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Removal of natural organic matter by an end-free gravity-driven membrane system combined with powdered activated carbon for household water supply

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ABSTRACT

There is a considerable need for household water treatment (HWT) systems that can supply safe and affordable drinking water for low- and middle-income countries. One HWT system, an end-free gravity-driven membrane (GDM) system, has been developed to produce potable water. GDM systems can remove turbid material and pathogens but cannot reduce natural organic matter (NOM) effectively. Because chlorination has been widely used for HWT in low- and middle-income countries, there are chances of trihalomethane (THM) formation with NOM content in water. To reduce NOM, an end-free GDM system combined with powdered activated carbon (PAC) was adopted. The raw water used was groundwater and lake water spiked with a humic acid solution. For raw water with low NOM concentration, batch operation without PAC addition was preferable to prevent a significant decrease in permeability because of PAC cake layer formation. For high NOM concentrations, PAC addition was required to reduce dissolved organic carbon (DOC) concentrations and to keep total THM formation under acceptable levels, the concentration of which was theoretically calculated. In this case, to prevent permeability and pH decreases from PAC addition, sufficient PAC should be added into the raw water to maintain the PAC concentration as low as possible while still satisfying DOC removal requirements. The end-free GDM system combined with PAC would have significant potential for HWT in low- and middle-income countries.

Keywords: Gravity-driven membrane; Household water treatment; Natural organic matter; Powdered activated carbon

1. Introduction

Approximately two billion people in the world have access to inadequate drinking water sources, such as untreated surface water, unprotected dug wells, or springs, mostly in low- and middle-income countries [1]. From this inadequate drinking water, 526,000 children under the age of five died from diarrhea in 2015 [2].

Recently, many household water treatment (HWT) solutions have been developed to prevent water-related diseases [3]. Injection of chlorine tablets or powders is one of the most widely used methods for HWT in low- and middle-income countries. Chlorination can deactivate pathogens with a relatively small amount of chlorine disinfectant. Additionally, chlorine tablets have advantages such as cost, safety, and convenience due to their single-use packaging and light weight [3,4]. However, before chlorination, the raw water should be filtered using a mesh or cloth filter to increase the chlorination efficiency. Users in rural areas of low- and middle-income countries often do not prefer chlorine tablets because of their aesthetic problems [5]. Aside from aesthetic issues, carcinogenic disinfectant by-products (DBPs), such as trihalomethanes (THMs) and haloacetic acids, are the most significant problems with chlorination [6].

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The factors influencing DBP formation include the concentration of natural organic matter (NOM), contact time with chlorine, chlorine dosage and residuals, pH, and water temperature. Most importantly, NOM is the principal precursor of DBP production [7]; and thus, in water with a high NOM concentration, the possibility of DBP formation is significantly increased [8].

NOM is pervasive in natural water and is one of the major contaminants in low-turbidity water [9]. NOM concentration is usually measured by indirect methods in terms of total organic carbon (TOC) or dissolved organic carbon (DOC). In several countries in the world, DOC concentrations in surface water are in the range of 5–15 mg L^{-1} [10–12]. NOM has no direct effects on human health but can cause undesirable color, adverse taste, and odor problems, along with the aforementioned formation of THMs during water treatment. When the DOC concentration of a water source is less than 5 mg L^{-1}, there is little effect on THM formation during chlorination. For DOC concentrations higher than this, however, there is a risk of health and aesthetic effects and THM formation during chlorination, depending on the DOC composition [13]. In low-income countries, the total trihalomethane (TTHM) was found to exceed the US Environmental Protection Agency (EPA) THM guideline for river water after 24 h of chlorination using point-of-use chlorination products. In addition, for rainwater, lake water, and earth pond water samples with 24 h chlorination, it was nearly at the level of the guideline [6,14]. Some countries have guidelines for TOC in potable water, e.g., 3 mg L^{-1} for Japan and Norway and 4 mg L^{-1} for Canada [15–17]. The US EPA sets the guideline under 50% for the TOC concentration in treated water when the raw water concentration is 8 mg L^{-1} [18]. There are several water treatment options for DOC removal, including adsorption, ozonation, membrane filtration, biodegradation, and coagulation with cationic additives [9]. Despite the diversity of these options, most options are not feasible for low-cost HWT and low- and middle-income countries. Gravity-driven membranes (GDMs) are one water purification method available in low- and middle-income countries. Frechen et al. introduced a flat sheet GDM system with the stable flux of 5 L m^{-2} h^{-1}, which could produce 20 L of filtered water per day using river water [19]. Clasen et al. reported that a GDM unit could produce an average of 8.8 L h^{-1} with a backwashing process using synthetic water with humic acid [20]. In low- and middle-income countries, 5 L d^{-1} per capita of safe water is needed for drinking and cooking. Additionally, 7 L d^{-1} per capita of safe water is required for bathing and personal hygiene. Therefore, based on a 5-person family, 25 L d^{-1} is required for drinking and cooking, whereas 60 L d^{-1} is needed with the addition of bathing and personal hygiene [21]. GDM systems can effectively remove turbidity and microorganisms, but not NOM. An ultrafiltration GDM filter was reported to reject 15%–35% of humic acid from river water and humic acid-spiked river water [22]. Powdered activated carbon (PAC) adsorption has been widely used for removing NOM in water treatment [23]. PAC can be combined with GDMs with relative ease compared with other methods, but this combination has not yet been studied.

The aim of this study, therefore, is to investigate whether an end-free GDM filtration system combined with PAC would be suitable for drinking water treatment, including NOM removal, as an HWT system by testing the reduction in NOM concentration in water samples, such as groundwater and lake water. Filtrate DOC was measured to observe the NOM reduction by PAC. In addition, TTHM formation for both raw and treated water was estimated by theoretical calculation. Furthermore, permeability was measured to assess whether the end-free GDM system could supply a sufficient filtrate quantity to a 5-person family.

2. Materials and methods

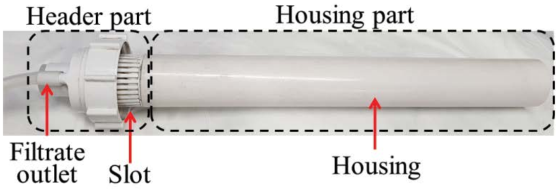
2.1. GDM filtration system setup

The GDM system was comprised of a 20-L plastic jerrycan, generally available anywhere in the world, and a GDM module connected to the jerrycan with a DIN51 screw, as shown in Fig. 1 [24]. The module contained hollow fiber membranes potted to the header. One side of the membrane fibers was individually sealed to allow the fibers to move freely [25]. The effective membrane area was 0.3 m^2, the average pure water permeability was 16.65 L m^{-2} h^{-1} kPa^{-1}, and the other specifications of the end-free GDM module are described in Table S1 (Supporting Information).

2.2. Raw water

Three kinds of raw water were used in this study: (1) humic acid-spiked groundwater (H.A.-G.W.), (2) lake water, and (3) humic acid-spiked lake water (H.A.-L.W.). The humic

(a) End-free GDM module



(b) End-free GDM system

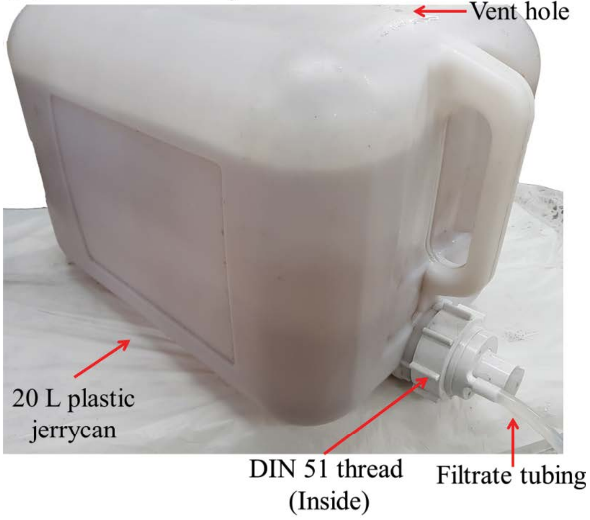


Fig. 1. (a) The end-free GDM module and (b) the end-free GDM system equipped with the module.

acid-spiked groundwater was prepared using commercial humic acid powder (Aldrich, USA) and groundwater. The average turbidity, DOC concentration, and UV absorbance at 254 nm (UV254) of the groundwater were 2.046 NTU, 0.876 mg L^{-1}, and 0.0158 cm^{-1}, respectively. First, 116.5 mg L^{-1} of the humic acid powder was dissolved into 1 L of distilled water, and the solution pH was increased to 10 using 0.1M sodium hydroxide. Then, pH was adjusted to 7 using 0.1M hydrochloric acid. After pH adjustment, the solution was diluted with groundwater to make a DOC concentration of 10 mg L^{-1}. The average turbidity, DOC concentration, and UV254 of the humic acid-spiked groundwater were 10.1 NTU, 9.7 mg L^{-1}, and 0.7855 cm^{-1}, respectively.

Lake water was used as a natural water source with low NOM concentration and low turbidity. The lake water sample used in this study was obtained from a lake in Wonju City in the Republic of Korea. The average turbidity, DOC concentration, and UV254 of the lake water were 23.1 NTU, 5.1 mg L^{-1}, and 0.0687 cm^{-1}, respectively. The humic acid solution was spiked into lake water to make a high DOC concentration sample as described above. The average turbidity, DOC concentration, and UV254 of the humic acid-spiked lake water were 25.1 NTU, 9.8 mg L^{-1}, and 0.444 cm^{-1}, respectively.

2.3. Powdered activated carbon

PAC (DARCO KB-B, Norit, The Netherlands) with an average particle size of 27–42 μm was used for NOM removal. The internal surface area and density of the PAC were 1,000 m^2 g^{-1} and 295 kg cm^{-3}, respectively, as shown in Table S2 of the Supporting Information. The PAC was directly added into the jerrycan in this study. Sodium phosphate buffer (0.1M) was also prepared to prevent a decrease in pH due to the PAC addition.

2.4. Experimental methods

2.4.1. Adsorption without the GDM filtration system

For preliminary adsorption tests, various amounts of PAC were added into a 250-mL flask containing the humic acid-spiked groundwater with a DOC concentration of 9.7 mg L^{-1} and another 250-mL flask with the lake water with a DOC concentration of 4.8 mg L^{-1}. A 30 mL of the mixture was sampled 2 h after addition and filtered with a 0.45-μm syringe filter (Chromafil CA-45/25-S, Macherey-Nagel, Germany).

2.4.2. Operation of the GDM filtration system

The GDM filtration system was operated as follows. First, the upright jerrycan was filled with raw water. Then, the GDM module was combined with the jerrycan, and the jerrycan with the module was laid down to filter the raw water, as shown in Fig. 1(b). After completion of each batch filtration, the jerrycan was placed upright and the module was unscrewed for the next batch filtration. Before starting the next operation, the concentrate was treated as follows. When the experimental condition was "Every batch," as shown in Table 1, the concentrate was fully emptied from the jerrycan after every batch filtration and recharged with raw water for the next batch filtration. When the condition was "No drainage," the concentrate was maintained in the jerrycan and the jerrycan refilled with raw water. "Every 5 batches" means the concentrate was fully emptied every five batches, and for the other batches, the concentrate was treated by the same method as the condition of no drainage.

The raw water was filtered by gravity; the water level started at 23 cm from the bottom of the jerrycan and ended at 10 cm. The effective water head for filtration was the sum of the water head of the raw water from the filtrate outlet level and the height of the siphon for the filtrate tubing. When the

Table 1
Experimental conditions of the GDM filtration system for the humic acid-spiked ground water (H.A.-G.W.), lake water, and humic acid-spiked lake water (H.A.-L.W.)

No.	Abbreviation	water source	Initial DOC (mg L_{-1})	PAC concentration in the jerrycan (mg L^{-1})	Total PAC input (g)	PAC Injection	Concentrate drainage from the jerrycan
1	H.A.-G.W. + PAC 0	Ground water	9.7	0	0	No PAC addition	Every batch
2	H.A.-G.W. + PAC 250			250	75	Every batch	Every batch
3	H.A.-G.W. + PAC 1,250 (once)			1,250	25	Once in the first batch	No drainage*
4	H.A.-G.W. + PAC 1,250			1,250	75	Every 5 batches	Every 5 batches
5	H.A.-G.W. + PAC 2,500 (once)			2,500	50	Once in the first batch	No drainage
6	H.A.-G.W. + PAC 3,750 (once)			3,750	75	Once in the first batch	No drainage
7	Lake water + PAC 0	Lake water	5.1	0	0	No PAC addition	Every batch
8	Lake water + PAC 500			500	300	Every batch	
9	H.A.-L.W. + PAC 0		9.8	0	0	No PAC addition	
10	H.A.-L.W. + PAC 500			500	300	Every batch	

* During 15 batches

raw water level was 23 cm, the effective water head was calculated to be 46 cm with the addition of the siphon effect. The filtrate flux was measured twice at the beginning and at the end of one batch of filtration. Next, manual cleaning was performed, which will be described in the following section. In the case of filtration with the humic acid-spiked groundwater, filtration was conducted for 15 batches, while filtration was carried out for 30 batches of the lake water and the humic acid-spiked lake water.

2.4.3. Adsorption with the GDM filtration system

For the humic acid-spiked groundwater, six different experimental conditions were tested as tabulated in Table 1: (1) H.A.-G.W. + PAC 0: no PAC injection during the processing of 15 batches and drainage of the concentration remaining in the jerrycan at the end of every batch filtration; (2) H.A.-G.W. + PAC 250: injection of 250 mg L^{-1} PAC into the jerrycan every batch and drainage of the concentration containing PAC at the end of every batch filtration (250 mg L^{-1} of fresh PAC was maintained in the jerrycan during filtration); (3) H.A.-G.W. + PAC 1,250 (once): injection of 1,250 mg L^{-1} PAC once at the first batch and no drainage of the concentration during the processing of 15 batches (which allowed the reuse of the injected PAC in the next batch filtrations); (4) H.A.-G.W. + PAC 1,250: injection of 1,250 mg L^{-1} PAC every 5 batches and drainage of the concentration every 5 batches; (5) H.A.-G.W. + PAC 2,500 (once): injection of 2,500 mg L^{-1} PAC once at the first batch and no drainage of the concentration during the processing of 15 batches; and (6) H.A.-G.W. + PAC 3,750 (once): injection of 3,750 mg L^{-1} PAC once at the first batch and no drainage of the concentration during the processing of 15 batches.

For both the lake water and humic acid-spiked lake water, two different experimental conditions were used. The first condition was no PAC injection and drainage of the concentration at the end of every batch filtration for (7) Lake water + PAC 0 and (9) H.A.-L.W. + PAC 0, as shown in Table 1. The other condition was injection of 500 mg L^{-1} PAC and drainage of the concentration at the end of every batch filtration for (8) Lake water + PAC 500 and (10) H.A.-L.W. + PAC 500.

2.4.4. Manual cleaning

Manual cleanings for the removal of the fouling layer from the membrane surface were carried out with two different methods, 'cleaning between batches' and 'long-term cleaning' conducted after processing 15 batches. All manual cleanings were conducted by manpower without any mechanical tools. The cleaning between batches was performed before starting every batch filtration, and it consisted of twisting 3 times and vertical shaking 10 times with the jerrycan full of raw water. For the twisting step, the module was rotated 90° clockwise and counterclockwise. For the vertical shaking step, the module was moved vertically up and down within a span of 20 cm.

Long-term cleaning was accomplished after filtering 15 batches in a separate bucket containing groundwater. It was conducted with vertical shaking 70 times near the header part, followed by vertical shaking 70 times for the middle region of the housing part. For vertical shaking for the middle region of the housing part, two-thirds of the module was submerged and moved up and down within a span of 20 cm. For vertical shaking near the header part, the module was fully submerged and moved up and down over a range of 10 cm.

2.5. Estimation of the TTHM formation

A model equation for TTHM was applied to estimate the formation of TTHMs in the raw and filtrate water assuming chlorination as a posttreatment, as follows [26]:

$$\text{TTHM} = 0.044\left(\text{DOC}\right)^{1.030}\left(t\right)^{0.262}\left(\text{pH}\right)^{1.149}\left(\text{Cl}\right)^{0.277}\left(\text{Temp.}\right)^{0.968} \quad (1)$$

where TTHM is the concentration of TTHM (μg L^{-1}), DOC is the DOC concentration (mg L^{-1}), t is the reaction time with chlorine reagents (h), Cl is the concentration of the chlorine reagents (mg L^{-1}), and Temp. is the temperature of the water (°C). In this study, it was assumed that the reaction time and the concentration were 30 min and 5 mg L^{-1}, respectively, by referring to a manual for commercialized chlorine tablets (Aquatabs®, Medentech. Ltd, Ireland).

2.6. Analytical methods

All raw water and filtrates were sampled at 3 min after the start of filtration. DOC was analyzed using a TOC analyzer (TOC-V CPH/CPN, Shimadzu, Japan). UV254 was determined using a UV-visible spectrophotometer (Cary 50 Probe, Varian, USA). pH was analyzed using a pH meter (Orion Star A211, Thermo Scientific, USA).

3. Results and discussion

3.1. PAC adsorption characteristics for the humic acid-spiked groundwater and lake water without GDM filtration

Fig. 2(a) shows DOC removal and pH changes according to PAC addition for the humic acid-spiked groundwater. The target DOC level after adsorption was set to 5 mg L^{-1}, which is the US EPA THM guideline and has also been suggested for human health in South Africa [18,27]. For the humic acid-spiked groundwater with an initial DOC concentration of 9.7 mg L^{-1} and no buffer addition, 1,000 mg L^{-1} PAC was needed to achieve the target DOC level. However, the addition of 1,000 mg L^{-1} PAC caused a problem in that the solution pH was decreased to approximately 3, as shown in Fig. 2(a). pH 3 is unfavorable for drinking water; even though it hardly causes health problems, the World Health Organization (WHO) suggests the pH for drinking water to be between 6.5 and 8.5 [28]. Therefore, to test PAC adsorption without a significant pH decrease, a buffer solution was used in all experiments using groundwater. With 0.1 and 0.01M phosphate buffer, 250 and 1,000 mg L^{-1} PAC was required to reduce the DOC concentration to below 5 mg L^{-1}, respectively. For 0.1M phosphate buffer, the pH was not changed, even with high PAC addition. However, the pH decreased to below 5 with 10,000 mg L^{-1} of PAC addition with 0.01M phosphate buffer.

Fig. 2(b) shows that the DOC concentration and pH decrease with PAC addition for lake water. No further significant DOC removal was observed at more than 500 mg L^{-1}

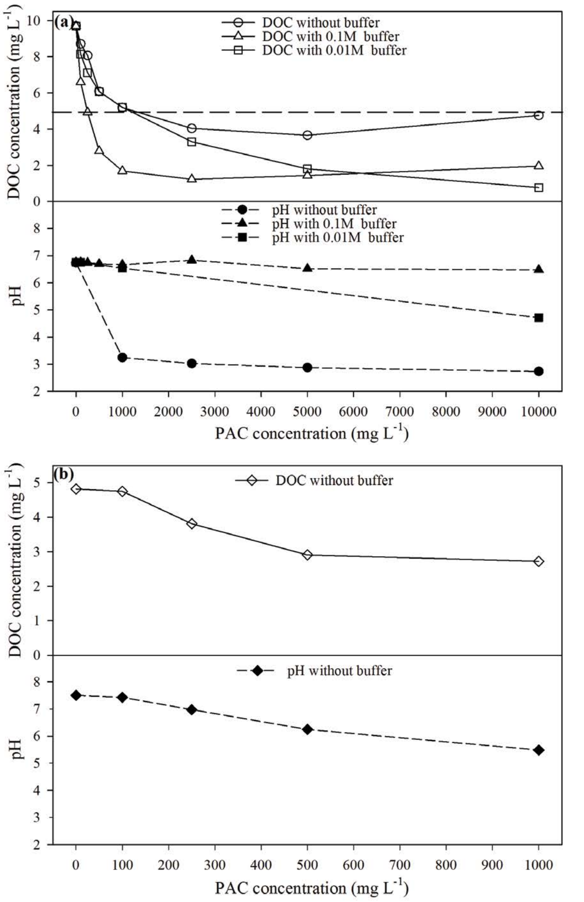


Fig. 2. Variations in DOC and pH by 2 h adsorption at each PAC concentration without GDM filtration for (a) humic acid-spiked ground water and (b) lake water.

of PAC addition. For 500 mg L^{-1} PAC, the pH decreased to 6.24. With the addition of more than 500 mg L^{-1} PAC, the pH fell to less than 6. For the lake water experiments, the phosphate buffer solution was not used because the pH of the water after all experiments was practically acceptable based on WHO guidelines [28].

3.2. Optimizing the PAC addition with the GDM filtration system using humic acid-spiked groundwater

3.2.1. Water permeability

Fig. 3 shows the normalized permeability with different PAC addition methods for the humic acid-spiked groundwater. After the 15th batch filtration, the GDM module was washed using the long-term cleaning process described above.

Fig. 3(a) shows the variation in the normalized permeability with the same total PAC dosage (75 g) but different PAC concentrations (250, 1,250, and 3,750 mg L^{-1} due to different addition methods (Table 1)), as compared with no PAC addition. At the end of the 15th batch with cleaning between batches, the permeability of 250 mg L^{-1} PAC addition at every batch was similar to that with no PAC addition, and it was nearly constant from the 7th to the 15th batches. However, when the PAC concentration was significantly higher, the permeability continuously decreased because of sizeable PAC cake layer formation on the membrane surface, especially near the header part (Fig. S1 in the Supporting Information). For 1,250 and 3,750 mg L^{-1} PAC, the normalized permeability decreased from 0.923 and 0.883 to 0.220 and 0.125, respectively, after the 15th batch. The greater the PAC concentration, the greater the permeability decrease, despite the same total PAC dosage. Seo et al. demonstrated that permeability decreased with high PAC addition concentration [29]. During processing of the 15 batches, a thicker PAC cake formed near the header part than the housing part (Fig. S1(a)). Yu et al. reported that the flux near the suction point was higher than that in other portions at the beginning of operation [30]. Similarly, the membrane near the header part was fouled more by PAC (Fig. S1(b)). Most of the PAC cake layer near the header part could be removed by long-term cleaning (Fig. S1(c)). Thus, after long-term cleaning, the permeability

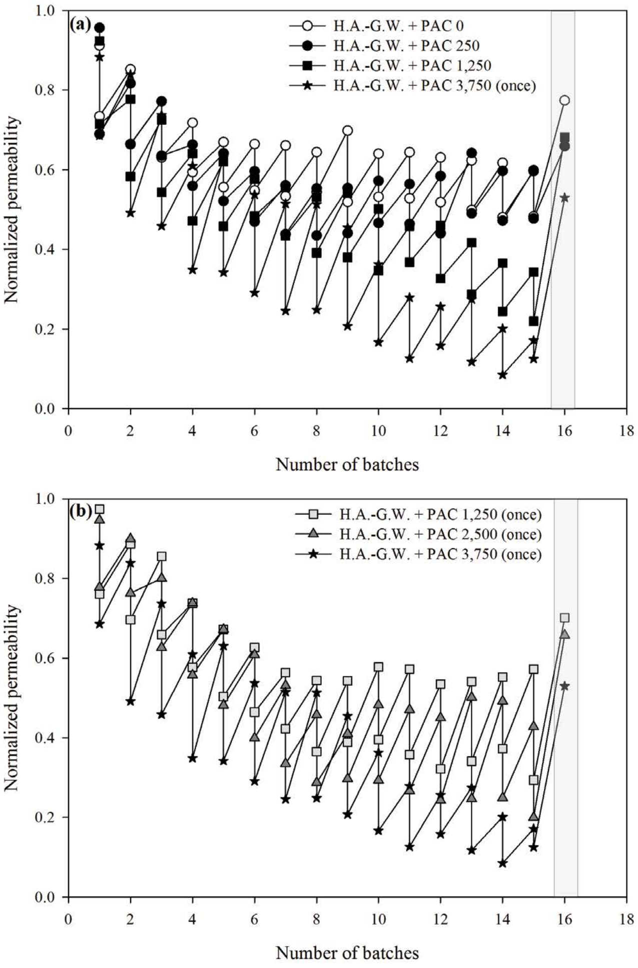


Fig. 3. Normalized permeability with different PAC addition methods for humic acid-spiked ground water (a) with the same total PAC dosage (75 g) but different PAC concentrations (250, 1,250, and 3,750 mg L^{-1} due to different addition methods) (Table 1) and (b) with different total PAC dosages (25, 50, and 75 g added at once) corresponding to different PAC concentrations (1,250, 2,500, and 3,750 mg L^{-1}), respectively. The gray boxes indicate the permeability measured after long-term cleaning following the 15th batch filtration.

increased from 0.125 to 0.530 for the humic acid-spiked groundwater with 3,750 mg L^{-1} PAC. The high PAC concentration played a role as a foulant by forming a cake layer together with humic acid on the membrane surface, thus reducing water permeability.

Fig. 3(b) shows the variation in the normalized permeability with the different PAC dosages (25, 50, and 75 g added once at the 1st batch), corresponding to different PAC concentrations (1,250, 2,500, and 3,750 mg L^{-1}, respectively (Table 1)). Similar results were observed as previously mentioned. After the 15th batch, the permeability decreased from 0.974, 0.947, and 0.883 to 0.294, 0.200, and 0.125 with 1,250, 2,500, and 3,750 mg L^{-1} PAC, respectively. The more PAC that was added, the more severely the normalized permeability decreased. The recovery of the normalized permeability was not significantly different among the three cases of Fig. 3(b); and thus, the efficiency of cleaning between batch filtrations hardly affected the overall permeability decrease during processing of the 15 batches. However, the permeability drop during each batch filtration became steeper as the PAC concentration increased. Therefore, in terms of permeability, a lower PAC concentration was better, irrespective of the total PAC dosage.

The average volumetric flow rates of the filtrate after processing 15 batches were 13.9, 12.9, 10.7, 6.9, 7.8, and 3.6 L h^{-1} for PAC concentrations of 0, 250, 1,250, 1,250 (once), 2,500 (once), and 3,750 mg L^{-1} (once), respectively, as shown in Figs. S2(a) and (b) (Supporting Information). Thus, the system could produce 86.4–333.6 L d^{-1} of the filtrate, which is sufficient for a 5-person family for bathing and personal hygiene as well as drinking and cooking (minimum of 60 L d^{-1}) [21].

3.2.2. DOC removal

Fig. 4 shows the DOC concentrations with different PAC addition methods for the humic acid-spiked groundwater. Fig. 4(a) shows the DOC concentrations with the same total PAC dosage but different PAC concentrations. For the filtration without PAC, the DOC concentration of the filtrate increased from 2.2 mg L^{-1} at the 1st batch to 8.8 mg L^{-1} at the 15th batch. For the initial batch filtration, humic acid molecules could be removed by adsorption because they were adsorbed on the membrane by ionic strength [31]. However, after the 5th batch, the DOC concentration of the filtrate exceeded the US EPA THM guidelines (dashed lines in Fig. 4). The more batches that were processed, the more adsorption sites on the membrane were reduced. After the membrane was fully saturated with humic acid, the humic acid molecules could easily pass through the membrane pores without any additional adsorption. The average DOC concentration of the filtrate was 3.9, 1.4, and 1.4 mg L^{-1} for 250, 1,250, and 3,750 mg L^{-1} PAC, respectively, and the filtrate DOC concentration did not exceed the guidelines in any of the three cases.

Fig. 4(b) shows DOC concentrations with the different PAC dosages and concentrations. The average DOC concentrations were 2.5, 1.6, and 1.4 mg L^{-1} for 1,250, 2,500, and 3,750 mg L^{-1} PAC, respectively, during the 15 batch filtrations. From the 8th batch to 15th batch, the DOC concentration of the filtrate for 1,250 mg L^{-1} PAC increased from 1.8 to 3.9 mg L^{-1}.

As previously discussed, the lower the PAC concentration, the higher the permeability. However, DOC was removed more with higher PAC concentrations, with no further difference over 1,250 mg L^{-1} PAC. Therefore, if the raw water is not significantly contaminated by NOM, it is preferable that the batch is operated without the addition of PAC. In contrast, for raw water with a significant amount of NOM, it is better to reduce DOC with adequate PAC addition to the GDM filtration system. It should be noted that the pH will drop sharply when a large amount of PAC is introduced (Fig. 2(b)).

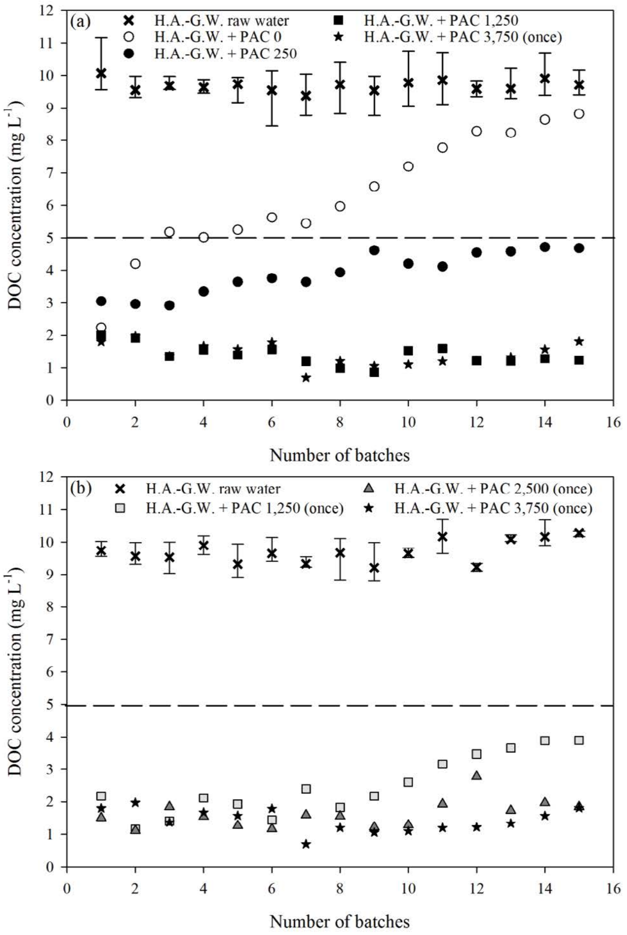


Fig. 4. DOC concentrations with different PAC addition methods for humic acid-spiked ground water (a) with the same total PAC dosage (75 g) but different PAC concentrations (250, 1,250, and 3,750 mg L^{-1} due to different addition methods) and (b) with different total PAC dosages (25, 50, and 75 g added at once) corresponding to different PAC concentrations (1,250, 2,500, and 3,750 mg L^{-1}), respectively. The dashed lines indicate the USEPA THM guideline, the 5 mg L^{-1} DOC limit when the DOC concentration of the raw water was 10 mg L^{-1}.

3.3. Application of PAC addition with the GDM filtration system for lake water

3.3.1. Water permeability

The humic acid-spiked lake water (the average DOC concentration was 9.8 mg L^{-1}) and the lake water (the average DOC concentration was 5.1 mg L^{-1}) were tested. Fig. 5 shows the normalized permeability during 30 batches of filtration with and without PAC addition for the lake water (Fig. 5(a)) and the humic acid-spiked lake water (Fig. 5(b)). For the lake water, the permeability with 500 mg L^{-1} PAC averaged 39% higher than that without PAC. This permeability trend is in contrast to the results for the humic acid-spiked groundwater shown in Fig. 3, in which the permeability was lower at higher PAC concentrations. The cake layer that formed on the membrane surface, in this case, was likely more permeable than that for the humic acid-spiked groundwater because of the higher turbidity and lower DOC of the lake water versus the humic acid-spiked groundwater. The lower DOC concentration might lead to a more permeable cake layer, and more particles in the raw water might have interfered with the approach of humic acid to the membrane surface, acting as a dynamic membrane [31,32].

When humic acid was spiked into the lake water, the result was somewhat different from the lake water case (Fig. 5(b)). During processing of the 30 batches, the permeabilities with and without PAC were very similar to one another. Since the turbidity of the humic acid-spiked lake water (25.1 NTU) was not increased significantly from the initial turbidity of the lake water (23.1 NTU), it is reasonable to conclude that the difference between Figs. 5(a) and (b) was caused by the DOC concentration increasing approximately two times due to the humic acid spiking. The increased amount of humic acid could reduce the porosity of the cake layer on the membrane surface, which in turn deteriorates its permeability. Therefore, the permeability difference was not significant in the humic acid-spiked lake water, unlike the lake water case.

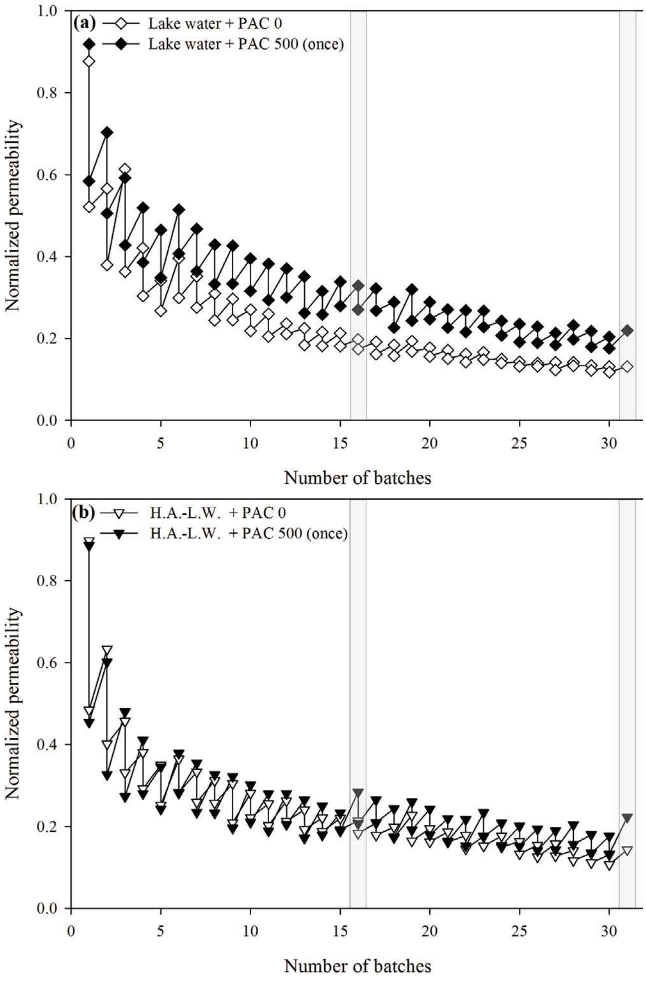


Fig. 5. Normalized permeability with and without PAC addition for (a) lake water and (b) humic acid-spiked lake water. The gray boxes indicate the permeability measured after long-term cleaning after every 15 batches.

The mean volumetric flow rates of the filtrate after processing 30 batches were 3.1 and 4.5 L h^{-1} for the lake water with PAC concentrations of 0 and 500 mg L^{-1}, respectively (Fig. S2(c) in the Supporting Information). For the humic acid-spiked lake water, the mean volumetric flow rates after processing 30 batches were 2.7 and 4.0 L h^{-1} for the PAC concentrations of 0 and 500 mg L^{-1}, respectively (Fig. S2(d) in the Supporting Information). The GDM system could produce at least 74.4 and 64.8 L d^{-1} of the filtrate for the lake water and humic acid-spiked lake water, respectively. Therefore, the GDM system could produce sufficient water for a 5-person family for drinking and cooking, as well as bathing and personal hygiene.

3.3.2. DOC removal

Fig. 6 shows the DOC concentrations with and without PAC addition for the lake water and humic acid-spiked lake water. For the lake water with a raw water DOC concentration of 5.1 mg L^{-1}, the average DOC concentrations of the filtrate were 3.5 and 1.7 mg L^{-1} without and with PAC addition, respectively, during processing of the 15 batches (Fig. 6(a)). For the humic acid-spiked lake water, the DOC concentrations decreased from 9.8 mg L^{-1} to 5.2 and 2.0 mg L^{-1} without and with PAC addition, respectively (Fig. 6(b)). The filtrate DOC concentration without PAC addition for the humic acid-spiked lake water exceeded the THM guideline.

For the lake water, the membrane without PAC addition rejected 1.6 mg L^{-1} DOC. This was calculated by subtracting the filtrate DOC (3.5 mg L^{-1}) from the raw water DOC (5.1 mg L^{-1}). With PAC addition, 0.5 mg L^{-1} DOC was removed by the suspended PAC before the formation of a PAC cake layer on the membrane surface. The removal of DOC for the initial four batches and for the four batches after long-term cleaning were less than those for the other batches. This implies that most of the PAC cake layer was formed after the initial four batches. After formation of the PAC cake layer, the PAC-coated membrane removed 3.1 mg L^{-1} DOC. The proportions of the removal with suspended PAC and the PAC-coated membrane were 9.8% and 60.8%, respectively. For the lake water with humic acid, the membrane without PAC addition rejected 4.6 mg L^{-1} DOC. With 500 mg L^{-1} of PAC addition, approximately 2.8 mg L^{-1} DOC was removed by suspended PAC before the formation of the PAC cake layer on the membrane surface. After formation of the PAC cake layer, the PAC-coated membrane removed 5.1 mg L^{-1} DOC. The proportions of the removal with the suspended PAC and the PAC-coated membrane were 28.6% and 52.0%, respectively. Most of the NOM in the water sources was removed by both the membrane and the PAC deposited on the membrane surface.

Fig. 7 shows the DOC removal with and without PAC addition for the lake water and the humic acid-spiked lake water. With PAC addition, DOC removal increased as the batches were processed, whereas DOC removal did not significantly increase without PAC addition. This supports the findings that a large portion of DOC was removed by the PAC deposited on the membrane surface.

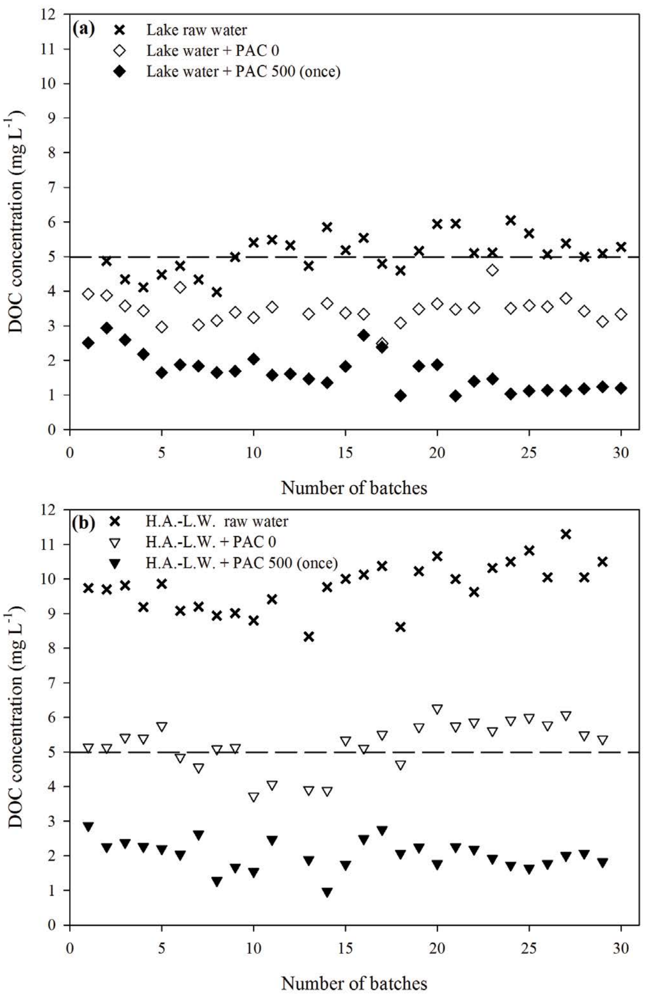


Fig. 6. DOC concentrations with and without PAC addition for (a) lake water and (b) humic acid-spiked lake water. The dashed line indicates the USEPA THM guideline (target DOC removal set under 50% for 10 mg L^{-1} DOC in the raw water).

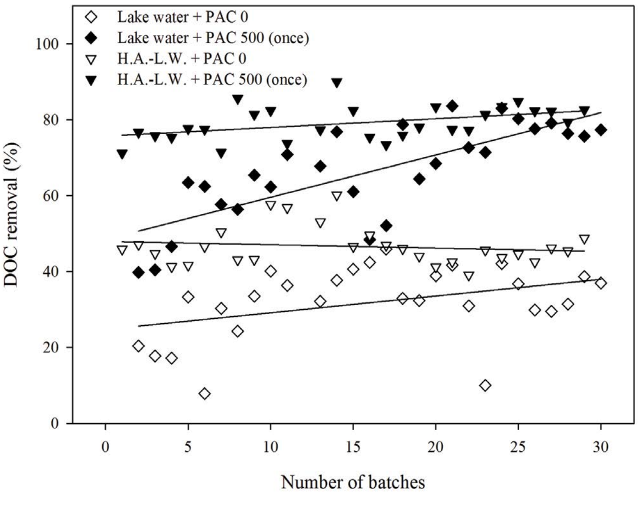


Fig. 7. DOC removal with and without PAC addition for lake water and humic acid-spiked lake water.

3.4. TTHM formation

According to the US EPA THM guideline, the maximum contaminant level (MCL) for TTHM is 80 µg L^{-1} [18]. TTHM may cause various cancers, along with reproductive and developmental problems [33]. Fig. 8 shows the estimated TTHM formation by chlorination of the filtrate from the GDM system with and without PAC addition for the humic acid-spiked groundwater, lake water, and humic acid-spiked lake water. For the humic acid-spiked groundwater, the raw water TTHM concentration was estimated to be 66.1 µg L^{-1} over the 15 batch filtrations. The average concentrations of TTHM for the filtrate were 44.6, 32.2, 21.0, 9.4, 13.4, and 9.9 µg L^{-1} with 0–3,750 mg L^{-1} PAC addition over the 15 batch filtrations, respectively. Thus, none of the filtrates exceeded the MCL for TTHM. However, the slope for the 'H.A.-G.W. + PAC 0' case is so steep that the TTHM concentration may exceed the MCL when the number of batches is higher than 16.

The TTHM concentrations for the lake water and humic acid-spiked lake water were 46.5 and 90.2 µg L^{-1}, respectively.

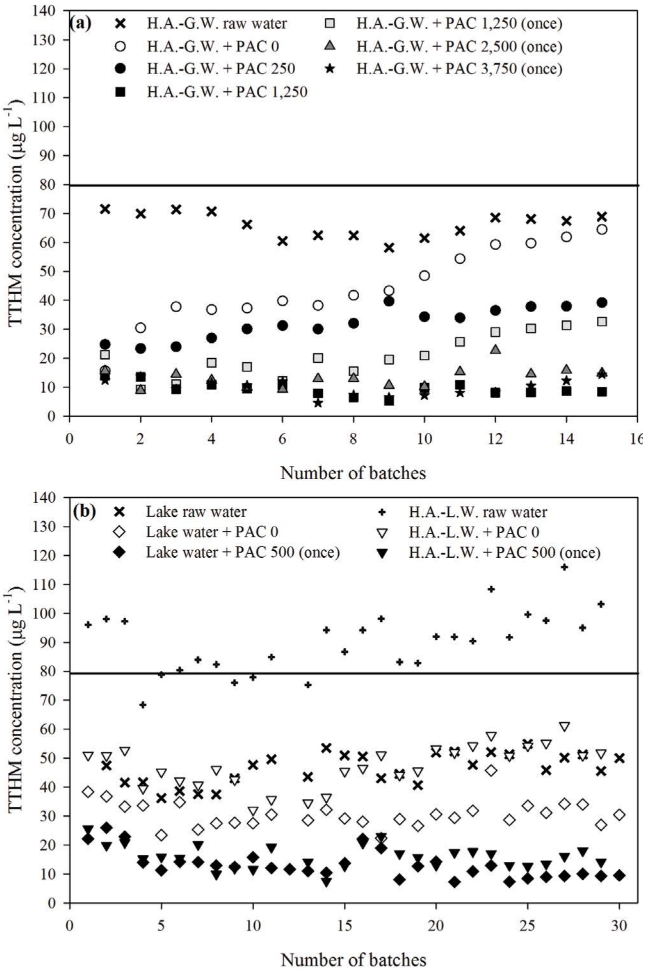


Fig. 8. Estimation of TTHM formation by chlorination of the filtrate from the GDM system with and without PAC addition for (a) the humic acid-spiked ground water and (b) the lake water and the humic acid-spiked lake water. The solid lines correspond to the maximum contaminant level for TTHM in the USEPA THM guidelines (80 µg L^{-1}).

The average TTHM concentrations for the filtrate for the lake water were 30.7 and 13.2 μg L^{-1} without and with 500 mg L^{-1} of PAC addition, respectively. Finally, those for the filtrate for the humic acid-spiked lake water were 47.3 and 16.1 μg L^{-1} without and with 500 mg L^{-1} PAC addition, respectively. Even though the TTHM concentrations were less than the MCL during the 30 batch filtrations, the values for the 'H.A.-L.W. + PAC 0′ case obviously increased after 12 batches. Without PAC addition, the TTHM concentration probably would increase over the MCL. In other words, the addition of adequate PAC in the GDM system is required to meet the TTHM guideline.

3.5. Other water quality indicators

The average turbidity and pH of the lake water were 23.1 NTU and 7.15, respectively. Filtrate turbidity and pH without PAC addition were 0.13 NTU and 7.09, respectively, and filtrate turbidity and pH with 500 mg L^{-1} of PAC addition to the lake water were 0.14 NTU and 6.53, respectively, without any addition of pH buffer solution. Both the filtrate turbidity and pH also satisfied the WHO guidelines for drinking water quality: below 5 NTU for turbidity and 6.5–9.5 for pH [28]. The GDM system with PAC addition will be an appropriate solution for natural water sources containing a significant amount of organic matter and will be further studied to investigate its performance and feasibility with various water sources.

4. Conclusions

NOM removal with an end-free GDM system combined with PAC was carried out for HWT using humic acid-spiked groundwater, lake water, and humic acid-spiked lake water as raw water sources. For the raw water with low NOM concentration, such as the lake water in this study, batch operation without the addition of PAC was preferable to prevent a significant decrease in permeability. For raw water with high NOM concentration, such as humic acid-spiked ground or lake water, the addition of PAC effectively reduced DOC concentrations and thus limited TTHM formation to levels below the regulatory limit. A high PAC concentration could reduce the permeability and sharply drop the pH of the filtrate. Therefore, PAC should be added to the raw water in an adequate amount to maintain a PAC concentration as low as possible but still satisfy DOC removal requirements. The GDM system could produce sufficient drinking, cooking, and personal hygiene water for a 5-person family. The end-free GDM system combined with PAC could thus be an applicable system for HWT in low- and middle-income countries.

Acknowledgements

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Supplementry Information

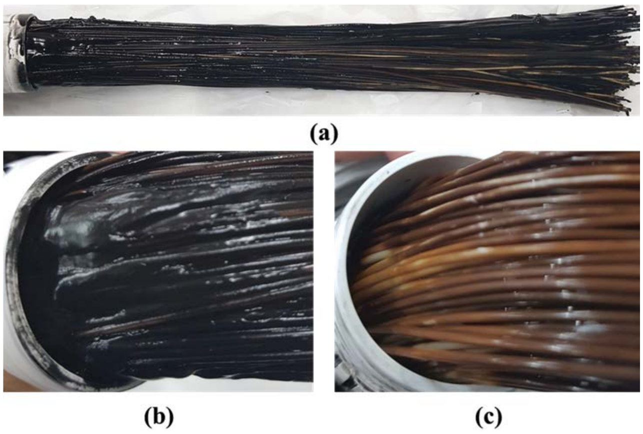

Fig. S1. (a) The whole GDM module and (b) its header part after 15 batches of operation using the humic acid-spiked ground water with 3,750 mg L^{-1} PAC, and (c) the header part after long-term cleaning following the 15th batch filtration.

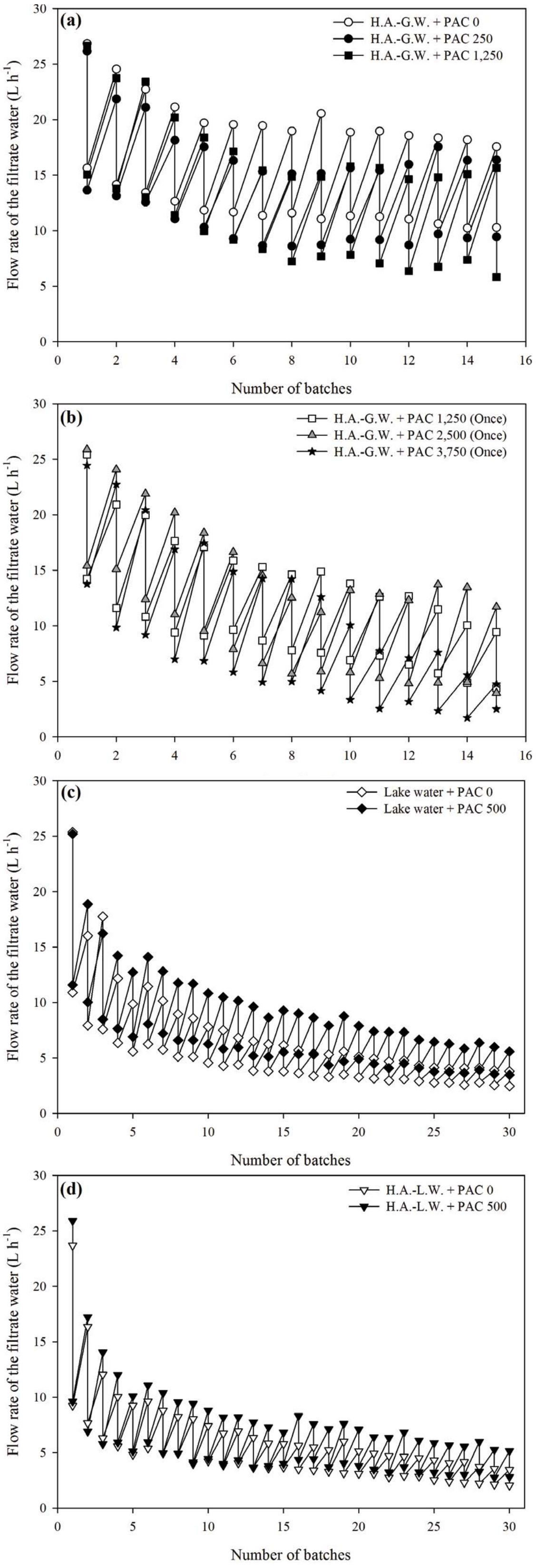

Fig. S2. Flow rate of the filtrate water for (a, b) humic acid-spiked groundwater, (c) lake water, and (d) humic acid-spiked lake water with and without PAC addition.

Table S1
Specifications of the hollow fiber membrane in the end-free GDM module

O.D./I.D.	1.21/0.71 mm
Effective area	0.36 m^2
Mean pore size	0.157 μm
Average pure water permeability	16.65 $L\ m^{-2}\ h^{-1}\ kPa^{-1}$
Membrane material	Polyvinylidene fluoride (PVDF)

Table S2
Specifications of the powdered activated carbon

Particle size	d5	min. 2.5 μm
	d50	min. 27 μm Max. 42 μm
	d95	Max. 125 μm
Methylene blue adsorption		31 $g\ mg^{-1}$
Internal surface area		1,000 $m^2\ g^{-1}$
Ash content		2 wt%
Density		295 $kg\ cm^{-3}$

* The d10, d50 and d95 are the intercepts for 10%, 50%, and 95% of the cumulative mass in the particle size distribution, respectively.