

Effect of granular activated carbon adsorption on mitigating microfiltration membrane fouling by algal organic matter

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ABSTRACT

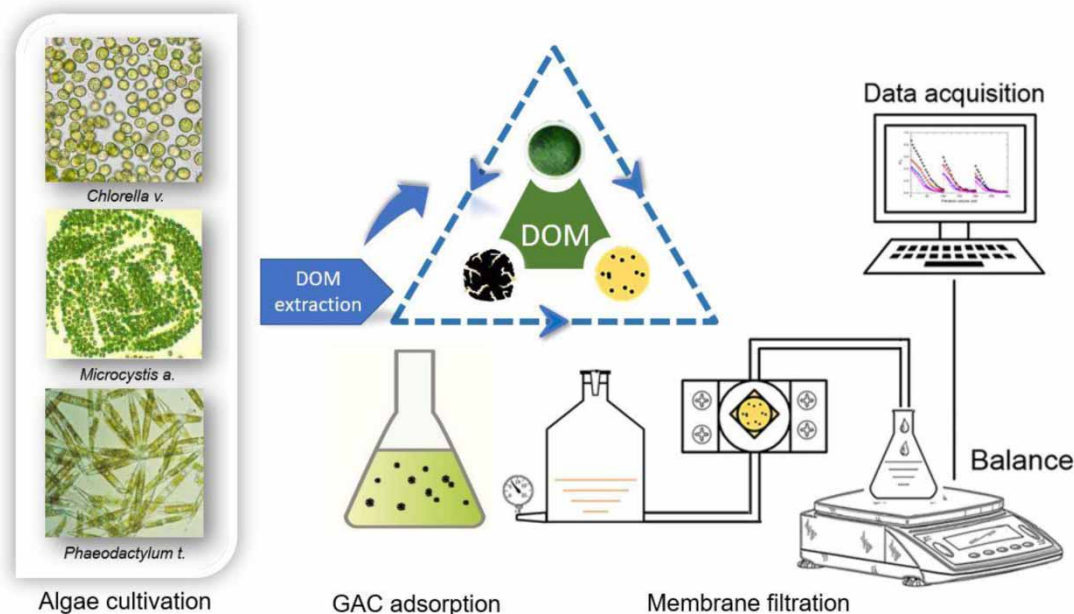
Algal blooms can seriously affect the operation of water treatment processes including low-pressure (micro- and ultrafiltration) and high-pressure (nanofiltration and reverse osmosis) membranes mainly due to the accumulation of algae-derived organic matter (AOM). This study investigated the effect of granular activated carbon (GAC) pretreatment on PVDF microfiltration performance for the removal of AOM. Dissolved organic matter (DOM) solution of commercial humic acid, extra- and intracellular organic matter from two species of algae, and Cyanobacteria were used for the investigation of the fouling potential of the membrane. A comparison study of different DOM removal and fouling behaviors of microfiltration (MF) after GAC adsorption as pretreatment was evaluated under variable GAC dosage and solution pH. Almost 15–20% improvement in flux and decline in irreversible fouling occurred due to the pretreatment using 1.0 g/L of GAC for an hour. The intracellular material caused higher membrane fouling than humic acid due to the hydrophilic nature of the AOM. Membrane fouling and decline in flux increased with increasing pH in the range of 5.0–8.0. The comparison results might help to provide insights into the real challenge of dealing with the treatment of algal-laden water.

Key words: activated carbon, adsorption, algal organic matter, membrane fouling, microfiltration

HIGHLIGHTS

- Up to 72.23 and 85.95% of DOC and UV₂₅₄ for CV-IOM can be removed by the GAC-MF process.
- A greater flux decline and irreversible fouling were observed from AOM than HA.
- Intermediate and standard blocking were the main fouling mechanisms for most DOMs.
- IOM from each algae shows greater flux decline, and more irreversible fouling than EOM.

GRAPHICAL ABSTRACT



1. INTRODUCTION

Climate change, population growth, and increased urbanization have contributed to the increasing frequency of eutrophication worldwide (Hoslett *et al.* 2018). The occurrence of harmful algal blooms in surface water has increased markedly over the last decade (Kudela *et al.* 2015). The metabolites of algae and other planktonic species are the major constituents of natural organic matter (NOM) in many surface water bodies, which are the sources of potable water in many areas. These substances cannot be easily removed by the traditional drinking water treatment processes such as coagulation–flocculation and sedimentation, creating problems for downstream units such as clogging of filters, increasing biofouling, reducing the efficiency of adsorption beds for the removal of trace contaminants, and increased disinfection byproducts formation (Lopes *et al.* 2017).

The extensive application of membrane processes, including microfiltration (MF) and ultrafiltration (UF), for drinking water treatment has significantly increased in the last two decades for their effective removal of pathogens such as *Cryptosporidium oocysts* and *Giardia cysts* and reduction of water turbidity with a comparable cost to conventional sand–charcoal filtration systems (U.S. Environmental Protection Agency 2005; Wong 2012). Microfiltration (MF, 0.1–10 μm) is widely applied in water treatment plants to remove particulate materials (Lehman & Liu 2009). However, membrane fouling caused by DOM significantly affects the filtration efficiency in water treatment. Membrane fouling due to the surrogate NOM such as commercial humic acid (HA) and Suwannee River NOM (SRNOM) is well-researched (Fang *et al.* 2010; Chiu *et al.* 2013; Kim & Dempsey 2013; Zhang *et al.* 2019a); however, fouling due to real cellular materials of algae or Cyanobacteria (most common eutrophic species) needs further attention due to the ubiquitous nature of the issue and absence of comprehensive research.

A previous investigation of membrane fouling by algal organic matters (AOMs) indicated that algal species and the derived AOM compositions significantly affected membrane fouling behavior (Huang *et al.* 2014b). An extended Derjaguin–Landau–Verwey–Overbeek (XDLVO) theory was applied to investigate the fouling behavior of AOM fractions from *Aphanizomenon flos-aquae* and *Anabaena flos-aquae*. The results indicated that the interface between membrane and neutral hydrophilic fraction presented the highest attractive energy, and controlled the membrane fouling in AOM microfiltration process (Huang *et al.* 2014a). Activated carbon (AC) adsorption is a process commonly used in water treatment plants to remove the residual organic pollutants, such as humic and fulvic DOM and ammonia. Growing problems with algal blooms have also indicated that AC adsorption is a promising solution for enhancing the removal of recalcitrant AOM (Pivokonsky *et al.* 2021). Granular activated carbon (GAC) adsorption, as one of the cost-effective and environmentally friendly processes

for water treatment plants to remove organic matter, has been extensively applied as a pretreatment process for membrane filtration to mitigate membrane fouling (Rasouli *et al.* 2017; Mayer *et al.* 2019). It is generally acknowledged that the performance of MF is influenced by the membrane type, feedwater characteristics, and operational conditions (Lehman & Liu 2009). A hybrid membrane-activated carbon process was applied for the treatment of oil field produced water and the results presented that GAC pretreatment enhanced the removal efficiency of COD and conductivity, and also reduced cake layer formation on membrane surfaces (Kose-Mutlu *et al.* 2017). A previous study presented that biopolymers, such as proteins and polysaccharides, could be effectively removed by GAC pretreatment prior to UF filtration to mitigate membrane fouling (Huck *et al.* 2009). Another study (Hatt *et al.* 2013) further found that coupling GAC to the downstream MF process provided a significant reduction in membrane fouling with improved product water quality and lower carbon usage rate than powder-activated carbon (PAC). Zhang *et al.* (2019b) investigated the effect of PAC on fouling by algal solution during ultrafiltration using two modes, i.e., the addition of PAC to the bulk feed and pre-depositing PAC onto the membrane surfaces. Both modes improved the removal of EOM from the algal solution; however, the influence of PAC addition on the EOM fouling was weak. The pH value, ionic strength, temperature, and chemistry are the main solution properties that play an important role in the AOM adsorption process (Kopecka *et al.* 2014). AOM molecules can be predominately positively or negatively charged depending on the solution pH (Safarikova *et al.* 2013). pH will also alter the characteristics (deprotonation/protonation) of functional groups on the GAC surface. Protonated and deprotonated AOM and GAC functional groups participate in various types of interactions (electrostatic, hydrophobic, and hydrogen bonding) during adsorption, thus substantially affecting the efficiency of the whole process (Abouleish & Wells 2015).

As mentioned above, most of the previous studies on the GAC/PAC adsorption-microfiltration process focused on NOM, and artificial organic micropollutants removal from drinking water treatment, and only a few of the investigations reported an integrated system for the treatment of algae-laden water. A comprehensive investigation of the combination of GAC and microfiltration membranes is not available. Further experimental data are necessary for process optimization and for designing such units. The pH point of zero charge (pHpzc) of GAC used in our work was determined to be 9.5 (Niasar *et al.* 2016), which shows the surface of GAC was positively charged within the working pH between 5.0 and 8.0. AOM has negative zeta potential values in the pH range of 2–10. If electrolyte/salt was added to increase the ionic strength, the AOM adsorption onto GAC would be reduced, thus the influence of ionic strength was not investigated from the practical perspective (Zhao *et al.* 2022). The objective of the current study is to investigate the effect of GAC dosage and solution pH on fouling potential and the flux of microfiltration due to several species of algae and Cyanobacteria.

2. MATERIALS AND METHODS

2.1. Algae cultivation and AOM extraction

The three species, *Chlorella vulgaris* (CV), *Microcystis aeruginosa* (MA), and *Phaeodactylum tricorutum* (PT), were obtained from the Canadian Phycological Culture Centre (CPCC) at Waterloo University (Waterloo, ON, Canada). The algal cells were cultivated in 2 L flasks in High Salt, 3N-BBM, and F/2, respectively, at 23 ± 2 °C under a fluorescent lamp (3,000 lx) with 16/8 h of light/dark cycle (Villacorte *et al.* 2015a). Algae and Cyanobacteria were harvested at the stationary growth phase and monitored by cell counting following the previous study (Zhao *et al.* 2020).

AOM solution was extracted by the following steps: (1) centrifugation of the harvested algal cultures at 3,700 rpm and 23 °C for 30 min (Thermo Scientific Sorvall, Legend T Plus); (2) subsequent filtration of the supernatant by a 1.2 µm filter (hydrophilic acrylic copolymer, Pall Corporation) to obtain extracellular organic matter (EOM); (3) the deposited algae on the filter were washed three times using Milli-Q water, then subjected to three freeze/thaw cycles (−18 °C for 12 h/40 °C for 2.0 h) to destroy the cells (Li *et al.* 2012), subsequently followed by centrifugation and filtration process as described above to obtain intracellular organic matter (IOM). The obtained AOM stock solutions were stored at 4 °C in a fridge for no more than 48 h before characterization or preparing the feed solution with dissolved organic matter (DOC) of 8.0 ± 0.5 mg/L for GAC adsorption and microfiltration after pH adjustment by 1.0 mol/L NaOH and 1.0 mol/L HCl solution. For comparison with the fouling behavior of AOM, humic acid (98% grade, Thermo Fisher Scientific Chemicals, Inc., USA) solution was used to prepare a working solution as the surrogate of NOM for the GAC-MF experiment.

2.2. GAC adsorption

The commercial GAC (Norit ROW 0.8 SUPRA, CAS Number: 7440-44-0) used in this study was purchased from Sigma-Aldrich Canada Co. The properties of GAC were investigated in a previous study in our group (Wan *et al.* 2019) shown as follows:

surface area $\approx 1,400 \text{ m}^2/\text{g}$, pore size $\approx 2 \text{ nm}$, total pore volume $\approx 0.7 \text{ cm}^3/\text{g}$, mesoporous area $\approx 634 \text{ m}^2/\text{g}$, and microporous area $\approx 766 \text{ m}^2/\text{g}$. The GAC was screened by mesh sieves to collect the GAC with a size range of 0.42–0.60 mm and followed by washing to remove the fines, then dried in an oven at $105 \text{ }^\circ\text{C}$, and stored in a desiccator before adsorption experiments.

The adsorption experiments were carried out in 500 mL Erlenmeyer flasks containing 400 mL of AOM solution using a Bench-top Orbital Shaker (Max Q 400, Thermo Scientific, ON, Canada) operated at temperatures of $23 \pm 1.5 \text{ }^\circ\text{C}$ under 200 rpm of shaking speed. Since surface and groundwater contain DOC in the range of 2–10 mg/L (Gumus & Akbal 2017), 1.0 g/L GAC was added into the DOM solution with an initial DOC of $8.0 \pm 0.5 \text{ mg/L}$. The pH of the solution was adjusted using 1.0 mol/L HCl or 1.0 mol/L NaOH to reach the pH values of 5–8 before adsorption. After GAC adsorption with a retention time of 1.0 h, the solution was filtered using a $1.2 \text{ }\mu\text{m}$ filter (hydrophilic acrylic copolymer, Pall Corporation) to remove GAC particles. The duplicated experiments have been conducted and reported with average values in this study.

2.3. Membrane and filtration unit

2.3.1. Fouling experiment assessment

The MF membrane used was a $0.45 \text{ }\mu\text{m}$ nominal pore size hydrophilic PVDF membrane (Millipore Corporation, USA) with an effective filtration area of $1.59 \times 10^{-3} \text{ m}^2$ in a dead-end stainless steel filter holder at a constant transmembrane pressure (TMP) of $50 \pm 0.5 \text{ kPa}$ by compressed air and operating temperature of $25 \pm 0.5 \text{ }^\circ\text{C}$. Before filtration, all fresh membranes were soaked in Milli-Q water for at least 24 h to remove possible organic contaminants. The filtrate weight was measured constantly by a digital balance (Denver SI-4002, Denver Instrument Co., USA) and data were automatically logged to a connected computer equipped with a data acquisition system shown in Supplementary Figure S1.

All DOM solutions were diluted using Milli-Q water to DOC of $8.0 \pm 0.5 \text{ mg/L}$ from a stock solution. Every filtration experiment was conducted for three continuous filtration cycles. Each cycle comprised three steps: (1) filtration with 100 mL Milli-Q water; (2) filtration of 100 mL feed solution; and (3) backwashing of the membrane by placing the reverse side of the membrane upwards and filtration of 100 mL Milli-Q water. The flux of feed solution filtration is named $J_{s,n}$, with the number n (1–3) representing the cycle number. J_n represents the average flux in the filtration of Milli-Q water. The total fouling (TF), the reversible fouling (RF), and the accumulative irreversible fouling (IF) of each filtration cycle can be calculated as follows (Elcik *et al.* 2016):

$$\text{TF}_n = \frac{J_0 - J_{s,n}}{J_0} \quad (1)$$

$$\text{IF}_n = \frac{J_0 - J_n}{J_0} \quad (2)$$

$$\text{RF}_n = \text{TF}_n - \text{IF}_n \quad (3)$$

2.3.2. Membrane fouling resistance and mechanism

To elucidate fouling mechanisms, the classic filtration models, including complete blocking, standard blocking, intermediate blocking, and cake filtration, were applied to understand the flux decline during the MF of the DOM solution under constant pressure. The instantaneous flux was calculated by numerically differentiating the cumulative volume filtered (V) per unit membrane area and analyzing it using blocking laws listed in Supplementary Table S1.

2.4. Analytical methods

DOC of AOM solution was measured using a TOC- V_{CPN} analyzer (TOC- V_{CPN} , Shimadzu, Japan) with a detection limit of 0.1 mg/L calibrated by a standard glucose solution. Temperature and pH were measured using a pH meter (Orion Model STAR A111, USA). The UV absorbance at 254 nm (UV_{254}) was measured by a UV/Vis spectrophotometer (UV-3600, Shimadzu, Japan) and the specific UV absorbance (SUVA , $\text{L mg}^{-1} \text{ cm}$) was calculated from UV_{254} value divided by DOC concentration.

3. RESULTS AND DISCUSSION

3.1. Effect of GAC dosage on organic removal efficiency

The effect of GAC dosage on the removal of DOM was conducted from a dosage of 0 to 1.5 g/L for different feed solutions, as shown in Figure 1. The percentage of DOM removal, in terms of DOC and UV_{254} , increased with the increase of GAC dosage,

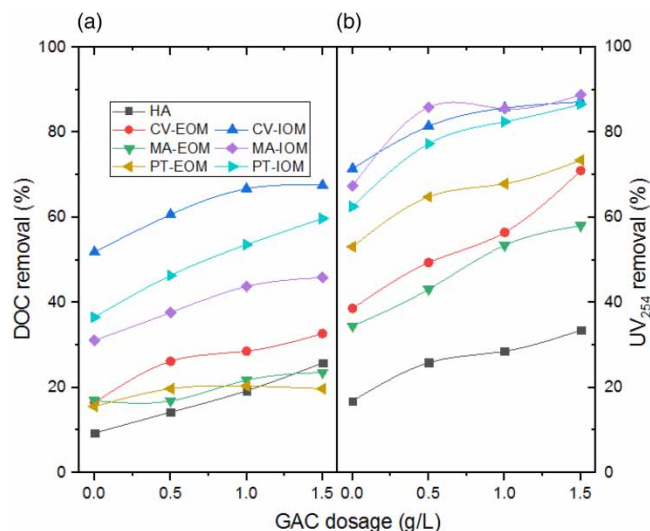


Figure 1 | Effect of GAC dosage on DOM removal in terms of DOC (a) and (UV_{254}) (b) after microfiltration with GAC adsorption pretreatment under pH of 7.0 and contact time of 1.0 h.

as the number of available adsorption sites increased by increasing the adsorbent dose. The removal of UV_{254} from each feed solution was higher than the removal of DOC. In terms of DOC for algal organic matter, the IOM for each algal species presented higher removal efficiency than that of EOM. With a dosage of 1.5 g/L GAC, the IOM of PT showed 40.03% of DOC removal higher than that from EOM, followed by 37.68% from CV and 22.34% from MA. With respect to UV_{254} , there was 38.99% of UV_{254} removal from IOM more than removed from EOM of CV, followed by 30.72 and 13.14% from MA and PT, respectively. This could be due to the higher aromatic or unsaturated components in IOM than in EOM from investigated algae (Zhang *et al.* 2013; Wang *et al.* 2014; Villacorte *et al.* 2015b; Li *et al.* 2018). Up to 23.21% of DOC and 24.06% of UV_{254} from PT-IOM was removed by the GAC-MF system with a GAC addition of 1.5 g/L more than DOC and UV_{254} were removed by the MF membrane without GAC addition.

It was indicated that GAC adsorption was effective to promote DOM removal; similar results also were proposed that DOCs of lower molecular weight substance were adsorbed onto GAC and DOCs of higher molecular weight can be removed by the membrane formed on the surface of the MF membrane (Kim *et al.* 2009). In comparison with DOM from AOM, humic acid presented relatively lower removal efficiency. It was also noted that the addition of GAC (1.5 g/L) presented (Figure 1) approximately 16.49 and 16.67% greater DOC and UV_{254} removal than without GAC adsorption.

3.2. Effect of GAC dosage on the flux and reversibility by DOM fouling

The normalized flux of each DOM for the MF with and without GAC addition is shown in Figure 2. The flux profiles demonstrated a feature of an initial sharp decrease (<40 mL) followed by a gradual decrease and a plateau during the later filtration phase. This phenomenon can be explained by the co-existence of irreversible pore blocking by low-MW fractions of the AOM and reversible cake layer formation resulting from the deposition of high-MW organics during the filtration period (Liu *et al.* 2017).

Specifically, the feed solution from AOM presented a significantly greater flux decline compared to humic acid, with more than 80% flux decline obtained at the end of the single cycle filtration (Figure 2(a)). A similar trend was also observed for the filtration of humic acid and AOM by Zhang *et al.* (2018). With 1.5 g/L GAC adsorption (Figure 2(b)), the filtration flux for each DOM was improved, with a maximum 15% improvement in flux occurring for HA, followed by PT-EOM, CV-IOM, CV-EOM, MA-EOM, and PT-IOM. It was noted that even though filtration flux was increased for all AOM after GAC adsorption, about an 80% decline in flux occurred for AOM. In comparison, flux for the humic acid solution declined by 60%.

Figure 3 shows the reversibility of fouling in terms of specific fouling contribution after each filtration cycle with different GAC additions. The results show that the irreversible fouling gradually increased at the cost of the reversible fouling decrease during the filtration cycles for each DOM. The decrease of irreversible fouling with the increase in GAC dosage indicated that GAC adsorption pretreatment improved the membrane reversibility considerably. Some protein-like compounds,

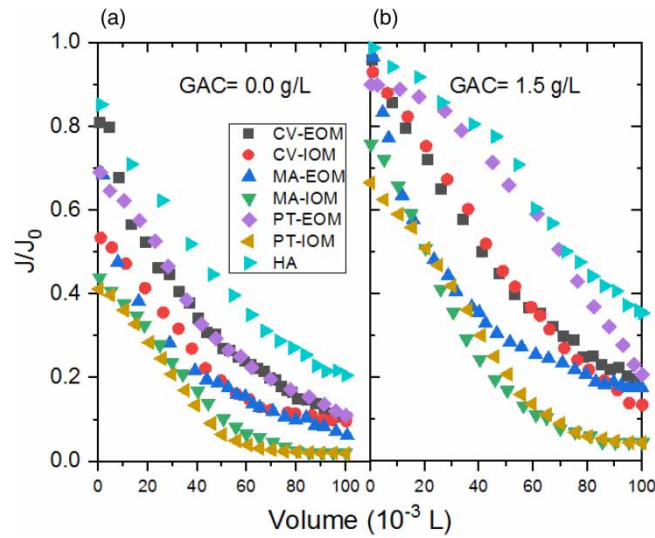


Figure 2 | Flux profile for first filtration cycle of the DOM solution with and without GAC adsorption pretreatment.

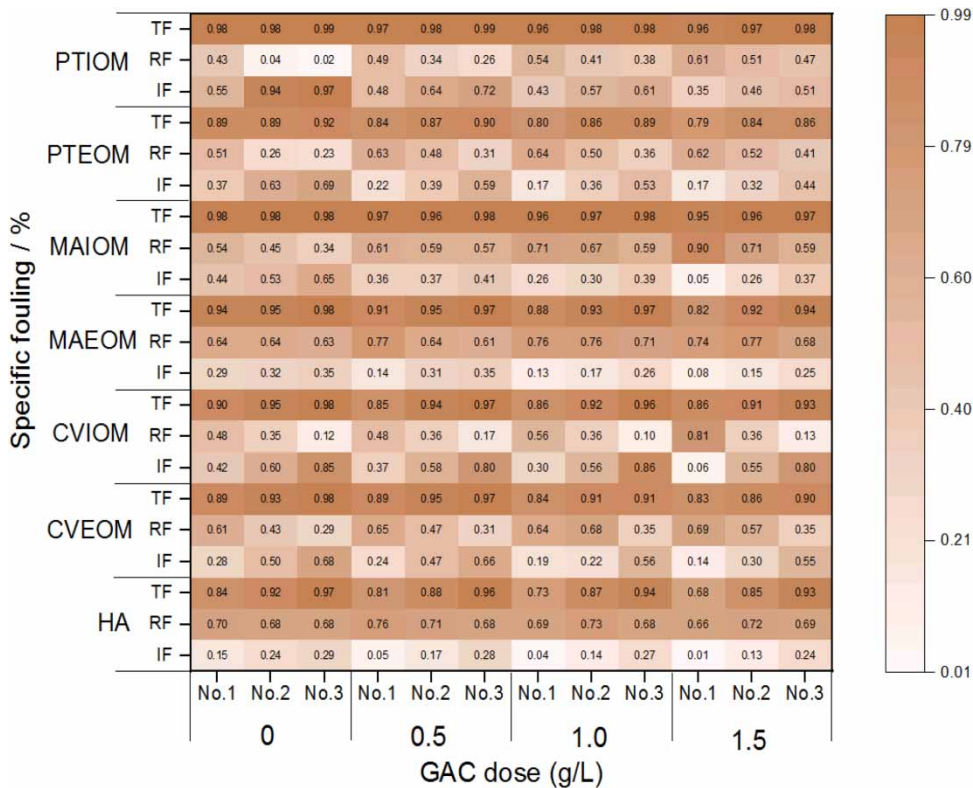


Figure 3 | Effect of GAC dosage on the reversibility of DOM fouling (TF, RF, and IF represent the total fouling, reversible fouling, and irreversible fouling, respectively, No. 1 to No. 3 denote the filtration cycle of each DOM).

hydrophobic in nature, and aromatic substances can be preferentially adsorbed by GAC, which was also validated by the UV₂₅₄ removal in this study. An earlier study used biologically active carbon for the removal of hydrophilic compounds for membrane filtration (Pramanik *et al.* 2018). In this work, humic acid was observed to contribute lower irreversible fouling than the AOM investigated, probably due to the higher hydrophilicity of the algal matter as shown in the earlier investigation

(Zhao *et al.* 2020). The EOM and IOM from three algal species presented a comparable total fouling at identical experimental conditions; however, the irreversible fouling from IOM was higher than that of EOM due to a higher percentage of hydrophilic protein-like substances with lower molecular weight (58.4%) than that in EOM (18.5%) (Zhou *et al.* 2014); probably by blocking of micropores of membrane or settling on already deposited substance resulting in the irreversible fouling.

3.3. Effect of pH on organic removal efficiency

The pH of the DOM solution not only alters the surface charge of the adsorbent, the dissociation of functional groups on the active sites of the adsorbent but also affects the ionization degree of the DOM in the solution (Kuśmierk & Świątkowski 2015; Zhang *et al.* 2019c). In this study, the pH dependence of DOM removal by microfiltration with GAC adsorption was performed in the pH range of 5.0–8.0. The initial pH of the solution can affect the characteristics (deprotonation/protonation) of functional groups on the GAC surface. Consequently, protonated and deprotonated AOM and GAC functional groups participate in multiple types of interactions during adsorption, including electrostatic, hydrophobic, and hydrogen bonding, thus substantially affecting the efficiency of the whole process (Abouleish & Wells 2015).

As shown in Figure 4, the removal of DOM by the GAC-MF combined system decreased with pH increasing from 5.0 to 8.0. A similar trend and relatively higher removal percentage of UV_{254} at lower pH for each DOM occurred, which indicated that aromatic and unsaturated compounds are favorably removed. The removal efficiency of each DOM decreased at neutral and alkaline pH. At alkaline conditions, the anionic species from DOM, such as the carboxyl, hydroxyl, and amide groups of DOM, are deprotonated, which resulted in the increase of negative charge of DOM, thus resulting in the decrease of DOM removal by GAC. AOM adsorption efficiency has been observed to increase with decreasing pH of the solution. A similar observation also proposed by the previous study stated that adsorption of AOM peptides of *M. aeruginosa* (expressed as DOC removal) on two GACs with pH_{PZC} of 5.5 and 6.7, respectively, was approximately twice as high at pH 5 than at pH 8.5 (Hnatukova *et al.* 2011). The IOM solution showed higher removal efficiency than humic acid and EOM from each algal species. IOM from each algal strain presented a higher removal rate than that of EOM, and HA presented the lowest removal efficiency which might result from its higher molecular weight ($MW \approx 39$ kDa) than that of algal species (Zhao *et al.* 2022).

3.4. Effect of pH on the flux decline and reversibility of DOM fouling

To probe the effect of feed solution pH on membrane permeate and degree of fouling after GAC adsorption for each DOM, experiments were performed at pH 5.0 and 8.0 for GAC adsorption with conditions mentioned above followed by three cycles

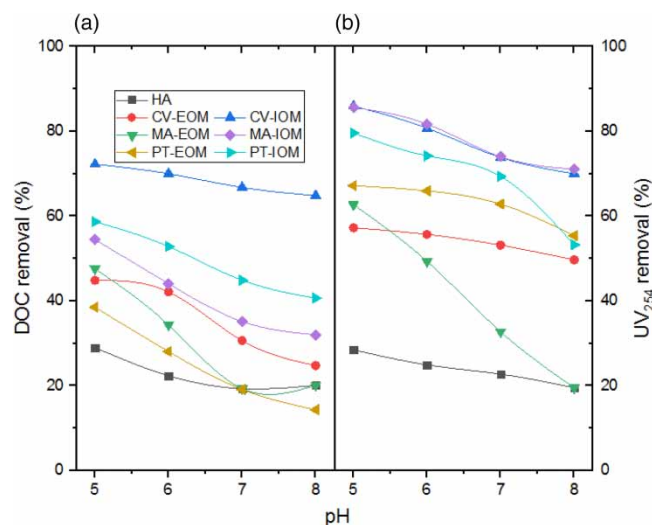


Figure 4 | Effect of solution pH on DOM removal in terms of DOC (a) and (UV_{254}) (b) after microfiltration with GAC adsorption pretreatment (GAC dosage of 1.0 g/L and contact time of 1.0 h).

of MF filtration without any additional pH control. As pH can alter the degree of ionization of the DOM presented in the solution, the electrostatic interaction between DOM and membrane would play a significant role. At higher pH, the repulsive force between negatively charged membrane and anionic species of DOM caused lower flux decline. On the contrary, at lower pH, the negatively charged membrane would attract protonated and positively charged DOM species, thus leading to increased fouling and a decrease in permeate flux (de la Casa *et al.* 2007).

In the present study, as seen in Figure 5, the flux decline increased at a higher initial pH of 8, which indicated that higher fouling occurred at a higher pH. More than 30% of the DOM of CV was removed by GAC adsorption (with about 50% total removal by combining GAC-MF treatment). These results implied that the effectiveness of GAC adsorption at lower pH can reduce the permeate flux decline and mitigate membrane fouling. This was also seen in a previous study where a decrease in the irreversible fouling of ultrafiltration occurred at lower pH for filtration of NOM (Dong *et al.* 2006). This finding implied that the electrostatic attraction between DOM and membrane was not the dominant fouling mechanism in the present experiments.

To obtain a better understanding of the fouling of each DOM, the fouling reversibility with pH variation was analyzed and the results are shown in Figure 6. The decrease of irreversible fouling with the decrease of solution pH indicated that GAC adsorption pretreatment at lower pH in the experimental range can cause membrane reversibility, due to the considerable removal of DOM by GAC adsorption at lower pH. In addition, the effective radius of DOM may decrease due to reduced inter-chain electrostatic repulsion at low pH, which can make the molecules smaller and easier to adsorb onto the membrane and flow through the micropores of the membrane matrix (Al-Amoudi 2010). Compared with humic acid, AOM presented higher irreversible fouling. A comparative study on membrane fouling potentials showed that higher irreversible fouling was caused by AOM derived from MA than that from humic acid (Li *et al.* 2014).

3.5. Fouling mechanisms of the AOM

To investigate the fouling mechanisms, the instantaneous flux of the first cycle of MF after GAC adsorption was fitted with the classic filtration models (shown in Table 1). The regression results are presented in Figure 7 and Table 1.

As shown in Table 1, among the four fouling models for each DOM solution, for CV-EOM and MA-IOM, membrane fouling was controlled by standard blocking with R^2 values of 0.997 for CV-EOM and 0.982 for MA-IOM. For the other DOM solutions, including humic acid, CV-IOM, MA-EOM, PT-EOM, and PT-IOM with the maximum R^2 values 0.977, 0.973, 0.958, 0.995, and 0.977, respectively, the fouling mechanisms were predominated by intermediate blocking and standard blocking. This result can mostly be attributed to the MW distribution of the DOM, in which the high-MW biopolymers (>13.5 kDa) might be removed by initial filtration through a 1.2 μm membrane (Fang 2010; Zhang *et al.* 2014), in addition

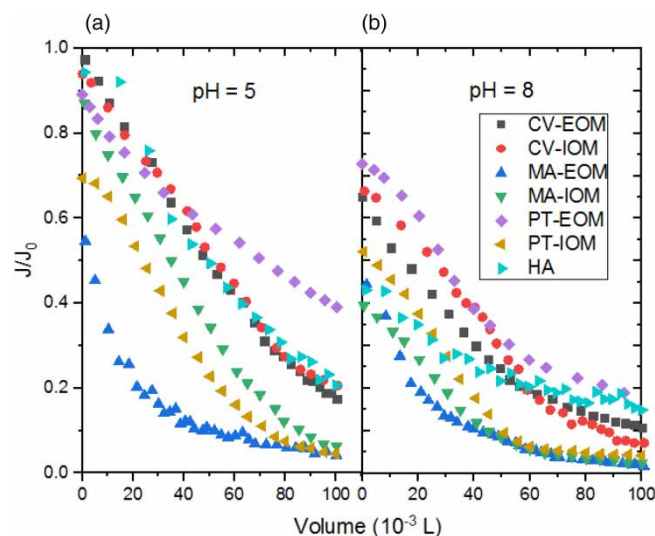


Figure 5 | Flux profile for the first filtration cycle of the DOM solution with GAC adsorption pretreatment under different solution pHs.

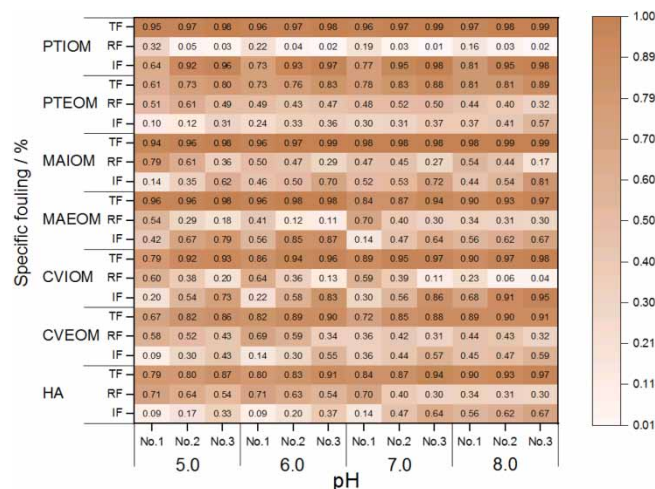


Figure 6 | Effect of solution pH on the reversibility of DOM fouling (TF, RF, and IF represent the total fouling, reversible fouling, and irreversible fouling, respectively; No. 1 to No. 3 denote the filtration cycle of each DOM).

Table 1 | R^2 values of fouling models for each DOM during the first cycle of MF after GAC adsorption (GAC dosage of 1.0 g/L, pH 7.0, and 1 h contact time)

Feed solution	Complete blocking	Standard blocking	Intermediate blocking	Cake filtration
HA	0.856	0.931	0.977	0.940
CV-EOM	0.990	0.997	0.993	0.953
CV-IOM	0.901	0.942	0.973	0.969
MA-EOM	0.622	0.937	0.958	0.938
MA-IOM	0.957	0.982	0.972	0.840
PT-EOM	0.983	0.992	0.995	0.980
PT-IOM	0.911	0.962	0.977	0.849

to the fact that the peptides from AOM (MW < 10 kDa) and medium-MW compounds (i.e., humic-like substances, ~ 1 kDa) with high affinity with GAC surface might more susceptible to adsorption onto GAC (Pivokonsky *et al.* 2021).

It could also be inferred that the comparable R^2 values of the fouling models implied that the fouling process was controlled by multiple mechanisms. This is attributed to the broad MW distribution of AOM (Fang *et al.* 2010; Li *et al.* 2018). The low-MW substance may be trapped inside membrane pores resulting in standard blocking, and the high-MW components may be deposited on the membrane surface to form a cake layer. A previous study on the UF membrane fouling potential of EOM also demonstrated that multiple mechanisms, including cake filtration and standard blocking, dominated the fouling formation (Li *et al.* 2014; Yan *et al.* 2017).

In a comparative study on membrane fouling potentials of algal extracellular and IOM, cake filtration has been identified as an important mechanism for flux decline.

It could be noted that multiple mechanisms might also take effect during filtration considering the relatively higher R^2 value (0.958 ~ 0.997); for instance, intermediate blocking and cake filtration dominated the fouling formation for humic acid, and standard blocking and intermediate blocking controlled the membrane fouling for most AOM, except for CV-IOM and humic acid for which intermediate blocking and cake filtration mechanisms governed the fouling formation. The bold figures of in Table 1 show the largest R^2 value among four fouling models for each DOM, which indicated the principal mechanism dominated the fouling formation for the DOM during the first cycle of MF after GAC adsorption. An earlier study demonstrated that cake filtration dominated the fouling during ultrafiltration of AOM from MA; however, the difference is mainly due to the type of filtration (Liu *et al.* 2017).

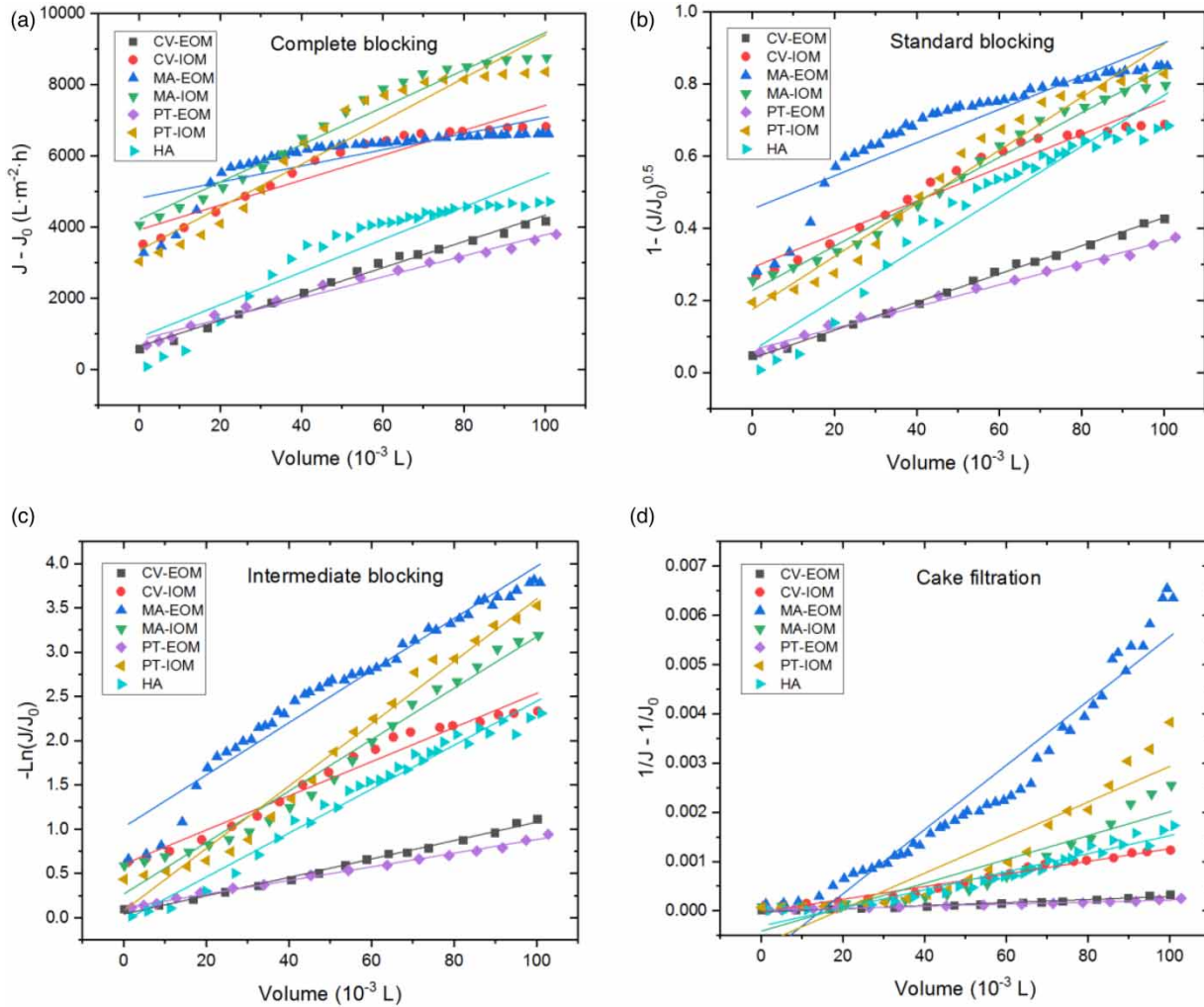


Figure 7 | Regression analysis of membrane fouling behavior using a classical fouling model for the first filtration cycle of individual DOM under pH of 7 with 1.0 g/L GAC adsorption.

4. CONCLUSIONS

The influence of GAC dosage and initial pH on microfiltration to remove DOM derived from three different algae, as well as humic acid, was investigated using a dead-end down-flow MF unit in batch scale. The combination of GAC adsorption and MF can significantly enhance DOM removal up to 72.23 and 85.95% for DOC and UV_{254} for CV-IOM. The addition of GAC can not only promote DOM removal but also mitigate the flux decline and reduce irreversible fouling. A lower initial pH value within the experimental range (5–8) showed positive effects for DOM removal and membrane reversibility. The total removal efficiency of AOM was higher than humic acid; however, a greater flux decline and higher irreversible fouling were observed from AOM than that of humic acid. The AOM derived from CV presented a better removal efficiency with less flux decline and irreversible fouling, followed by the Cyanobacteria, MA, and the diatom, PT. The fouling models implied that intermediate blocking and standard blocking were the dominant membrane fouling mechanisms for most DOM except the CV-IOM and humic acid where intermediate blocking and cake filtration controlled the fouling process. Although IOM from each algal species demonstrated relatively higher removal performance than EOM, considering the greater flux decline and irreversible fouling compared to EOM, to maintain the algal cell integrity and avoid lysis to release IOM are important considerations for membrane treatment of algae-laden water.

ACKNOWLEDGEMENTS

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DATA AVAILABILITY STATEMENT

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

CONFLICT OF INTEREST

The authors declare there is no conflict.

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