Comparison of biological activated carbon (BAC) and membrane bioreactor (MBR) for pollutants removal in drinking water treatment


ABSTRACT

Biological activated carbon (BAC) and membrane bioreactor (MBR) were systematically compared for the drinking water treatment from slightly polluted raw water under the same hydraulic retention time (HRT) of 0.5 h. MBR exhibited excellent turbidity removal capacity due to the separation of the membrane; while only 60% of influent turbidity was intercepted by BAC. Perfect nitrification was achieved by MBR with the 89% reduction in ammonia; by contrast, BAC only eliminated a moderate amount of influent ammonia (by 54.5%). However, BAC was able to remove more dissolved organic matter (DOM, especially for organic molecules of 3,000 ~ 500 Daltons) and corresponding disinfection by-product formation potential (DBPFP) in raw water than MBR. Unfortunately, particulate organic matter (POM) was detected in the BAC effluent. On the other hand, BAC and MBR displayed essentially the same capacity for biodegradable organic matter (BOM) removal. Fractionation of DOM showed that the removal efficiencies of hydrophobic neutrals, hydrophobic acids, weakly hydrophobic acids and hydrophilic organic matter through BAC treatment were 11.7%, 8.8%, 13.9% and 4.8% higher than that through MBR, while MBR achieved 13.8% higher hydrophobic bases removal as compared with BAC.

Key words | biological activated carbon (BAC), drinking water treatment, membrane bioreactor (MBR), pollutants removal

NOMENCLATURE

AOC | assimilable organic carbon
BAC | biological activated carbon
BDOC | biodegradable dissolved organic carbon
BET | Brunauer-Emett-Teller
BOM | biodegradable organic matter
DBPFP | disinfection by-products formation potential
DO | dissolved oxygen
DOC | dissolved organic carbon
DOM | dissolved organic matter
GAC | granular activated carbon
HAAFP | haloacetic acids formation potential
HiM | hydrophilic organic matter
HoA | hydrophobic organic acids
HoB | hydrophobic organic bases
HoN | hydrophobic organic neutrals
HRT | hydraulic retention time
MBR | membrane bioreactor
MF | microfiltration
MW | molecular weight
NF | nanofiltration
OUR | oxygen uptake rate
PAC | powdered activated carbon
PEG | polyethylene glycols
POM | particulate organic matter
PVC | polyvinyl chloride
SEC | size exclusion chromatography
SRT | sludge retention time
THMFP | trihalomethanes formation potential
TOC | total organic carbon

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INTRODUCTION

Nearly 50% of surface water supplies in China had been contaminated due to the discharge of domestic and industrial wastewater without sufficient treatment, with ammonia and organics as the main pollutants. Organic matter in source water adversely affects drinking water treatment from many aspects. Apart from the problems of color, taste and odour, organic matter can result in the more difficult destabilisation of colloids, the formation of disinfection by-products, and the bacterial regrowth in distribution systems (Murray & Parsons 2004; Huang et al. 2008).

Biological activated carbon (BAC) process has been widely studied and applied in China for the production of drinking water with high quality (Xu et al. 2007). BAC is able to remove biodegradable organic matter (BOM) efficiently, which is the most undesirable fraction of organic matter in water. An additional benefit of BAC is the substantial reduction of trihalomethanes formation potential (THMFP) in the treated water. BAC filtration provides simultaneous adsorption of refractory organic matter and biodegradation of BOM in a single reactor (Seredyn’ska-Sobecka et al. 2006). Furthermore, in addition to the biodegradation of organic compounds dissolved in water, the biofilms on the external surfaces and macropores of granular activated carbon (GAC) are also capable of metabolising the organic matter previously adsorbed by the carbon (Scholz & Martin 1997). With the bioregeneration, less thermal regeneration of the activated carbon would be required, which results in lower energy consumption and operating costs.

Membrane filtration processes, such as nanofiltration (NF), ultrafiltration (UF) and microfiltration (MF), play very important roles in drinking water purification in recent years due to ever-increasing standards for drinking water quality, improvement of membrane materials and decrease of costs. UF and MF are effective for separating particles, suspended solids and microorganisms, and have been considered as attractive options to solve the issues related to pathogenic bacteria and protozoan oocysts (Choo et al. 2005; Humbert et al. 2007). However, both of them are usually not effective in the removal of organic substances, especially those with low molecular weight (MW) (Tomaszewska & Mozia 2002; Choi & Dempsey 2004).

Membrane bioreactor (MBR) technology has gained particular interest and been applied to full-scale municipal wastewater treatment up to now (Lyko et al. 2007). MBR enables unit processes of membrane filtration and biodegradation to be accomplished in one single reactor, and offers several advantages over conventional treatment processes, such as reduced footprint, high biomass concentration and excellent finished water quality. MBRs and their hybrid processes with pre-ozonation or powdered activated carbon (PAC) have also been studied for the drinking water treatment (Williams & Pirbazari 2007). Unfortunately, the results about the effectiveness of MBR for organic removal seem to be controversial. Li & Chu (2003) found that 60% of total organic carbon (TOC) was removed in their submerged MBR; whereas Sagbo et al. (2008) only achieved satisfactory treatment efficiency when combined with PAC.

As two kinds of advanced water treatment methods, BAC and MBR have many properties in common, such as physical filtration of particles and biodegradation of organic matter and ammonia. However, it is not clear yet which one is more efficient for the production of drinking water. In this paper, the effectiveness of BAC and MBR for the treatment of slightly polluted raw water was systematically compared. The advantages and disadvantages of both processes were also analysed, which might provide some reference data for water works in selecting the suitable advanced treatment processes.

MATERIALS AND METHODS

Experimental set-up

Mini-pilot-scale BAC and MBR were constructed for this investigation (Figure 1). The BAC filter consisted of a 60 mm inner-diameter Plexiglas pipe, with a height of 2.0 m. Coal-based GAC (Ø1.5 mm × 3.0 mm, ZJ-15, Ningxi, China) was employed in the BAC; the bed depth was 1.0 m. The GAC had a BET surface area of 920 m² g⁻¹, with
the iodine number of 860 mg g⁻¹. The MBR had an activated sludge reactor with an effective volume of 2.0 L, and the membrane module was directly immersed inside it. A hollow fibre UF membrane module (Litree China) was employed, which was made of polyvinyl chloride (PVC), with nominal pore size of 0.01 μm and total membrane area of 0.4 m² (corresponding to the specific membrane area per reactor volume of 200 m² m⁻³). Both BAC and MBR were fed with raw water through a constant level tank. The BAC effluent was adjusted by using a flowmeter, while MBR effluent was drawn directly from the membrane module with a suction pump. Continuous aeration was provided at the bottom of the MBR to supply oxygen for activated sludge and generate strong turbulence for membrane cleaning, and on the top of GAC layer to saturate influent water of BAC with dissolved oxygen (DO).

**Operation conditions**

During the experimental period, the flux of the UF membrane in the MBR was set at a constant value of 10 L m⁻² h⁻¹. The detailed information on the membrane fouling could be found in a previous paper by Tian et al. (2009). Both BAC and MBR were operated with the same hydraulic retention time (HRT) of 0.5 h. BAC was backwashed once a week. Except for membrane cleaning, no sludge discharge was conducted for the MBR during the experiments, which corresponded to a sludge retention time (SRT) of more than 80 days. The volumetric ratio of air and influent water was kept at 20:1 in the MBR, while the ratio was approximately 5:1 for the BAC to saturate the influent with DO. The suction pump of MBR was controlled by a timer based on a sequence of 8 min on and 2 min off in each cycle. A predetermined amount of PAC (1.5 g L⁻¹) was added into the bioreactor of MBR at the beginning of start-up to support bacterial growth; while there was no further PAC addition during the following experiments. Thus, the MBR used in this investigation could be regarded as a traditional one. The PAC (coal-based, Xinhua, Shanxi, China) had a particle size smaller than 200-mesh (95%), with a BET surface area of 1,030 m² g⁻¹ and iodine number of 950 mg g⁻¹.

Before this investigation was performed, the BAC and MBR had been operated for more than 3 months feeding with the same raw water, and the stable state had been achieved. Thus, the adsorption capacity of the GAC in the BAC and PAC in the MBR was believed saturated, and microorganisms had colonized on the carbon surface. However, the microorganisms could metabolise both the organic matter in influent water and that previously adsorbed on the carbon (Seredyn’ska-Sobecka et al. 2006), thus recovering the adsorption capacity of the activated carbon to some extent. Therefore, the balance between biodegradation and adsorption was established. The information on the biomass concentration in the MBR could be found in a previous paper by Tian et al. (2009).

**Raw water**

The polluted raw water used in the study was simulated by mixing domestic wastewater into local tap water (Harbin, China) at a ratio of 1:30. Meanwhile, 1 mg L⁻¹ of humic acid was also added to the simulated raw water. The ammonia concentration of the raw water was maintained at 3 ~ 4 mg L⁻¹ by dosing NH₄Cl (analytical grade). During the experiments, the raw water had average temperature of 25.2 ± 2.5°C, pH 7.17 ± 0.16.
Analytical methods

Water quality analysis was conducted following the standard methods. COD$_{Mn}$ was analysed by the potassium permanganate oxidation method. NH$_3$-N concentration was determined by the colorimetric method using a spectrometer (UV754, Cany, China); UV$_{254}$ was also determined by using the spectrometer. TOC and dissolved organic carbon (DOC, pre-filtration through a 0.45 μm membrane) were measured by the TOC analyser (TOC-VCPH, Shimadzu, Japan). Turbidity was monitored by a turbidimeter (TURBO550, WTW, Germany). DO concentration was measured by the DO electrometer (pH/Oxi 340i, WTW, Germany) with a probe (Cellox®325).

THMFP and halocarboxylic acids formation potential (HAAFP) were determined following US EPA Method 551.1 and 552.2, except that the incubation time after chlorine dosing was shortened from 7 to 3 days. The THMFP presented was the sum of CHCl$_3$, CHBrCl$_2$, CHBr$_2$Cl and CHBr$_3$; the HAAFP was the sum of CH$_2$ClCOOH, CH$_2$BrCOOH, CHCl$_2$COOH, CCl$_3$COOH, CHBrClCOOH, CBrCl$_2$COOH, CHBr$_2$COOH, CBr$_2$ClCOOH, and CBr$_3$COOH.

Biodegradable dissolved organic carbon (BDOC) was measured with the method established by Servais et al. (1987) with some modification: the incubation was conducted in the dark at 22°C for 3 days in this study. The BDOC was defined as the difference between original DOC and final DOC after incubation. Assimilable organic carbon (AOC) measurement was carried out using a method modified by Liu et al. (2002).

Size exclusion chromatography (SEC) was used to determine the apparent MW distribution of UV-active substances in the water samples. The measurement was carried out by using a high performance liquid chromatograph (LC-10A, Shimadzu, Japan) with a UV detector (SPD-10A), using a Waters Ultrahydrogel 250 column (7.8 × 300 mm). To suppress the nonsize exclusion effects (electrostatic repulsion and specific adsorption), the mobile phase comprised 0.1 M NaCl, 0.002 M KH$_2$PO$_4$, and 0.002 M Na$_2$HPO$_4$, and was buffered to pH 6.8 (Perminova et al. 2005). The flow rate was set at 0.4 mL min$^{-1}$. Polyethylene glycols (PEG) were employed to calibrate the relationship between the MW and the retention time. Injection volume of water samples was 25 μL.

Dissolved organic matter (DOM) was fractionated into five fractions by using Amberlite XAD-8 and XAD-4 resins according to Qiao et al. (2006): hydrophobic bases (HoB); hydrophobic neutral fraction (HoN); hydrophobic acids (HoA); weakly hydrophobic acids (WHOA); hydrophilic matter (HiM). DOM fractions were subjected to DOC analyses. The resins were cleaned and conditioned as described by Leenheer (1981) and Imai et al. (2001).

RESULTS AND DISCUSSION

Comparison of turbidity removal by BAC and MBR

Figure 2 shows the turbidity removal performance of BAC and MBR during the experiments. It could be seen that influent turbidity was decreased from 1.88 ± 0.62 NTU to 0.70 ± 0.16 NTU in the BAC, with a removal efficiency of nearly 60%, while more than 96% of reduction was achieved by the MBR, and the turbidity in the effluent was lowered to the level of 0.07 ± 0.02 NTU. MBR exhibited much higher turbidity removal capacity due to the separation of UF membrane.

Comparison of NH$_3$-N removal by BAC and MBR

In distribution systems, 0.25 mg L$^{-1}$ of ammonia is sufficient to cause the growth of nitrifying bacteria, and thus lead to
bacteriological deterioration of drinking water quality (Csanady 1992). As shown in Figure 3a, the raw water had average NH$_3$-N concentration of 3.49 ± 0.49 mg L$^{-1}$. BAC treatment decreased influent NH$_3$-N to 1.63 ± 0.63 mg L$^{-1}$, with the removal efficiency of 54.5 ± 14.5%. By contrast, MBR managed to decrease more than 89% of influent NH$_3$-N, with the effluent concentration as low as 0.38 mg L$^{-1}$ on average.

To determine the biological activity of nitrifying bacteria in the BAC and MBR, the oxygen uptake rate (OUR) was measured in the experiments. During the OUR measurements, 6.0 g of GAC in the BAC and 50 mL of mixed liquor in the MBR were taken out and transferred to conical flasks (effective volume 1.0 L). After that, the conical flasks were filled up with the pre-oxygenated NH$_3$-N solution (4.0 mg L$^{-1}$, at the same level as the raw water). Then, the DO probes were immediately inserted in the solution and the flasks were completely sealed. The solution in the flasks was mixed with a magnetic stirrer at 150 rpm. The change of DO concentrations was recorded in real time, as shown in Figure 3b. It could be seen that, although DO concentrations in the two flasks decreased to almost the same level after 200 min of consumption (1.34 mg L$^{-1}$ for BAC vs. 1.41 mg L$^{-1}$ for MBR), it was obvious the OUR by the nitrifying bacteria in BAC was much faster than that in the MBR. According to the DO changes during the first 30 min (linear segment), the OUR of the nitrifying bacteria in the BAC and MBR could be calculated as 15.9 μg O$_2$ g$^{-1}$ GAC min$^{-1}$ and 1.05 μg O$_2$ mL$^{-1}$ mixed liquor min$^{-1}$, respectively.

It could be figured out that approximately 15 mg L$^{-1}$ DO would be required when complete nitrification is considered in this study. However, aeration was provided on the top of the GAC layer in the BAC, which could only saturate the influent with DO (7 ~ 8 mg L$^{-1}$). So it is reasonable to infer that the DO concentration restricted the bio-oxidation of NH$_3$-N in BAC. On the other hand, the configurations of MBR solved this problem, since aeration was provided at the bottom of the MBR continuously, which resulted in the saturation of mixed liquor with DO all the time. As a result, nearly complete nitrification was achieved by the MBR.

**Comparison of organic matter removal by BAC and MBR**

**DOM removal**

Total organic matter in water might be classified into particulate fraction and dissolved fraction. Particulate organic matter (POM) could be easily eliminated even in conventional treatment processes (coagulation, sedimentation and sand-filtration), while DOM is one of the major concerns due to the potential hazards to health and difficulty to be removed. From Figure 4a and b, it could be seen that the raw water had average DOC and UV$_{254}$ concentrations of 5.398 ± 0.517 mg L$^{-1}$ and 0.086 ± 0.008 cm$^{-1}$, respectively. BAC decreased influent DOC by 26.3% on average, which was 4.8% higher than the
21.5% removal achieved by the parallel MBR. As for UV254, the removal efficiency obtained by BAC was 29.9%, which was nearly one-fold higher than that by MBR (15.1%).

GAC layer in the BAC possessed substantial adsorption capacity for DOM in raw water, especially for UV-active substances. The high concentration of organic compounds adsorbed on the activated carbon could facilitate the growth of microorganisms on the GAC surface. The biofilms worked to regenerate the granular activated carbon in turn. Thus, adsorption and biodegradation took place simultaneously in the BAC (Seredyn’ska-Sobecka et al. 2006). On the other hand, there was only 1.5 g L\(^{-1}\) of PAC in the bioreactor of MBR; the activated carbon content was significantly lower than that in BAC, which pointed to the fact that biodegradation rather than adsorption played the dominant role in the DOM removal in MBR. As a result, BAC exhibited higher removal efficiency for DOM than MBR throughout this investigation.

**Total organic matter removal**

TOC and COD\(_{Mn}\), as the surrogate parameters representing the content of total organic matter, have been widely used in the field of drinking water treatment. There was 5.952 ± 0.711 mg L\(^{-1}\) of TOC and 4.79 ± 0.56 mg L\(^{-1}\) of COD\(_{Mn}\) in the raw water during the study, respectively. It could be observed from Figure 5a that BAC and MBR obtained essentially the same removal efficiencies for TOC...
(27.8% by BAC vs. 28.6% by MBR). However, 33.5% of influent CODMn was decreased by MBR treatment, which corresponded to a 10.7% enhancement as compared with the 22.8% removal obtained by BAC (Figure 5b). There was still POM contained in the BAC effluent, such as crumbs of the biofilms on the carbon surface, with the concentration averaging 0.309 mg L\(^{-1}\) in the experiments. However, the UF membrane in the MBR was able to intercept particles and colloids completely, with the effluent free of POM. This might be the reason that MBR achieved higher removal for total organic matter in comparison with BAC.

**Disinfection by-products formation potential (DBPFP) removal**

As shown in Figure 6, there were 249.1 ± 18.7 μg L\(^{-1}\) of THMFP and 168.5 ± 10.9 μg L\(^{-1}\) of HAAFP contained in the raw water on average, respectively. BAC and MBR removed essentially the same amount of influent THMFP, with the removal efficiencies of 35.8 ± 4.3% and 34.1 ± 8.5%, respectively. On the other hand, only 24.7 ± 3.9% of influent HAAFP was eliminated by MBR, while the removal efficiency through BAC treatment reached 36.9 ± 4.8%, which was 12.2% higher than that achieved by MBR.

**BOM removal**

In order to further examine the removal of organic matter that related to the bacterial regrowth and biological stability in the distribution system, the performance of BAC and MBR for BDOC and AOC elimination was also studied and compared. As shown in Figure 7, BAC decreased BDOC from 0.576 ± 0.214 mg L\(^{-1}\) in the raw water to 0.226 ± 0.089 mg L\(^{-1}\) in the effluent (removed by 57.2 ± 14.3%); while the slightly higher concentration of 0.259 ± 0.114 mg L\(^{-1}\) was observed in the MBR effluent, corresponding to the reduction of 51.7 ± 12.9%. On the other hand, the raw water had an average concentration of 771.3 ± 145.9 μg L\(^{-1}\) for AOC. BAC and MBR were shown to decrease influent AOC by 49.3 ± 6.1% and 54.9 ± 7.5%, respectively. Thus, it might be concluded that BAC and MBR had essentially the same capacity for removing BDOC and AOC from the raw water.

**MW distribution and fractionation of DOM removed by BAC and MBR**

The apparent MW distributions of DOM in the raw water, as well as the effluents of BAC and MBR, were also measured using SEC method (Figure 8a). It could be seen that DOM with the MW range of 7,000 ~ 300 Daltons predominated in the raw water. The intensity of the absorbance peak between 4,000 and 300 Daltons was decreased after both BAC and MBR treatment. However, the BAC process was able to decrease more organic molecules of 3,000 ~ 500 Daltons when compared with MBR.

Results of the fractionation of DOM in the raw water as well as the BAC and MBR effluents were illustrated in Figure 8b. The raw water contained HoB, HoN, HoA, WHoA, and HiM in the concentrations of 0.681 mg L\(^{-1}\), 0.829 mg L\(^{-1}\), 1.066 mg L\(^{-1}\), 0.488 mg L\(^{-1}\) and 2.276 mg L\(^{-1}\) respectively. The performance of BAC and MBR for BDOC and AOC elimination was also studied and compared. As shown in Figure 7, BAC decreased BDOC from 0.576 ± 0.214 mg L\(^{-1}\) in the raw water to 0.226 ± 0.089 mg L\(^{-1}\) in the effluent (removed by 57.2 ± 14.3%); while the slightly higher concentration of 0.259 ± 0.114 mg L\(^{-1}\) was observed in the MBR effluent, corresponding to the reduction of 51.7 ± 12.9%. On the other hand, the raw water had an average concentration of 771.3 ± 145.9 μg L\(^{-1}\) for AOC. BAC and MBR were shown to decrease influent AOC by 49.3 ± 6.1% and 54.9 ± 7.5%, respectively. Thus, it might be concluded that BAC and MBR had essentially the same capacity for removing BDOC and AOC from the raw water.

**Figure 6** | Comparison of THMFP and HAAFP removal by BAC and MBR.

**Figure 7** | Comparison of BDOC and AOC removal by BAC and MBR.
on average, respectively. BAC decreased these five fractions by 16.4%, 36.3%, 24.7%, 22.2%, and 27.6%, respectively; while the removal efficiencies through MBR treatment were shown to be 30.2%, 24.6%, 15.9%, 8.3%, and 22.8%, respectively. It could be seen that BAC could remove much more influent HoN, HoA, WHoA, and HiM as compared with MBR (11.7%, 8.8%, 13.9%, and 4.8% higher, respectively). Only for HoB, the removal efficiency achieved by BAC was 13.8% lower than that by MBR.

CONCLUSIONS

In this investigation, BAC and MBR were systematically compared for the drinking water treatment from slightly polluted surface water with the same HRT of 0.5 h. The following conclusions could be drawn:

(1) MBR exhibited excellent turbidity removal capacity due to the separation of the membrane; while only 60% of influent turbidity was removed by BAC.

(2) BAC removed a moderate amount of NH$_3$-N from the raw water (by 54.5%). By contrast, MBR was highly efficient for reducing influent NH$_3$-N (89%).

(3) BAC was able to remove more DOM in raw water than MBR due to simultaneous adsorption and biodegradation; however, POM was detected in the effluent. As a result, the removal efficiency of total organic matter by BAC was lower than that by MBR.

BAC and MBR exhibited essentially the same capacity for BOM removal.

(4) DOM with the MW range of 4,000 – 300 Daltons was reduced by both BAC and MBR; while BAC was more effective for the elimination of organic molecules of 3,000 – 500 Daltons.

(5) Fractionation of DOM showed that the removal efficiencies of HoN, HoA, WHoA, and HiM through BAC treatment were 11.7%, 8.8%, 13.9%, and 4.8% higher than that through MBR; while MBR achieved 13.8% higher of HoB removal than BAC.

Based on the conclusions shown above, it might be recommended that if the raw water has high content of ammonia and/or POM the MBR process should be selected; while if there is a large amount of DOM, especially hydrophobic DOM in the raw water, the BAC should be preferably considered.

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