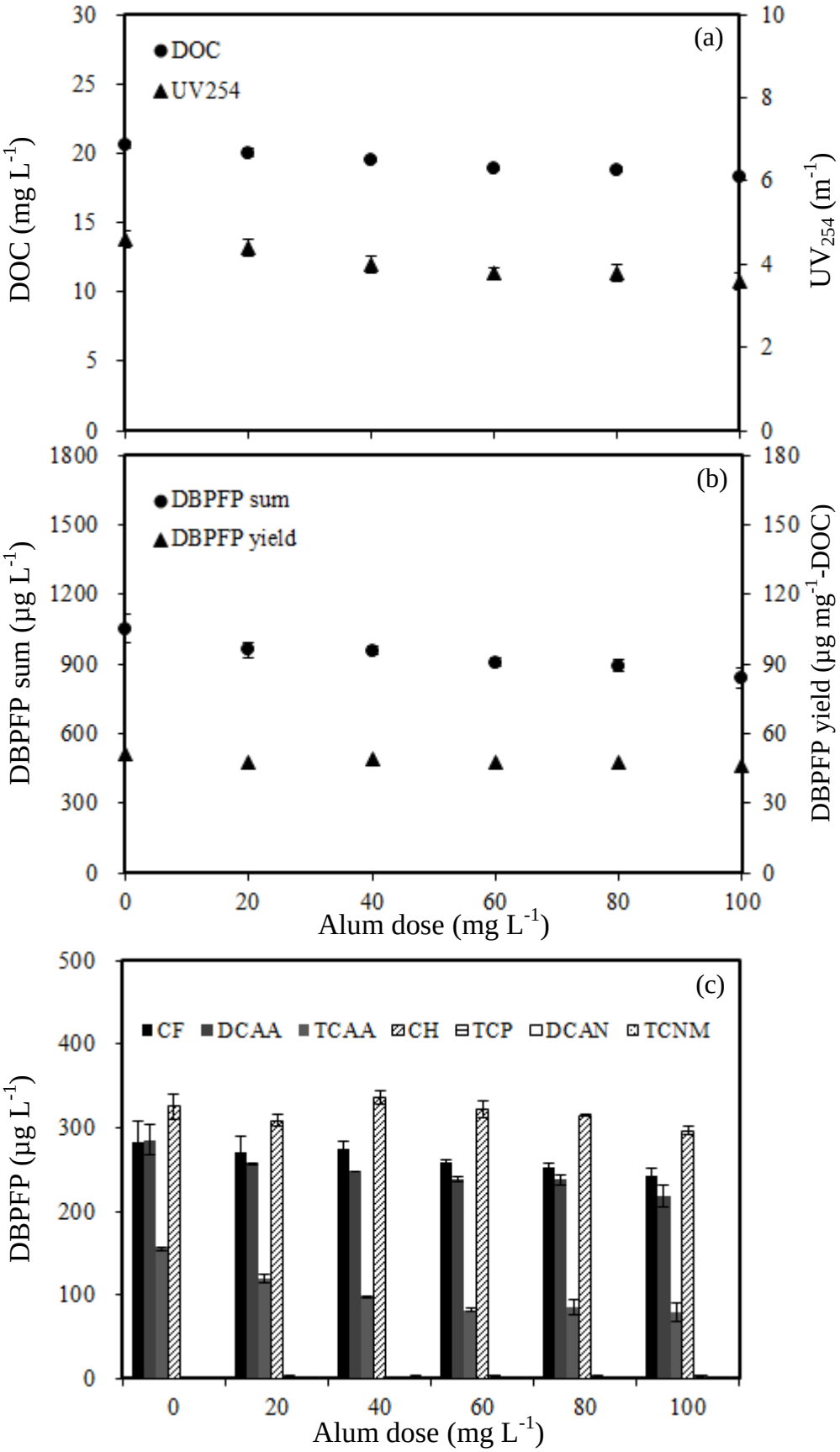


Fig. 1. Treatment results for the SMP water after enhanced coagulation and sedimentation as a function of the alum dosage: (a) DOC and UV_{254}; (b) overall DBPFP sum and DBPFP yield; (c) the formation potentials of different DBP species.

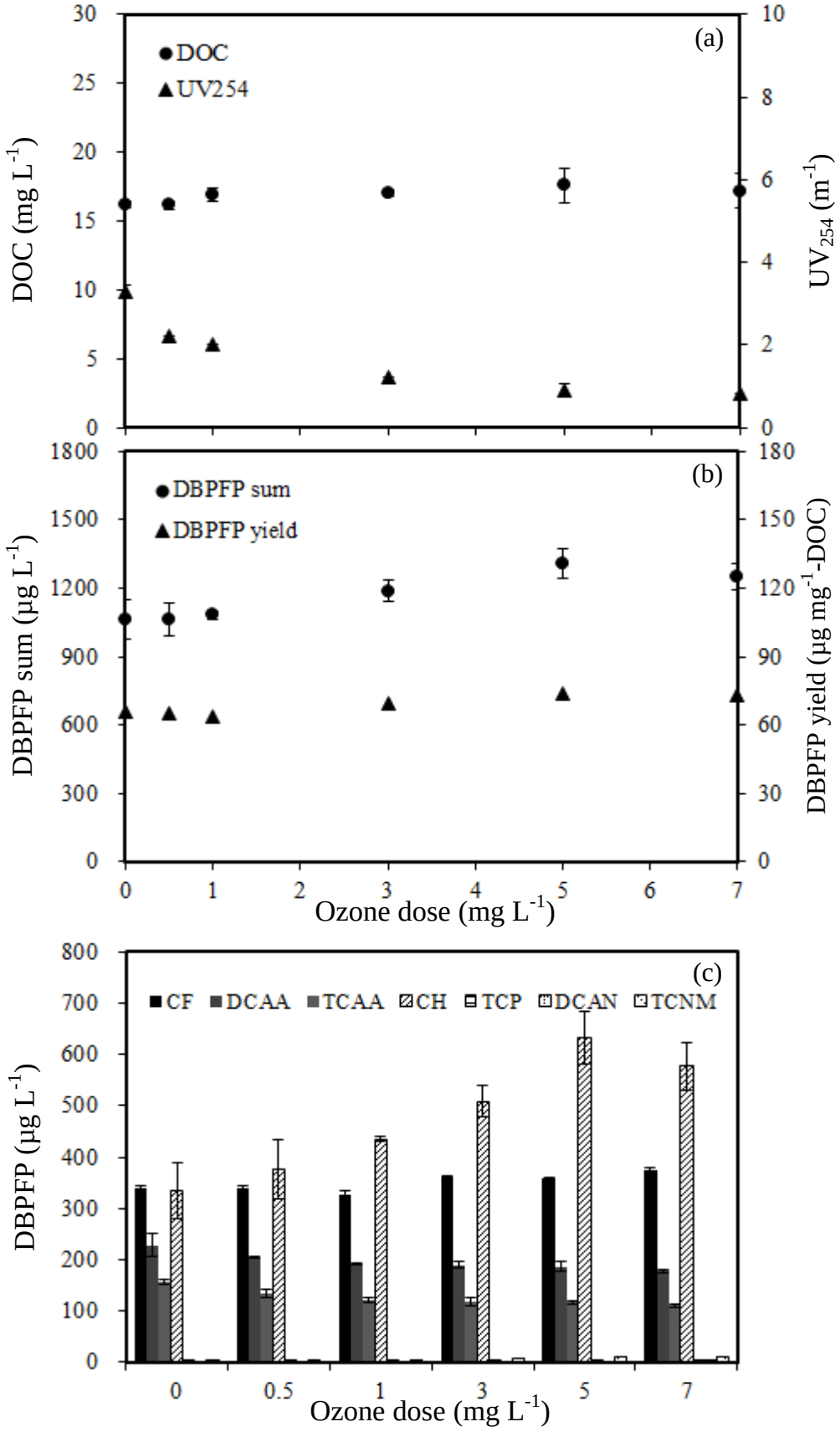


Fig. 2. Treatment results of the SMP water after ozonation as a function of the ozone dosage: (a) DOC and UV_{254}; (b) overall DBPFP sum and DBPFP yield; (c) the formation potentials of different DBP species.

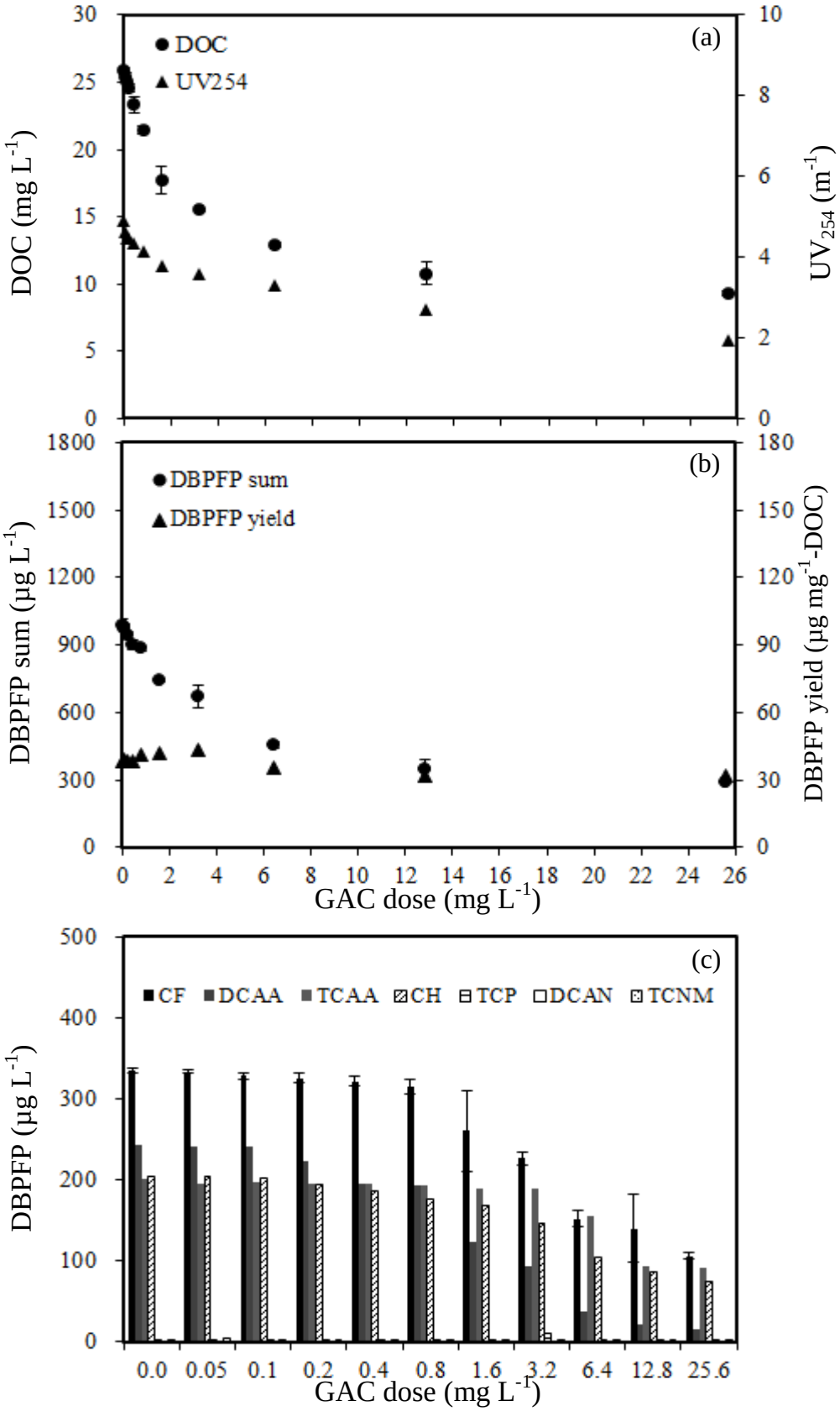
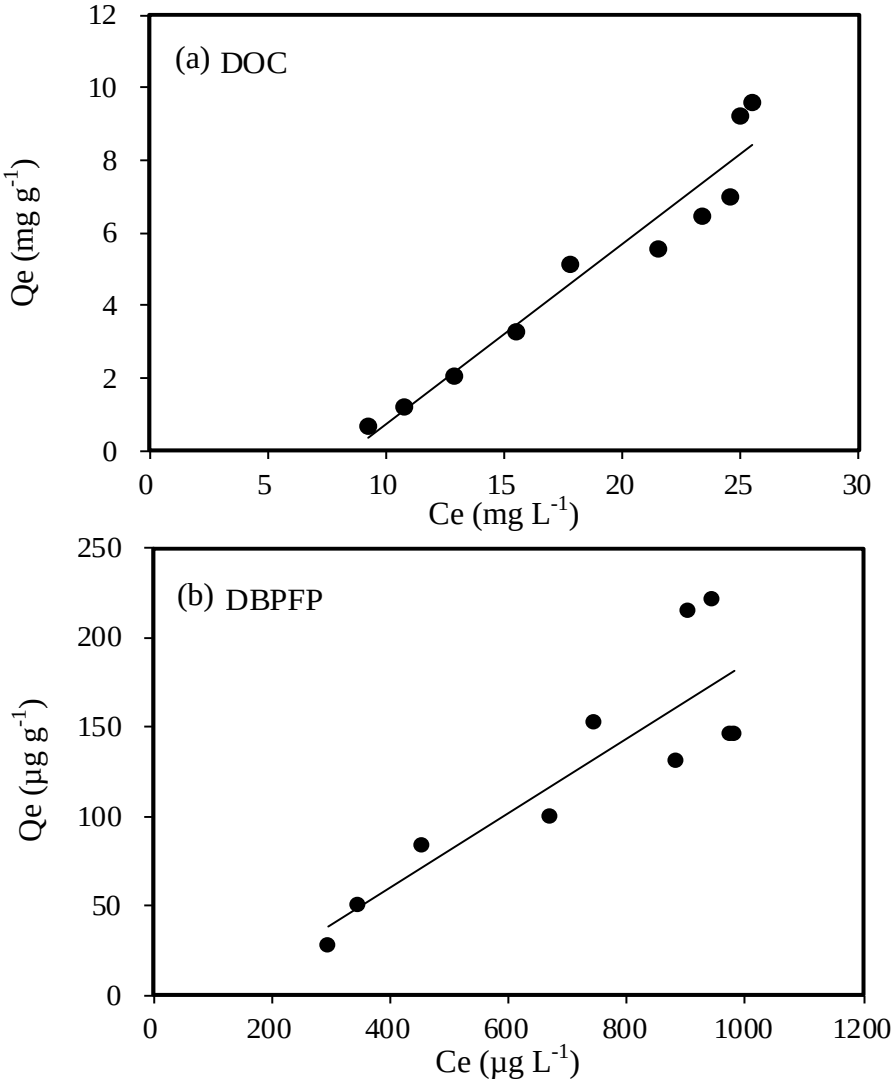


Fig. 3. Treatment results of the SMP water after GAC adsorption as a function of the GAC dosage: (a) DOC and UV_{254}; (b) overall DBPFP sum and DBPFP yield; (c) the formation potentials of different DBP species.



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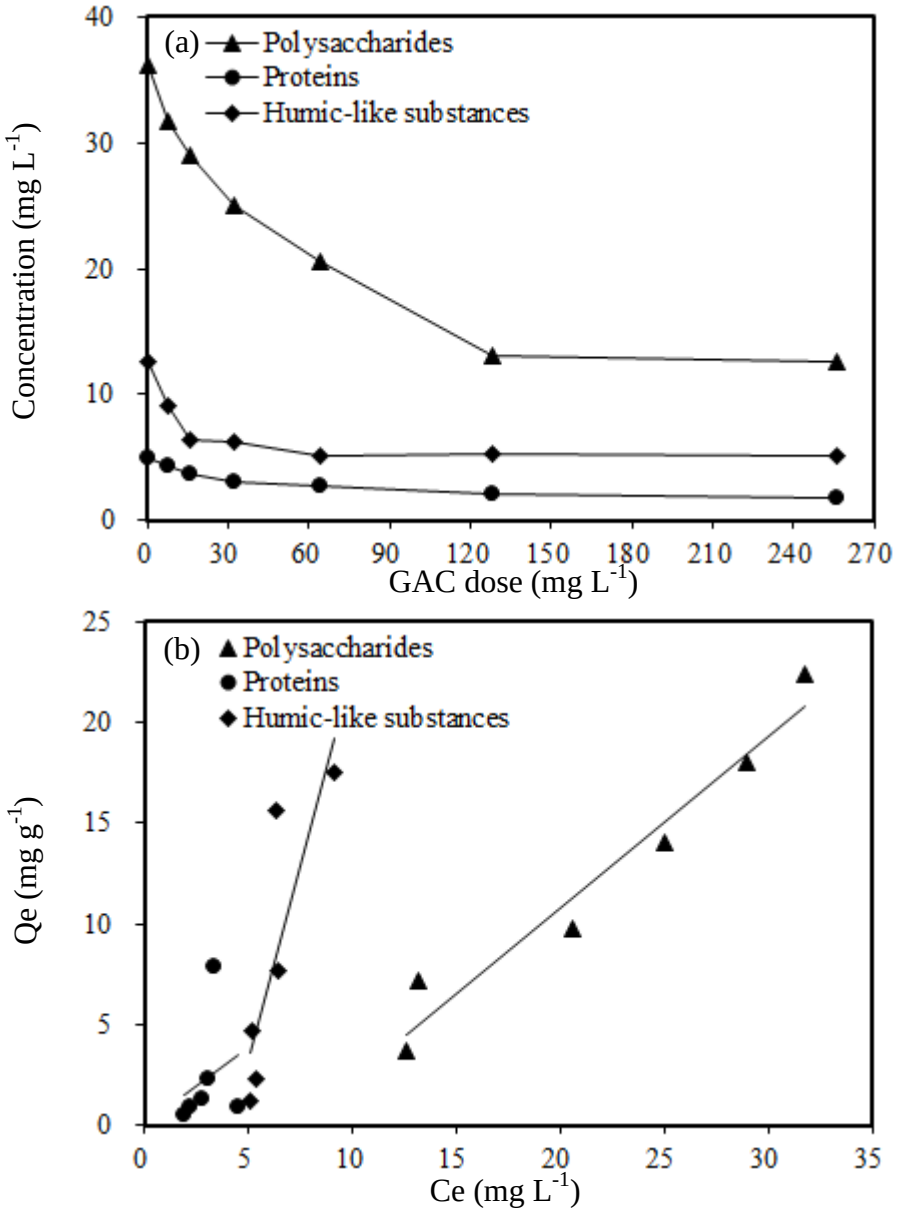

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