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Presence of powdered activated carbon/zeolite layer on the performances of gravity-driven membrane (GDM) system for drinking water treatment: Ammonia removal and flux stabilization

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Abstract: Gravity-driven membrane (GDM) filtration is a promising alternative for decentralized water supply, while its widespread application was hindered by the poor removals of organics and ammonia during long-term operation. In this study, powered activated carbon (PAC) and granular zeolite were selected as typical adsorbents to investigate the impacts of pre-deposited adsorbent layers on contaminant removal and membrane fouling. Results showed that the pre-deposited PAC layers exhibited higher removal of organics than the control, while the zeolites deposited layers exhibited low removal of organics. The presence of PAC only enhanced the  $NH_4^+$  removal st subsequent stable stage, while zeolites were effective in deal with sudden hig'  $1/H_4^+$  concentration due to ion exchange. The presence of mixed adsorbents layers had similar organic removal with PAC and NH<sub>4</sub><sup>+</sup> removal with zeolite. The pre-deposited Pr.C layers could effectively alleviate membrane fouling in short-term UF tests, while the stable fluxes  $(5.88-6.54 \text{ L/(m^2 \cdot h)})$  in long-term GDM operation were slightly 'ov er than the control (6.63  $L/(m^2 \cdot h)$ ). The zeolites deposited layer aggravated membrane injuling in both short-term ultrafiltration and long-term GDM (5.03-3.84 L/( $m^2 \cdot h$ )), but a highest stable flux (6.10 L/( $m^2 \cdot h$ )) was observed for GDM using the mixed adsorbents. The pre-deposited adsorbent layers resulted in increased concentrations of biomass, *tri-phosphate* (ATP) and extracellular polymeric substances (EPS), forming cake *i* yers with a denser structure than the control. Finally, the fouling mechanism for GDM using different adsorbent layers was proposed based on fouling analysis and characteristics of biological fouling layer. The results and conclusion in this study could provide helpful information for the application of GDM with pre-deposited adsorbent layer in treating raw water with organics and/or sudden high ammonia concentration to produce potable water.

Keywords: Gravity-driven membrane, Ultrafiltration, PAC, Zeolites, Ammonia, Stable flux

### **1. Introduction**

The global access to safe drinking water is still a grand challenge to the development of human civilization (Montgomery and Elimelech, 2007), especially in low-income countries or areas where centralized water supply is not available. Gravity-driven membrane (GDM) system has the merits of low hydraulic pressure (40-100 cm), easy operation, without physical/chemical cleaning and high reliability, ensuring it an attractive process for decentralized water supply (Pronk et al., 2019). Bench-scale or pilot -scale experiments with different module configuration for seawater treatment were corrud out (Wu et al., 2017a). The contaminant removal behaviors of GDM are largely dependent on the biological layer on the surface of ultrafiltration (UF) membranes. The unstable removal of contaminants was one of the critical obstacles for the widespread application of GDM. Organics and ammonia are two typical contaminants in micro-polluted survey water (Liao et al., 2015). On one hand, the organic removals were usually less war 20% when only GDM system was employed for water supply (Ding et al., 2017b; Tan, et al., 2018a), and negative removals for organics have also been reported (Akhondi e. al., 2015; Wu et al., 2016). On the other hand, low ammonia removals were obser ed and the removals increased when the feed concentrations decreased from 1.4 to 0.6-0.5 ".g/L (Du et al., 2019). However, no existing studies involving feed ammonia concentrations more than 2.0 mg/L in GDM systems. Meanwhile, it would last certain time (e.g., a few days) to achieve high removals of ammonia during the start-up period or sudden high feed ammonia loading, leading risk for the safety of water supply.

The removals of contaminants in GDM systems greatly depended on the biological active fouling layer (Pronk et al., 2019), where the enrichment of ammonia-oxidizing bacteria (AOB) and nitrite oxidizing bacteria (NOB) promoted the removals of ammonia (Chang et al., 2014). Derlon et al. (2014) revealed that hydrolysis of organic matter due to the growth of biological layer in GDM was responsible for the permeate quality deterioration. Recently, a

series of approaches (e.g., pretreatment, operation condition) were investigated to improve the membrane performance (Chang et al., 2017; Zhang et al., 2021), and adsorption is a commonly employed pretreatment technique. The hybrid activated carbon and GDM process could effectively enhance contaminant removals (Tang et al., 2018b). The technique of pre-deposited adsorbents has been widely employed in low pressure membrane filtration systems (Anantharaman et al., 2020; Chen et al., 2019). The combination of pre-deposited adsorbents with GDM have several advantages. For example, it could remove contaminants due to adsorption and provide suitable conditions for biological growth. Meanwhile, the pre-deposited adsorbent layer was added once before the operation of the system, without additional operation. Thus, pre-deposited adsorbent layer was an appropriate method for the enhancement of biological activity and contaminant removals in GDM systems, and the feasibility of the combined GDM process has been proven in our previous studies (Ding et al., 2018a; 2018b).

Different types of adsorbents have been employed to improve the removals of organics and ammonia, such as powered activated carbon (PAC), carbon nanotubes and zeolites (Anantharaman et al., 2020; then et al., 2019). The adsorption performance of PAC and zeolites in short-term test has hern widely reported (Almutairi and Weatherley, 2015; Cai et al., 2013; Hu et al., 2017; Xue et al., 2018). However, the adsorption capacity would be saturated during long-term operation, and the microorganism in the cake layer would grow, influencing the permeate water quality. Therefore, differences in the contaminant removals by UF membranes in short-term test and GDM systems in long-term operation might be obtained. Recently, modification and preparation of zeolites with specific characteristics have been carried out to enhance organic removals to alleviate membrane fouling (Hazrati et al., 2018). A biomimetic dynamic membrane which was fabricated by physical absorption and filtration of carbon nanotubes and laccases on membrane surface could enhanced

contaminant removal and fouling control (Chen et al., 2019). Moreover, there was not a consistent view for the impact of pre-deposited PAC layer on membrane fouling. Some researchers demonstrated that pre-deposited PAC layer could alleviate membrane fouling, and the extent of membrane fouling correlated with the grain size of PAC (Cai and Benjamin, 2011; Cai et al., 2013), while the pre-deposited PAC layer might result in lower permeate fluxes (Hu et al., 2017; Li et al., 2020). During long-term GDM operation, the impact of pre-deposited activated carbon layer on membrane fouling varied, and the stable fluxes might increase, decrease or remain unchanged (Ding et al., 2018b; Shac et al., 2017; Song et al., 2019).

Overall, previous studies involving adsorbent in GCM filtration primarily focused on removals of organics or low-concentration ammonia using PAC, no existing reports about zeolite as well as the mixture of both PAC and zeolite. The current study focused on the impacts of pre-deposited adsorbent layer, or membrane performance in GDM systems during long-term operation of feed water with high ammonia. The contaminant removal and membrane fouling in GDM systems using PAC, zeolite or their mixture under different dosages were investigated. The objectives of this study were the following: (a) to evaluate the influence of pre-deposited Pr.C or zeolite layer on removals of organics and ammonia during short-term UF or long-term GDM operation, and (b) to investigate the membrane fouling using different types and dosages of pre-deposited adsorbent layer.

#### 2. Materials and methods

#### 2.1 Experimental setup

The experimental setup driven by pressure in this study is presented in Fig. 1. Firstly, the role of pre-deposited adsorbent layer in the performance of UF membrane was investigated in short-term test. Specifically, the UF membranes were carried out under a pressure of 70 kPa driven by  $N_2$  using custom-made UF cell. Two selected adsorbents with different dosages

were added into feed water and were pre-deposited on membrane surface before UF operation compared with the control group without any adsorbent layer. For each short-term UF test, 400 mL of feed solution was filtrated under dead-end mode without stirring to prevent the breakage of deposited layer. Then, GDM systems were operated driven by water level difference between feed water tank and permeate tank (i.e., 0.75 m), using the experimental setup illustrated in Fig. 1. Similarly, the adsorbents were pre-deposited on membrane surface, and the GDM systems were carried out without any disturbance for more than two months operation. The dead-end filtration mode, which was employed in most GDM systems (Derlon et al., 2014; Wu et al., 2017a;  $\Gamma$  ing et al., 2020), was used in the current study. GDM systems were operated under room to membrane (18-22°C) in dark place. Parallel tests were done for all the UF (n=2) and GD'A to ts (n=2).

The UF cells were made using polymeth it reinacrylic (PMMA) and the effective inner diameter of each cell was 68 mm, resulting in an effective membrane area of 36.3 cm<sup>2</sup>. Polyethersulfone (PES) UF membranes were purchased from MICRODYN-NADIR (Germany), with a molecular weigh cutoff (MWCO) of 150 kDa. UF membranes were soaked in ultrapure water for at least twenty four hours to remove preservatives before use (Chang et al., 2015), and new membrane was employed in each test.



Fig. 1. The schematic diagram of experimental setup: (a) for short-term UF test and (b) for

long-term GDM operation. PAC200 and PAC800 represented PAC with a dosage of 200 and 800 g/m<sup>2</sup>, respectively, while GZ500 and GZ2000 were abbreviated as zeolites with a dosage of 500 and 2000 g/m<sup>2</sup>, respectively. PAC800+GZ2000 was short for the mixed adsorbent with 800 g/m<sup>2</sup> of PAC and 2000 g/m<sup>2</sup> of zeolite.

#### 2.2 Feed water and adsorbents

The feed water was prepared by diluting domestic sewage (Tang et al., 2020) with tap water at a dilution ratio of 30, and high ammonia concentrations were maintained by adding NH<sub>4</sub>Cl in the feed water. The characteristics of feed water was remained unchanged in the long-term operation by replacing feed water with fresh one every day. The characteristics of feed water quality were as follows: DOC = 2.68-3.36 mg/L,  $JV_{254} = 0.043-0.055$  cm<sup>-1</sup>, NH<sub>4</sub><sup>+</sup>-N = 2.4-3.1 mg/L, pH = 6.9-7.4, dissolved oxygen (LO) of around 9.5 mg/L.

Two types of commercially available adsorbents, PAC (Macklin, China) and zeolite (Zhengzhou, China) were used in this work. Ir a dition to the great removals for organics and ammonia, both PAC and zeolite wergeheep and easy to obtain for practical operation. PAC was cleaned by soaking in acidic solution (pH = 2, HCl) for 24 h followed by soaking in alkaline solution (pH = 12, NaOH).  $7.^{ft}$  that, PAC was further soaked in pure water for another 12 h, and then dried bef re u.e. In comparison, zeolites were activated by soaking in 0.3 mol/L NaCl solution at 10.0°C for 2 h, and then were flushed using pure water and dried before use. PAC and ze slite with different dosages as well as their mixture were added in feed water to form pre-coated adsorbent layers on membranes surface by gravity. The nominal size, specific surface area and total pore volume of PAC were 80  $\mu$ m, 1687 m<sup>2</sup>/g and 1.49 cm<sup>3</sup>/g, respectively. In contrast, the zeolites characterized by larger grain size (500  $\mu$ m), lower specific surface area (46.04  $m^2/g$ ) and total pore volume (0.088 cm<sup>3</sup>/g). The PAC dosage of 200 g/m<sup>2</sup> was identified according to previous literature (Ding et al., 2018; Shao et al., 2017), while the dosage of 500  $g/m^2$  was chosen because this dosage was the minimal value to ensure the membrane surface deposited with zeolites. To investigate the role of dosage in GDM performance, a high dosage of 2000g/m<sup>2</sup> (Four times higher than the low

dosage) was selected. PAC200 and PAC800 were short for PAC with the dosages of 200 and 800 g/m<sup>2</sup> (calculated by per unit area of membrane), respectively, while GZ500 and GZ2000 represented zeolite dosages of 500 and 2000 g/m<sup>2</sup>, respectively. The mixture of PAC (800 g/m<sup>2</sup>) and zeolite (2000 g/m<sup>2</sup>) were abbreviated as PAC800+GZ2000.

#### 2.3 Water quality analytical measurements

The DOC concentrations of feed and effluent were measured using an automatic total organic carbon analyzer (multi N/C 2100S, Analytic Jena, Germany). UV<sub>254</sub> was determined using an UV/vis spectrophotometer (T6, Puxi, China). The N<sup>LL</sup><sup>+</sup> concentration was detected by the colorimetric method using the same spec rophotometer. The fluorescence excitation-emission matrices (EEMs) of organic matters were characterized by a fluorescence spectrophotometer (F-7000, Hitachi, Japan). The samples were pre-filtrated through a 0.45-µm filter before analyzing DOC,  $UV_{134}$  and EEM. The pH and DO values were measured using a portable digital instrument (HQ30d, HACH, USA).

### 2.4 Filtration flux and resistance analysis

The flux (J) was continuously n. v. itored using an electronic balance which related to a computer. The flux was calculated using eq.1,

$$J = \frac{V}{S \times t} \tag{1}$$

where V was filtration volume (L), S was effective membrane area  $(m^2)$ , and t was filtration time (h).

Membrane filtration resistances (R, m<sup>-1</sup>) were calculated according to Darcy's law (eq.2):

$$R = \frac{\Delta P}{J \times \mu} \tag{2}$$

where  $\Delta P$  was operation pressure (Pa),  $\mu$  was viscosity of water (Pa·s). The total resistances ( $R_t$ ) were composed of intrinsic membrane filtration ( $R_m$ ), resistance caused by cake layer

 $(R_c)$  and pore blocking caused by membrane  $(R_p)$ . The detailed information about the calculation of these resistances were summarized in previous study (Ding et al., 2014).

#### 2.5 Characterization of biological fouling layer

At the end of GDM tests, optical coherence tomography (OCT) (model 930 nm Spectral Domain, Thorlabs GmbH, Dachau, Germany) was used to characterize the physical structure of the biological fouling layer. The OCT observations were carried out by selecting 15-20 points optionally to determine thickness and roughness using ImageJ (version 1.52s, Wisconsin, USA).

The mass of volatile and total solids of the biological touling layer adhered to the membrane surface were determined, following the method described elsewhere (Chomiak et al., 2015). The extraction of extracellular polymeric substances (EPS) from the biological fouling layer was conducted by the ultration and centrifugal method, as described previously (Adav and Lee, 2008). The concentrations of proteins and polysaccharides were tested by the bicinchoninic acid method and the anthrone-sulfuric method, respectively (Ding et al., 2017a). The tri-phosphate (^T.) content was measured in the biological fouling layer adhered to the membrane surface, using the BacTiter-Glo (Promega Corporation) kit and protocol, as described in previous studies (Berney et al., 2008; Ding et al., 2017a). The ATP content was normalized by the effective membrane surface.

#### 3. Results and discussion

#### 3.1 Contaminant removal performance during short-term operation

To investigate the role of precoated adsorbents on membrane surface in contaminant removal, the variations of DOC,  $NH_4^+$  and fluorescence substances during short-term UF tests using zeolites, PAC and their mixture are presented in Fig. 2. As shown in Fig. 2a, the UF membrane just removed a part of organics, with an average removal of 18% for DOC. The low organic removals have also been reported in previous literature (Akhondi et al.,

2015; Chang et al., 2019; Ding et al., 2017b; Tang et al., 2018a; Wu et al., 2016). The presence of zeolites on membrane surface had little impact on DOC removal, regardless of zeolite dosages. Whereas, PAC significantly improved the removals of organic matters, and higher DOC removal was observed with increased PAC dosage. Then, the mixture of zeolite and PAC exhibited the advantages of both adsorbents, with 78% of DOC. The enhanced removals of organic matters could be attributed to the excellent adsorption capacity of PAC, and the adsorption behaviors of PAC for NOM with different fractions were analyzed in detail by Velten et al. (2011). The hybrid PAC-UF process could improve DOC removal by 45% when compared to an UF unit alone (Zhang et al., 20'5).

As illustrated in Fig. 2b, the UF unit alone had not recroval of  $NH_4^+$  with a concentration in the permeate (2.64 mg/L) like that in the feed (2.65 mg/L), indicating that the necessity of UF hybrid process. The  $NH_4^+$  were decreased to 0.52 and 0.41 mg/L for UF permeate using zeolites with 500 and 2000 mg/L, respectively, and the removals were 65% and 84%, respectively. In comparison, less than 20% of  $NH_4^+$  was removed in the PAC-UF hybrid process. The presence of both zoolite and PAC resulted in a removal of 76% for  $NH_4^+$ , obviously higher than those in PAC-UF and slightly lower than those in zeolite-UF process. The excellent  $NH_4^+$  removals by zeolites could be attributed to the ion exchange of  $NH_4^+$  with cations in zeolites, as also reported in previous literatures (Huo et al., 2012; Soetardji et al., 2015; Xue et al., 2018). A synergetic effect of zeolite and PAC in removing  $NH_4^+$  was found by Liao et al. (2015). The lower  $NH_4^+$  removal of both zeolite and PAC than zeolite alone was probably due to the large difference between the sizes of both adsorbents under dead-end filtration, resulting in the zeolites wrapped in PAC.

Four typical fluorescence peaks were observed in the EEM spectra of feed water (Fig. 2c), peak A (Ex/Em = 235/340-355, aromatic proteins), B (Ex/Em = 280/320-330, tryptophan protein-like substances), C (Ex/Em = 245/410-430, fulvic acid) and D (Ex/Em =

290-320/410-430, humic acid) (Chen et al., 2003). Although UF membrane removed more protein-like substances than humic acid, the total removal of fluorescent substances was quite low using UF alone (Fig. 2d) (Wang et al., 2017). Similarly, the presence of zeolites on membrane surface had no impact on fluorescence substances (Figs. 2e-f). In contrast, the pre-deposited PAC layer greatly decreased the fluorescent substances, especially for the fulvic acid-like and humic acid-like substances (Figs. 2g-h). Recently, the adsorption performance of both zeolites and PAC on fulvic acid and humic acid was reported by Islam et al. (2020). As expected, an excellent removal was observed for fluorescent organics when both zeolite and PAC were used (Fig. 2i).

In summary, during the short-term UF test, the pre-deposited zeolite layer took a great role in the high removals for  $NH_4^+$  due to ion exchange, while excellent removals of organic matters (DOC and fluorescence substances) were observed using PAC. High removals of  $NH_4^+$  and organic matters were found when the mixture of zeolite and PAC was applied.

Solution



**Fig. 2.** Effect of adsorbent type and dosage on contaminant removals during short-term UF tests: (a) DOC, (b)  $NH_4^+$  and (c)-(1) fluorescence substances identified by EEM for (c) influent, (d) control, (e) GZ50°, (f) GZ2000, (g) PAC200, (h) PAC800 and (i) PAC800+GZ2000.

### 3.2 Removal performance during long-term GDM operation

#### **3.2.1 Organic removal**

The variations of DC C of feed and GDM permeate with operation time during long-term operation are shown in Fig. 3. The DOC concentrations in the feed water ranged from 2.68 to 3.36 mg/L, and an average removal of 19% was found for the control GDM (Fig. 3a). Similarly, the pre-deposited zeolite layers did not enhance the removals of DOC, and the average DOC removals were 22% for GZ500 and GZ2000, respectively. In contrast, much higher DOC removals were found in GDM systems when PAC was pre-deposited on membrane surface, with average values of 50% and 75% for PAC dosages of 200 and 800 g/m<sup>2</sup>, respectively. In addition, the DOC concentrations in the GDM permeate using

pre-deposited mixed adsorbents layer (i.e., PAC800+GZ2000) were similar to those using PAC800. Therefore, the organic removals for GDM during long-term operation were similar with those during short-term UF tests (see Fig. 1). After the GDM systems operated for 30-40 days, the DOC removals gradually decreased in this study. Decreased organic removals with operation time has also been reported in published literatures (Ding et al., 2017b; Shao et al., 2017). This was because the particulate organic matter be transformed into DOC due to the biological activity (Shao et al., 2017). Meanwhile, the hydrolysis of biological fouling layer deteriorated the water quality of the GDM permeate (Derlor e. al., 2014). However, the adsorption of pre-deposited PAC adsorbents may be gr.du. 11y saturated during long-term operation. The DOC removals at the end of the GDM peration were 39% and 54% for PAC200 and PAC800, respectively, still much higher the control GDM (13%). Moreover, the PAC might be partly regenerated in the presence of microbe (Zhang et al., 1991). When the adsorption capacity of PAC was "ur. out, only biological degradation worked (Korotta-Gamage and Sathasivan, 2017) Therefore, the improvement in DOC removal could be maintained for a long time.

Fig. 4 illustrates the effect of adsorbent type and dosage on the removals of fluorescence EEM spectra during long-tern. 'GDM operation. Similar with feed water under short-term UF test (Fig. 2c), still four typical EEM peaks were observed under different operation time. Generally, the removals of fluorescent organics gradually decreased with elapsed time, especially for peaks C and D. This was probably due to the microbial growth secretion, as also found in our previous work (Ding et al., 2018a). When compared to the feed water, the control GDM and the GDM pre-coated with zeolites just removed part of proteins, as presented in Figs. 4a-d. The higher removals of proteins than humic acids in GDM were also reported by Tang et al. (2018c). In contrast, all the fluorescent peaks disappeared when GDM was pre-deposited with PAC, even after operation for 60 days. The results indicated that

pre-deposited PAC layer exhibited excellent removals for aromatic proteins, tryptophan protein-like substances, humic acid-like substances.

Overall, during long-term GDM operation, the GDM alone just removed a few general and fluorescent organics. The pre-deposited zeolite layer had hardly positive influence on organic removal, irrespective of zeolite dosage. The pre-deposited PAC layer, in particular for higher PAC dosage, removed most dissolved organics including aromatic proteins, tryptophan protein-like substances and humic acid-like substances. When mixed adsorbents were employed, the organic removals were similar with the using PAC at high dosage. Additionally, the lower organic removals with the operation time were observed for DOC and fluorescent substances.



**Fig. 3.** Effect of adsc bent type and dosage on the removals of DOC during long-term GDM operation. (The  $NH_4^+$  dat, with standard deviations are summarized in Table S2)



**Fig. 4.** Effect of adsorbent type and dosage on the removals of 1 uorescence organic matters during long-term GDM operation: (a) influent, (b) control (c) PAC200, (d) PAC800, (e) GZ500, (f) GZ2000 and (g) PAC800+GZ2000.

#### 3.2.2 Ammonia removal

A good ammonia removal could be obtaine<sup>4</sup> when feed ammonia concentration was less than 1.5 mg/L (Chen et al., 2021; Dv et al., 2019). The feed  $NH_4^+$  concentrations were maintained at 2.4-3.1 mg/L to investigate the effect of adsorbent type and dosage on  $NH_4^+$ removals during long-term GDM ope at on, as shown in Fig. 5. In the first 16 days, the  $NH_4^+$ removals were quite low in the centrol GDM as well as GDMs with pre-deposited PAC layers, and  $NH_4^+$  concentrations in GDM permeate decreased significantly after operation for about 3 weeks (i.e., 17-2); days). These results indicated that ammonia oxidizing bacteria (AOB) and nitrite oxidizing bacteria (NOB) were enriched in the systems (Chang et al., 2014). Then, the permeate  $NH_4^+$  were maintained stable 30 days later, and the average  $NH_4^+$ concentrations were 0.49, 0.35 and 0.32 mg/L for the control GDM, GDM with PAC200 and GDM with PAC800, respectively. The removals of  $NH_4^+$  were primarily due to biological degradation in the control GDM, and the presence of PAC just slightly enhanced  $NH_4^+$ removals. Biological activated carbon has been used in membrane bioreactor to improve the removals of  $NH_4^+$  (Du et al., 2017; Tian et al., 2009), while PAC might hardly enhance  $NH_4^+$ 

removal in GDM systems (Shao et al., 2017). Despite the high  $NH_4^+$  removals in the control GDM, the presence of PAC shortened the duration before reaching 0.5 mg/L  $NH_4^+$  in permeate.

Zeolites were commonly used in water treatment to enhance the NH<sub>4</sub><sup>+</sup> removals, such as in biological filter (Feng et al., 2013; Yang et al., 2017) and ion exchange tower (Almutairi and Weatherley, 2015). Compared to the control, GDMs with pre-deposited zeolite layer exhibited excellent  $NH_4^+$  removals at the beginning of operation, while the permeate  $NH_4^+$ concentrations increased sharply with the peak values on Dav 19. Then, ammonia oxidizing bacteria (AOB) and nitrite oxidizing bacteria (NOB) vere enriched and NH<sub>4</sub><sup>+</sup> gradually decreased in the permeate. The  $NH_4^+$  concentrations in the permeate of GDM with GZ500 were less than 0.1 mg/L after operation for 40 days, while it took about two months when the permeate  $NH_4^+$  reached 0.1 mg/L for GDM with  $\frac{372000}{1000}$ . The  $NH_4^+$  removal behaviors in the GDM with mixed adsorbents were similar to the GDM with GZ2000. The high removals for  $NH_4^+$  could be attributed to ion exchange between  $NH_4^+$  and cations in zeolites (Wang and Peng, 2010), and higher removal were expected under higher zeolites dosage due to the larger exchange ability. When the exchange ability was run out, the removals of  $NH_4^+$ gradually decreased, and it vuld take a longer duration to adsorb NH<sub>4</sub><sup>+</sup> in GDM with pre-deposited zeolite havers once AOB and NOB were enriched. However, Tang et al. (2018a) found that  $NH_4^+$  removals were improved without  $NH_4^+$  release in a GDM with pre-coated zeolite layer, and the results might be due to the lower  $NH_4^+$  concentrations in the feed water (~0.4 mg/L). With respect to the pre-deposited layer using both PAC and zeolite, the change of NH<sub>4</sub><sup>+</sup> in permeate of GDM with PAC800+GZ2000 was similar to that of GDM with GZ2000.

Therefore, although there was not a significant difference in  $NH_4^+$  concentrations in permeate of the control and GDM with pre-deposited PAC layer in the first month, the

presence of pre-deposited PAC layer increased the  $NH_4^+$  removals after operation for one month. It was not a good approach for treating high  $NH_4^+$  solutions using pre-deposited zeolite layer during long-term operation, but the regeneration of zeolites made the GDM systems with pre-deposited zeolites layer could deal with sudden higher  $NH_4^+$  loading. In addition, the  $NH_4^+$  removals could not be enhanced in presence of both PAC and zeolite.



**Fig. 5.** Effect of adsorbent type and dosage on the removals of  $NH_4^+$  during long-term GDM operation. (The  $NH_4^+$  data with standard deviations are summarized in Table S2)

#### 3.3 Flux development

#### 3.3.1 Flux decline during short-term operation

The pre-deposited adsorbent layer on membrane surface could influence membrane flux and resistance. The effect or adsorbent type and dosage on the filtration flux and resistance during short-term UF tests are illustrated in Figs. 6a-b. The normalized flux decreased to 0.24 at the end of UF test for the control UF test. As membrane fouling was primarily caused by organic matters rather than  $NH_4^+$ , zeolites which were not effective in removing organics could not alleviate membrane fouling. In fact, the presence of zeolites obviously aggravated membrane fouling (Fig. 6a). The initial normalized fluxes were about 0.5 when zeolites were pre-deposited on membrane surface, and the final normalized fluxes were just 0.10 and 0.07 for GZ500 and GZ2000, respectively. In contrast, the presence of PAC significantly

alleviated membrane fouling, with the final normalized flux of 0.58 and 0.73 for PAC200 and PAC500, respectively. Although the pre-deposited PAC layers on membrane surface might increase hydraulic resistance, the removals of organic matters which were the primary foulant in UF tests reduced the fouling loading, resulting in higher fluxes than the control UF. Wu et al. (2017b) demonstrated that membrane fouling could be effectively eliminated when GAC was employed under disturbance condition, while Li et al. (2020) found that PAC could aggravate or eliminate membrane fouling depending on feed water quality. When the mixture of both zeolite and PAC were deposited simultaneously, the mixtal normalized flux was obviously decreased, similar to the GDMs using zeolites a'one. The final normalized flux was 0.39, higher than zeolites deposited UF but lower than PAC deposited UF, indicating that the UF fouling using zeolites and PAC could be explained by individual adsorbent.

When compared to the control UF test, the order resistance increased with an increase in zeolite dosage, and a higher PAC dosage left to a lower total resistance, as showed in Fig. 6b. Generally, the pre-deposited adsorbent layers could decrease the part of membrane pore blocking ( $R_p$ ). When compared to the control GDM,  $R_p$  decreased by 17% and 14% for GDM with GZ500 and GZ2000, respectively, while a decrease of 63% and 66% for  $R_p$  was observed for GDM with PACLO0 and PAC800, respectively. There was also an obvious decrease in  $R_p$  for the GDM with mixed adsorbents. The decrease in  $R_p$  was attributed to water purification for zeolites and PAC by adsorption, and the deposited layers could prevent foulant into entering the membrane pores. The flux decline caused by irreversible fouling could be effectively alleviated using dynamic membrane, as summarized in previous review (Anantharaman et al., 2020).



**Fig. 6.** Effect of adsorbent type and dowing on the filtration flux and resistance (a)(b) during short-term UF tests and (c)(d) during long-term GDM operation: (a)(c) flux and (b)(d) resistance. (The flux data with standard deviations are summarized in Table S3-S4)

### 3.3.2 Flux development of long-term GDM

During long-term CDM operation, the fluxes decreased sharply in the first 10 days, forming cake layer gradually. In the period of 10-35 days, the fluxes decreased slowly, and biological action in the cake layer was gradually intensified, characterized by heterogeneous structure of the biological cake layer. Finally, the stable fluxes were obtained in days 35-65, and this phenomenon has been widely reported in published literature (Peter-Varbanets et al., 2010; Peter-Varbanets et al., 2011). The flux of control GDM stabilized at  $6.63\pm0.09 \text{ L/(m}^2 \cdot \text{h})$  (LMH), while the stable flux of GDMs were decreased due to the pre-deposited zeolites layer, with the values of  $5.03\pm0.18$  and  $3.84\pm0.13$  LMH for GZ500 and GZ2000,

respectively. This result indicated that zeolites had adverse impact on stable flux of GDMs due to the intrinsic characteristics of zeolites and their deposited layers. Meanwhile, the pre-deposited zeolite layer could further adversely impact biological fouling layer, as demonstrated in short-term UF test (Fig. 6a).

When PAC was deposited in GDM systems, the stable fluxes for PAC200 and PAC800 were 5.88±0.14 and 6.54±0.14 LMH, respectively, slightly lower than the flux in control GDM. The fluxes in PAC deposited GDMs experienced an increase in 18-25 days, and this phenomenon has been found in Ding et al. (2018a). Li et al. (2014) found that GAC adsorption did not have a significant impact on membrane tooling. The presence of PAC did not result in an obvious increase in membrane resistance, with initial resistance of  $1.8 \times 10^{10}$ and 2.2×1010 m-1 for PAC200 and PAC800, respectively. As more organic matters which were the primary membrane foulants could 'te prived at higher PAC dosage, the higher PAC dosage might lead to a higher stable flux. Ding et al. (2018a) demonstrated that the stable flux decreased to 3.0 LMH in the presence of PAC (250 g/m<sup>2</sup>) from 4.5 LMH for the control. The stable flux could be enhanced when adsorbents and membranes were separated using plexiglass mesh in a GAC-GDM process by eliminating resistance caused by adsorbents (Tang et al., 2012). Moreover, the mixed adsorbents deposited on membrane surface made the flux submize at 6.13 LMH, indicating that the PAC could offset the adverse impact of zeolites. This was because organic matters could be adsorbed by PAC, and the void volume of zeolites alone were filled with PAC grain with smaller sizes, as discussed in Section 3.5.

As presented in Fig. 6d, the resistance distribution showed that the total resistances correlated well with stable fluxes. All the pre-deposited adsorbent layers enhanced resistances compared to the control. The cake layer resistance ( $R_c$ ) shared more than 90% of the total fouling resistance, and this result was consistent with previous study (Chang et al., 2019).  $R_p$ 

decreased due to the pre-deposited adsorbent layers. Therefore, the presence of pre-deposited layer was beneficial to membrane cleaning. Similarly, Ding et al. (2018a) found that the irreversible fouling in GDM could be alleviated by the deposited cake layer. Moreover, biological activity could be improved in the pre-deposited adsorbent layer, forming secondary protective screen (Ersahin et al., 2012). The  $R_p$  were decreased by 46-48% with the increase in zeolites dosage when compared to the control GDM. The  $R_p$  was eliminated by pre-deposited zeolite layer primarily due to the formed physical barrier, and zeolites at a dosage of 500 g/m<sup>2</sup> were enough to spread out on membrane curfue. In comparison,  $R_p$  was decreased by 49% and 59% for PAC dosages of 200 ar.d 200 g/m<sup>2</sup>, respectively, and the mixed adsorbents decreased the  $R_p$  by 48%. Thus, both playsical barrier and organic removal could attribute to the fouling in GDM, especially of higher PAC dosage. Moreover, membrane pore blocking was primarily responsive for irreversible fouling (Jiang et al., 2003; Mourouzidis-Mourouzis et al., 2008). Vec.all, although the stable fluxes decreased a bit, membrane fouling caused by pore blocking (i.e., irreversible fouling) could be eliminated in the presence of zeolites and/or PAC

## 3.4 Characterization of biological fouling layer

The biological fouling layers were characterized at the end of the GDM operation, with the results presented in Fig. 7. As shown in Fig. 7a, the presence of zeolites made the biomass higher than the control GDM by 99%-160%. With respect to EPS in cake layer, the presence of zeolites greatly increased the contents of protein and polysaccharide, while both the protein and polysaccharide concentrations were not obviously influenced by pre-deposited PAC layer at higher dosage (PAC800). Thus, the pre-deposited adsorbents in GDM surface would increase biomass and EPS, leading to more severe fouling than that in control GDM. Our previous study (Ding et al., 2018a) also demonstrated that pre-deposited adsorbent layer

could increase EPS content, while EPS in cake layer of GAC pre-deposited GDM was higher than that in sand pre-deposited GDM due to the higher adsorption capacity of GAC than sand.

When compared to the control GDM, the pre-deposited adsorbent layers improved the ATP contents significantly, in particular for GDM using zeolites (Fig. 7d). The result indicated that biological activity was enhanced in cake layer and the biomass increased, as also reported in previous study (Shao et al., 2017). Compared to the ATP in control GDM, the ATP contents in cake layer of GDM increased by 135% and 195% for GZ500 and GZ2000, respectively. This was because the zeolite grain size was larger (500 µm), and the large pore volumes in the adsorbent layer provided suitable conditions for biological growth, but led to lower stable fluxes. In comparison, the preserve of deposited PAC on membrane surface only slightly enhanced the ATP cortents with an increase of 22% and 36% for PAC200 and PAC500, respectively. Altinu ,h the organic matters adsorbed by PAC could be served as the nutrients of microorganisms (Zhang et al., 1991) which might grow on the surface of adsorbent layer, the impact of PAC on biological fouling layer was not significant. In addition, the ATP in cake 'aver of GDM with PAC800+GZ2000 was higher than the control by 40%, which was circular with the GDM with PAC800. Therefore, PAC was the dominant factor for the piological growth in the mixed adsorbents. In this study, the pre-deposited zeolite layer had much more obvious influence than PAC layer, although PAC exhibited larger organic adsorption capacity. The difference in adsorbent grain structure might be the major factor in determining biomass, ATP and EPS.

Moreover, the OCT scanning technique was used to characterize the biological fouling layer. The OCT image of a virgin membrane was shown in Fig. S1 (Supporting Information). As presented in Fig. 8, the thickness of cake layer decreased with the presence of PAC, but the cake layer was denser than that in the control and the roughness also increased. In

comparison, the thickness and roughness of cake layer in the zeolites deposited GDM were larger than that in the control GDM, and the large grain sizes provided suitable conditions for biological growth on heterogeneous layer surface and in void volumes. This could also explain the reason why biomass and EPS increased obviously using zeolites.



**Fig. 7.** The characteristics of the biological fouling layer under different conditions. The red asterisk labeled on one  $\xi$  oup represents the significant difference (p < 0.05) between this GDM and the control GDM (i.e., without pre-deposited adsorbent layer).



**Fig. 8.** OCT images of biological fouling layer for (a) control and pre-deposited layer using (b) GZ500, (c) GZ2000, (d) PAC200, (e) PAC800 and (f) PAC800+GZ2000. The yellow arrow represents the boundary between membrane sum ce and biological fouling layer. The thickness ( $\delta$ ) and roughness (Ra) of the biological fouling layer were listed on the right. Note: NA, not available.

### 3.5 Fouling mechanisms

The deposited PAC layer could effectively eliminate membrane fouling during short-term UF tests (Cai et al., 1013, Ding et al., 2014), but it exhibited adverse impact on stable flux during long-term GDM operation. The fouling mechanism in GDM systems using different types of adsortent are illustrated in Fig. 9. As presented in Figs. 9a-b, the PAC layer could make the calle layer denser than the control GDM, increasing biomass content and corresponding hydraulic resistance. As PAC decreased organic loading by adsorbing or degrading organic matters, the PAC dosage resulted in significant difference in organic matters. The decreased organic loading could lower fouling resistance, especially for higher PAC dosage. Considering the smaller grain sizes, dense PAC deposited layers formed on membrane surface, and cake layers occurred on the surface of deposited layers with the inner deposited layers and membrane surface slightly influenced by contaminants in feed water.

Thus, the stable flux, cake layer structure and biomass were not significantly influenced by PAC dosage.

In contrast, the deposited zeolites layers aggravated membrane fouling in both short-term UF tests and long-term GDM operation. This could be attributed to the larger hydraulic resistance, lower adsorption capacity for organic matters and higher biomass in the cake layer. The formed EPS and SMP could aggravate membrane fouling, as reported in previous study (Meng et al., 2017). Moreover, the large grain sizes of zeolites resulted in the formation of loosely deposited layers, and foulants were deposited on the surface and inner volume of zeolites layer as well as the membrane surface (Fig. 9c). As shown in Fig. 9d, when the mixed adsorbents using PAC and zeolites were employed, the PAC grains were filled in the void volumes of zeolites, explaining the effect of adsorbent sizes on membrane fouling (Cai et al., 2013).



Fig. 9. Fouling mechanism in GDM systems: (a) Control, (b) PAC, (c) zeolites, (d) PAC+zeolites.

According to the contaminant removals, PAC was recommended to choose for organic removal and zeolite was employed for sudden high-concentration ammonia of raw water. The stable fluxes decreased in the presence of pre-deposited zeolite layer, while similar stable fluxes were obtained when PAC was deposited on GDM surface. Moreover, membranes in GDM systems were operated without any cleaning, and the adsorbents in pre-deposited layer were seldom regenerated or replaced. Thus, the capital cost would be increased a little due to the addition of adsorbents, while the operating cost may be decreased due to the improved contaminant removals. By selecting appropriate adsorbent(c) the proposed GDM with pre-deposited adsorbent layer would deal with micro-pon ted surface water with high concentrations of organics or ammonia, ensuring the CDM an attractive technology for decentralized water supply.

### 4. Conclusions

In this study, zeolites and PAC wit. diaferent dosages were deposited on UF membrane surface to investigate their impacts on stable flux and contaminant removal. The following concluding remarks could be obtained.

(1) The pre-deposited FAC layers showed higher removals of DOC,  $UV_{254}$  and fluorescence substances (anothatic proteins, tryptophan protein-like substances, humic acid-like substances) than the control, and high PAC dosage resulted in high removals of organics. In contrast, the zeolites deposited layers exhibited low removals of organics, regardless of zeolites dosages. The mixed deposited layer using PAC and zeolite led to excellent organic removals, similar to that using PAC alone.

(2) The presence of PAC only enhanced the  $NH_4^+$  removal at stable stage, with final  $NH_4^+$  concentrations of 0.07-0.10 mg/L in the permeate of GDM with pre-deposited PAC layers. Due to ion exchange, the pre-deposited zeolite layers made it effective for the GDM systems in dealing with sudden higher  $NH_4^+$  loading but not for long-term high  $NH_4^+$ 

26

solutions. The mixed deposited layer using both PAC and zeolite showed similar to that using zeolite alone.

(3) The pre-deposited PAC layers could effectively alleviate membrane fouling in short-term UF tests, while the stable fluxes (5.88-6.54 LMH) in long-term GDM operation were slightly lower than the control GDM (6.63 LMH). The zeolites deposited layer aggravated membrane fouling in both short-term ultrafiltration and long-term GDM. The stable flux for the GDM using mixed adsorbents (6.10 LMH) was similar to that using PAC. The deposited adsorbent layer could increase filtration resignance of GDM systems, but decrease the pore blocking resistance.

(4) The pre-deposited adsorbent layers resulted in moreased concentrations of biomass, tri-phosphate (ATP) and extracellular polymeric substances (EPS), forming cake layers with a denser structure than the control one. The cake any er structures were further identified using optical coherence tomography (OCT) into ges.

#### CRediT authorship contributior statement

An Ding: Conceptualization, Methodology, Editing, Supervision. Ruilin Song: Data curation, Data analyses, Writing. Hao Cui: Data curation, Data analyses. Haiyan Cao: Data curation, Data analyses. Huu Hao Ngo: Conceptualization, Methodology, Editing. Haiqing Chang: Conceptualization, Methodology, Writing, Editing. Jun Nan: Conceptualization, Methodology, Editing. Guibai Li: Conceptualization, Methodology, Supervision. Jun Ma: Conceptualization, Methodology, Editing.

#### **Declaration of competing interest**

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

27

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### **Appendix A. Supporting Information**

Supplementary data related to this article or be found online.

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## **Highlights**:

- > PAC enhanced the removals of organics in short- and long-term UF processes
- $\blacktriangleright$  Zeolites could deal with sudden rather than long-term high NH<sub>4</sub><sup>+</sup> concentration
- $\blacktriangleright$  Mixed adsorbents had similar organic removal with PAC and NH<sub>4</sub><sup>+</sup> removal with zeolite
- > Pre-deposited adsorbent layers increased fouling in GDM but reduced pore blocking
- > Low stable flux was due to increase in ATP and EPS of biological fouling layer