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Effects of preadsorption by carbon black on membrane filtration of natural organic matter

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ABSTRACT

This study aimed to assess the performance of two carbonaceous adsorbents, i.e. self-dispersible carbon black (CB) particles (130 nm) and powdered activated carbon (PAC; 151 μm), in the hybrid treatment with microfiltration or ultrafiltration. It was revealed that, although the dissolved organic carbon (DOC) removal by CB was less than that by PAC, addition of CB prior to the membrane filtration significantly reduced membrane fouling, whereas PAC addition brought about a severe membrane fouling. The difference between these two adsorbents was explained by the dominance of aromatic organic matter in lake water, selective adsorption of organics by the adsorbents, and a change of the cake structure of the adsorbents during the membrane filtration.

Keywords: Activated carbon; Adsorption; Carbon black; Fouling; Membrane filtration; Natural organic matter

1. Introduction

The use of low pressure membrane filtration process, including microfiltration (MF) and ultrafiltration (UF), is prone to severe fouling by natural organic matter (NOM) and not very effective in removal of organic micropollutants. Either preadsorption by powdered activated carbon (PAC) [1] or simultaneous organic adsorption using a high dose (≈20 g/L) of PAC [2] has been employed to improve the water quality and reduce membrane fouling. In several cases, PAC exacerbated membrane fouling in filtration of humic acid solution [1,3] or natural water [4–6]. The increased fouling by PAC was described to be caused by the combined effect between PAC and unadsorbed NOM [4], of which molecular weight (MW) was lower than 300 Da or larger than 17,000 Da [1]. Thus, new adsorbents that can reduce membrane fouling are being explored.

Carbon black (CB) nanoparticles have been widely used in commercial products, e.g. pigments, rubber and plastic additives. Consequently, CB is disposed of after being used as a waste. Alternatively, CB has a potential to be used as an adsorbent since it can bind a substantial amount of contaminants by making use of its large specific surface area, but it has not yet been evaluated in water treatment process employing low pressure membrane filtration. Thus, this study aimed to investigate the effects of preadsorption by CB in comparison with PAC on membrane fouling in filtration of surface water containing a substantial amount of NOM.

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2. Materials and methods

2.1. Source water, adsorbents, and adsorption test

Water was collected from Lake Mälaren (Stockholm, Sweden) and filtered through membranes with a 0.45 μm nominal pore size. The filtered water thus obtained had a dissolved organic carbon (DOC) concentration of 8.2 mg/L, UV_{254} absorbance of 0.22 cm^{-1} and pH 8.1. Calcium and magnesium concentrations of 24.1 mg/L (0.6 mM) and 4.5 mg/L (0.19 mM), respectively, were sufficient for promoting rapid aggregation of CB particles [7]. Hydrophobic acids accounted for 82% of total DOC and 83% of total DOC was the organics having MW of 30–0.5 kDa while macromolecular organics (MW $\approx$ 100 kDa) contributed only to 7% of the total DOC. Self-dispersible CB nanoparticles (Aquablack-001; Tokai Carbon Co. Ltd., Japan) and PAC (151 μm; Shirasagi S-10, Japan Environment Chemicals Ltd., Japan) were evaluated in this study. The volumetric mean size of CB was determined as 130 nm by the dynamic light scattering method (Nanotrac, Nikkiso Co. Ltd., Japan). A trace CB concentration (0–10 mg/L) was determined by the multiplying factor of 13.6 (mg/L) per unit UV/Vis absorbance (cm^{-1}) at 400 nm.

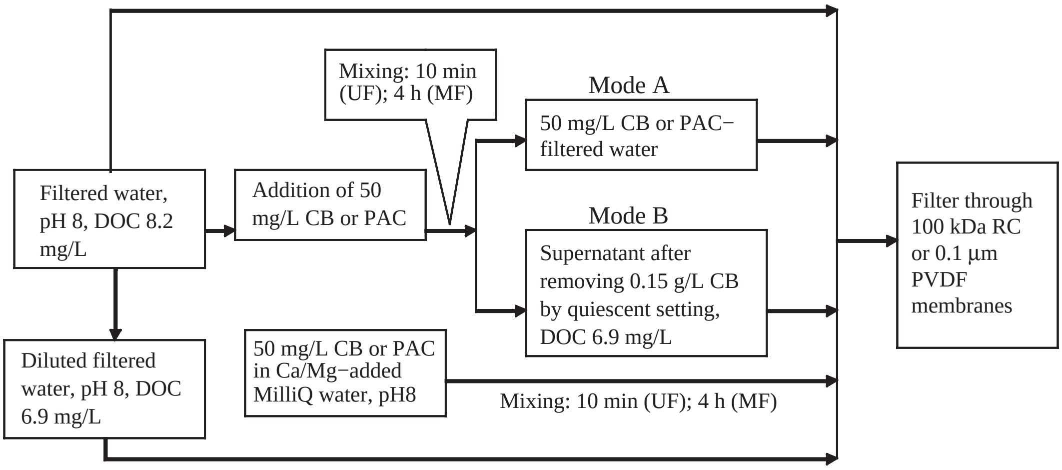
The adsorption tests employed a conventional jar test apparatus with 0.5 L glass beakers. A predetermined amount of CB or PAC was added into each 0.3 L of filtered water and mixed at rates of 200 rpm for 30 min and 100 rpm for 90 min, respectively. CB or PAC was removed by filtering water sample through filters with a 0.1 μm nominal pore size.

2.2. Filtration experiments

Membrane filtration was performed in a dead end mode with 100 kDa regenerated cellulose (PLHK, Millipore) membrane (UF) or 0.1 μm PVDF (Durapore) membrane (MF) using a 50 mL unstirred cell. The pressure was maintained constant at 100 kPa for UF and 43 kPa for MF. The filtration protocol is shown in Fig. 1. Preadsorption step was conducted in a jar test apparatus with 50 mg/L of CB or PAC. Filtered water/adsorbent slurry was mixed at a rate of 200 rpm for 2.5 min and filtered by 100 kDa UF filters within 10 min. Mixing was carried out for 4 h before the MF experiments to ensure CB aggregate size that is great enough to be completely rejected by membrane. The feed waters after adsorption by CB were prepared in two ways: CB dispersed in filtered water (Mode A) or supernatant of CB dispersed in filtered water (4 h after settling; Mode B). Filtration of diluted filtered water having the same DOC concentration of 6.9 mg/L as the supernatant (Mode B) was also conducted.

2.3. Fouling resistance

Since CB or PAC might aggravate filtration resistance, fouling resistance (R_f) of organics was assessed separately from the resistance caused by CB or PAC [6]. Based on the resistance-in-series model, the total filtration resistance (R_T) can be expressed as a sum of resistances of a virgin membrane (R_m), the adsorbent material (R_{ads}), and organic foulants (R_f) as shown in Eq. (1). The term "R_f" also included a combined fouling of adsorbent and NOM.



Filtered water: 0.45 μm prefiltered water obtained from Lake Mälaren (Sweden)

Fig. 1. Schematic filtration protocol of fouling assessment for UF and MF.

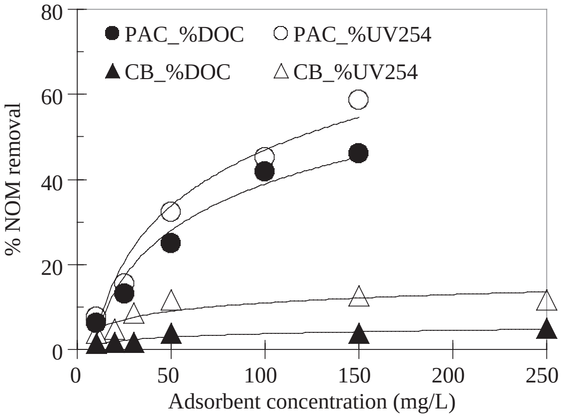


Fig. 2. Removals of NOM by CB or PAC in batch adsorption tests. Initial DOC concentration of 8.2 mg/L, $UV_{254} = 0.22$ cm^{-1}.

$$\frac{\Delta P}{\mu J} = R_T = R_m + R_{\text{ads}} + R_f \tag{1}$$

In each batch run, R_{ads} was obtained by Eq. (2),

$$R_{\text{ads}} = \frac{\alpha_{\text{ads}} C_{\text{ads}} V}{A} \tag{2}$$

where α_{ads} (m/g) is the specific cake resistance, A the effective membrane surface area (13.4 cm^2), V cumulative filtered volume, and C_{ads} is the bulk concentration of CB or PAC. The specific cake resistance was obtained from the slope of plotting (t/V) versus (V/A^2) [8] of the filtration experiments using CB or PAC dispersed in the Ca/Mg added MilliQ water, which contained 24 mg/L Ca^{2+} and 4.5 mg/L Mg^{2+} ions. The fouling resistance (R_f) was then calculated from Eq. (1) by subtracting R_m and R_{ads} from R_T.

3. Results and discussion

3.1. Adsorption test

PAC exhibited a significantly higher NOM removal than CB as seen in Fig. 2. The NOM removal rate was greatly enhanced by increasing the dose of PAC. By contrast, NOM removal by CB appeared nearly constant despite the increasing dose from 50 to 250 mg/L. This might suggest that only a portion of NOM can be adsorbed into aggregates of CB particles. As revealed by our earlier publication [9], macromolecular organics were incorporated into the CB aggregates. Thus, a 50 mg/L CB or PAC was used in the adsorption/membrane filtration experiments. It should be noted that, at a CB dose of 50 mg/L, DOC removal of 4% was considerably lower than UV_{254} removal of 12% as shown in Fig. 2. However, it was found later that DOC removal was higher than UV_{254} rejection in the CB/UF (Fig. 6).

3.2. Fouling resistance (R_f)

Filtration resistances in filtration of CB or PAC suspension (R_{ads}) in the Ca/Mg added MilliQ are shown in Fig. 3a. As can be seen, CB particles contributed to the filtration resistance. In contrast, PAC macroparticles did not cause membrane fouling since they formed a highly permeable, porous layer [1]. To compare the effects of organic removal by CB or PAC on membrane fouling, the fouling resistance (R_f), which excluded R_{ads} (Eq. (1)), was presented in Fig. 3b. It should be noted that the fouling resistance (R_f) shown in Fig. 3b is one order of magnitude greater than the adsorbent resistance (R_{ads}) shown in Fig. 3a. The fouling resistance (R_f) was in the order of FilWat + PAC >> Filtered water (FilWat) > FilWat + CB as shown in Fig. 3b. Though CB

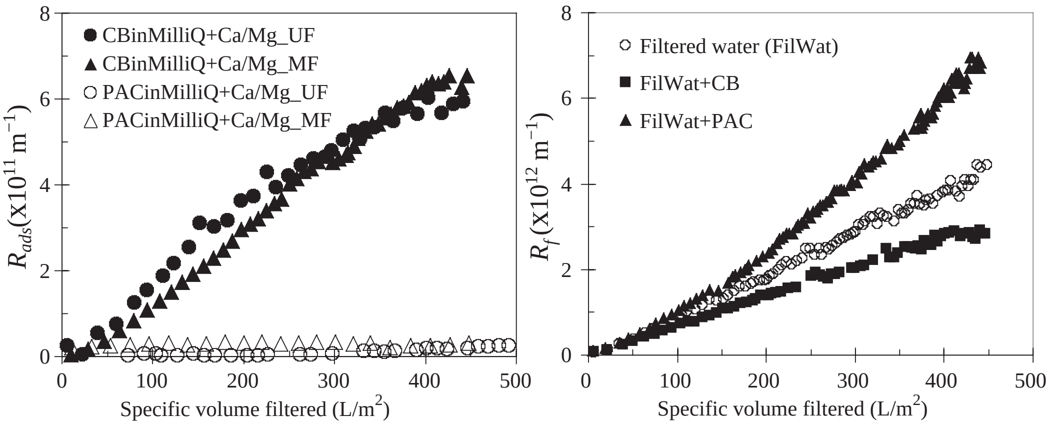


Fig. 3. (a) Filtration resistance (R_{ads}) of 50 mg/L CB or PAC dispersed in Ca/Mg-laden MilliQ water. (b) Fouling resistance (R_f) in filtration of filtered waters without and with pretreatment by CB or PAC with UF membranes (Mode A).

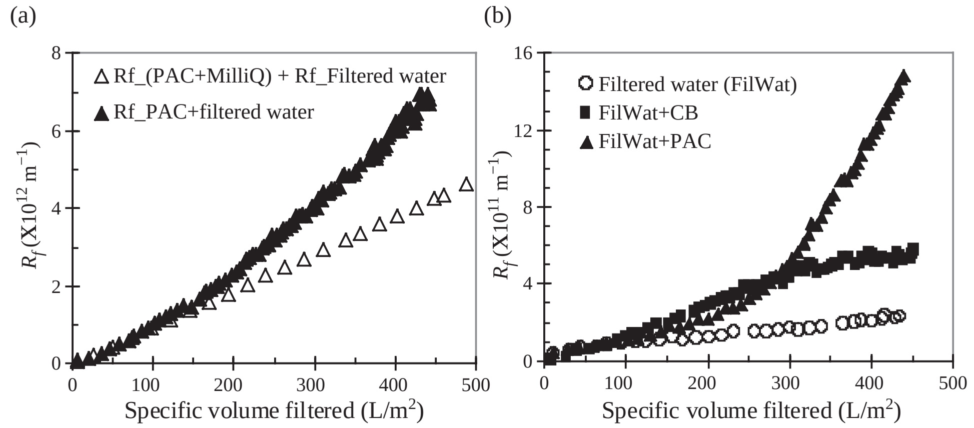


Fig. 4. (a) Fouling resistance (R_f) due to the combined fouling effect of PAC and NOM with UF membrane. (b) Fouling resistance (R_f) in filtration of filtered waters without and with pretreatment by CB or PAC with MF membrane (Mode A).

removed only 4% of total DOC (Fig. 2), preadsorption by CB considerably reduced R_f, which indicated that CB removed the NOM fraction that caused membrane fouling. Since the increasing rate of R_f was linear for FilWat + CB (Fig. 3b), the resistance after CB treatment simply correlated to a specific volume filtered and the amount of deposit. Contrarily, fouling resistance of UF membrane increased substantially after PAC preadsorption although PAC showed a much higher NOM removal than CB. PAC and NOM plausibly caused a combined fouling effect as seen from the significantly higher fouling resistance than the sum of the resistances by PAC alone and filtered water without PAC (Fig. 4a). It was described that the increased fouling was caused by NOM binding to PAC and/or to membrane surface, which built a low permeable layer on the membrane surface [4]. The fouling resistance over the course of filtration showed a concave curve, suggesting a change in cake structure due to association of organic micromolecules into cake voids. This explanation would be supported by steadily increasing NOM rejection as filtration proceeded (Fig. 6).

The fouling resistance (R_f) of MF (Fig. 4b) was lower than that of UF (Fig. 3b) by an order of magnitude. In Fig. 4b, the R_f was in the order of FilWat + PAC >> FilWat + CB > Filtered water (FilWat), indicating that the addition of CB or PAC exacerbated fouling of MF membrane. The R_f of FilWat + CB increased at a rate nearly twice as high as filtered water alone. After 450 L/m^2 was filtered, R_f of FilWat + PAC ($R_f \approx 1.5 \times 10^{12}$ m^{-1}) was almost three times larger than R_f of FilWat + CB ($R_f \approx 5.8 \times 10^{11}$ m^{-1}). The R_f for FilWat + PAC exhibited a concave-up slope, resulting in much higher fouling resistance than FilWat + CB. The concave-up curve with PAC dispersed in filtered water might be caused by pore blocking [10] and hindered back diffusion of macromolecular organics from the membrane surface [9], while a concave-down curve

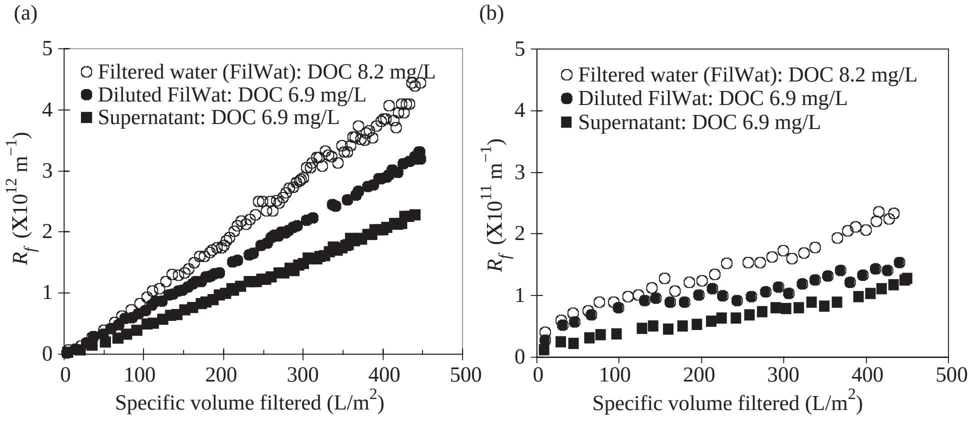


Fig. 5. Fouling resistance (R_f) of supernatant of CB dispersed in filtered water and diluted filtered water with (a) UF membranes and (b) MF membranes (Mode B).

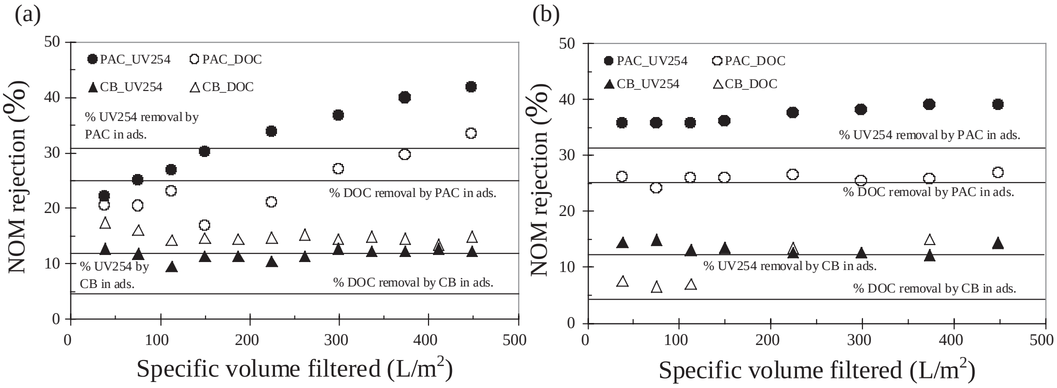


Fig. 6. NOM removals with (a) UF and (b) MF of filtered water treated by PAC or CB.

with CB dispersed in filtered water represented cake filtration [10].

To confirm if CB removed a fraction of NOM which caused membrane fouling, a further study was performed with supernatant of CB in filtered water and diluted filtered water (Mode B; Fig.5). These two feed solutions had the same DOC concentration. Potential fouling materials were present in the diluted water, while they might be excluded from the supernatant by CB adsorption. With UF membrane (Fig. 5a), the increasing rate of fouling resistance (slope of R_f versus specific volume filtered) reduced slightly by dilution and nearly halved by CB adsorption. With MF membrane (specific filtered volume <100 L/m^2), the increasing rate of R_f was almost the same for filtered water and the diluted water, while it was reduced considerably by CB (Fig. 5b). The results demonstrated that addition of CB resulted in the decrease in fouling resistance, which indicated that CB can adsorb NOM that cause membrane fouling.

3.3. *Organic removal*

NOM removals in filtrations of filtered water pretreated by CB or PAC are presented in Fig. 6. With UF membrane, organic adsorption by PAC (10 min) was not in equilibrium and thus the initial NOM removal was lower than that observed in the adsorption test (2 h). In Fig. 6a, NOM removal by PAC/UF steadily increased as filtration proceeded and UV$_{254}$ rejection increased at a higher rate than DOC removal. This result was in agreement with the intensified fouling by PAC due possibly to void filling of PAC cake by aromatic organics. Thus a change in cake structure was observed merely in UF. With MF membrane, NOM removal by PAC/MF was constant as filtration proceeded since organic adsorption was equilibrated prior to the filtration.

In contrast, NOM removal by CB/UF and CB/MF was nearly constant during the filtration as seen in Fig. 6a and b. This may be because 10 min was enough to reach equilibrium for CB adsorption, and the adsorbable organic matter was removed in 10 min. In CB/UF system, DOC removal was apparently higher than UV$_{254}$ rejection and considerably higher than the DOC removal observed in the adsorption test (Fig. 2). The result indicated that the total DOC rejection was attributed to the selective removal of hydrophilic organic matter by CB adsorption and the UF membrane.

4. Conclusion

PAC adsorbed a substantial amount of organic matter but increased fouling in both UF and MF. It was suggested by UV$_{254}$ removal of PAC/UF that aromatic organics were migrated and sorbed in cake voids, resulting in steady increases in NOM removal and fouling resistance throughout UF. In contrast, although CB particles caused filtration resistance, adsorption of the potential fouling fraction of NOM lowered the fouling resistance considerably. The hydrophilic surface of CB selectively adsorbed hydrophilic NOM, but hydrophobic NOM passed through the CB cake formed on UF membranes. In all feed waters, however, the filtration resistances were much lower for MF than UF, which suggested the potential advantage of using MF in combination with CB.

Acknowledgements

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Reference

[1] C.F. Lin, Y.J. Huang and O.J. Hao, Water Res., 33 (1999) 1252-1264.

[2] H. Oh, M. Yu, S. Takizawa and S. Ohgaki, Desalination, 192 (2006) 54-62.

[3] C.W. Li and Y.S. Chen, Desalination, 170 (2004) 59-67.

[4] M. Zhang, C. Li, M.M. Benjamin and Y. Chang, Environ. Sci. Technol., 37 (2003) 1663-1669.

[5] F. Saravia and F.H. Frimmel, Desalination, 224 (2008) 168-171.

[6] J. Kim, Z. Cai and M.M. Benjamin, J. Membr. Sci., 310 (2008) 356-364.

[7] J. Lohwacharin, S. Takizawa and S. Ohgaki. Sep. Sci. Technol., 43 (2008) 1852-1870.

[8] G. Foley, J. Membr. Sci., 274 (2006) 38-46.

[9] J. Lohwacharin, K. Oguma and S. Takizawa, Effects of selective adsorption of NOM by carbon black on variation of filtration resistances, Proc. IWA Conf. on Natural Organic Matter: from Source to Tap, Bath, UK, 2008, pp.151-157.

[10] [10] L.J. Zeman and A.L. Zydney, eds., Microfiltration and Ultrafiltration, Principles and Applications, Marcel Dekker, New York, 1996, pp. 397-446.