Membrane fouling propensity after adsorption as pretreatment in rainwater: a detailed organic characterisation

L. Sabina, B. Kus, H.-K. Shon and J. Kandasamy

ABSTRACT

Organic characterisation in rainwater was investigated in terms of dissolved organic carbon (DOC) and molecular weight distribution (MWD) after powdered activated carbon (PAC) adsorption. PAC adsorption was used as pretreatment to membrane filtration to reduce membrane fouling. The MW of organic matter in rainwater used in this study was in the range of 43,000 Da to 30 Da. Each peak of organic matter consisted of biopolymers (polysaccharides and proteins), humic and fulvic acids, building blocks, low MW acids (hydrolysates of humic substances), low MW neutrals and amphiphilics. Rainwater contained the majority of hydrophilic compounds up to 72%. PAC adsorption removed 33% of total DOC. The removal efficiencies of the hydrophobic and hydrophilic fractions after PAC adsorption were 50% and 27%, respectively. PAC adsorption was found to preferentially remove the hydrophobic fraction. The majority of the smaller MW of 1,100 Da, 820 Da, 550 Da, 90 Da and 30 Da was removed after PAC adsorption. The MFI values decreased from 1,436 s/L^2 to 147 s/L^2 after PAC adsorption. It was concluded that PAC adsorption can be used as a pretreatment to membrane filtration with rainwater.

Key words | flocculation, hydrophobic and hydrophilic fraction, membrane filtration, molecular weight size distribution, PAC adsorption, rainwater

L. Sabina
B. Kus
H.-K. Shon
J. Kandasamy (corresponding author)
Faculty of Engineering,
University of Technology,
Sydney, P.O. Box 123,
Broadway NSW 2007,
Australia
E-mail: *jaya.kandasamy@uts.edu.au*

INTRODUCTION

Rainwater is recognized as a valuable water resource that can be exploited to provide a sustainable water supply and augments potable water supply in urban areas. Rainwater contains contaminants including particles & microorganisms. Rainwater harvested from roofs can contain animal and bird faeces, mosses and lichens, windblown dust, particulates from urban pollution, pesticides, and inorganic ions from the sea (Ca, Mg, Na, K, Cl, SO_4), and dissolved gases (CO_2, NOx, SOx). High levels of pesticide are also found in rainwater.

Yoo *et al.* (2006) studied a reuse system using membrane process treating rainwater runoff from an urban parking area, which contained non-point pollutants. The rainwater reuse system consisted of a pre-filter, membrane and disinfection. Hollow fiber membrane having pore size of 0.4 μm made of polyvinyl di-fluoride (PVDF) was used in this system because of its stable flux and strength. The treated water met for all the parameters of the guideline values regulated by Korean standard for reclaimed water. Turbidity was less than 0.3 NTU in the final effluent. COD concentration decreased from 23.0 mg/L to 13.1 mg/L and BOD_5 decreased from 5.3 mg/L to 1.7 mg/L after treatment by pre-filter and membrane process. *E. coli* was completely removed by this system (Yoo *et al.* 2006).

Membrane technology is a successful technology in wastewater reuse which has can be used for treatment of rain water. However, membrane fouling has been a major obstacle. In this study, the objectives were (i) to characterise organic matter in rainwater in terms of dissolved organic

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carbon (DOC) and molecular weight distribution (MWD) of DOC, (ii) to investigate powered activated carbon (PAC) adsorption as pretreatment, and (iii) to evaluate membrane fouling index after PAC pretreatment.

EXPERIMENTAL METHODOLOGIES

Rainwater

The rainwater samples used in these experiments were collected from a 150 square meter Colorbond (steel) roof and guttering of a 7 year old residential house in Campbelltown, in the southern part of Sydney, Australia. The tank was installed 2 years ago using only PVC fittings. The tank has a total capacity of 2,500 litres with dimensions of 2 meters high and 0.6 meter wide. The catchment area of the roof has no noticeable leaves or debris in the guttering and does not have a first flush system installed before the runoff enters the tank. The outlet of the tank is located 90 millimeters from the base of the tank and passes through PVC fittings before entering a pump. The outlet of the pump also has PVC fittings that join into the brickwork of the house before exiting through a conventional outdoor tap.

The pH of the rainwater samples were an average of 5.2 at 21°C, and the conductivity was 24.8 μs/cm at 21°C.

XAD fractionation of rainwater

Organic fractions in rainwater can be classified as hydrophobic (HP) and hydrophilic (HP) fractions. XAD-8 resin was used for fractionating dissolved organics into HP fraction (XAD-8 adsorbable; mostly hydrophobic acids with some hydrophobic neutrals). The remaining fraction escaping the XAD-8 was the HL component. The resin in the column was washed in the following order; pure water, 0.1 N NaOH, pure water, 0.1 N HCl and pure water. After filtering all the samples, they were then acidified to pH 2 due to the reduction of HP interaction between feed and resins. The acidified samples passed through the resins at a low velocity (2 ml/min). The effluents which underwent the XAD-8 resin were taken as the HL fraction. The adsorbed HP on the XAD-8 was eluted with 0.1 N NaOH.

PAC adsorption

Adsorption with PAC was conducted using 1 L of rainwater. The PAC used in the experiments was washed with distilled water and dried in the oven at 103.5°C for 24 hours. They were kept in a desiccator before using in the adsorption experiments. The characteristics of PAC used are given in Table 1. PAC was stirred with mechanical stirrer at 100 rpm for 1 hour. The ambient temperature was 25°C.

Membrane fouling index

The membrane used in this study had a 0.45 μm pore size and 47 mm diameter (Milipore Ltd.). The dead-end cell experimental setup is shown in Figure 1. An applied pressure of up to 200 kpa was used. Rainwater, with and without pretreatment, was pumped to a flat sheet membrane module. Silt density index (SDI) and modified fouling index (MFI) were investigated.

Dissolved organic carbon (DOC)

DOC was measured using carbon analyser (TOC-V, Shimadzu, Japan). All samples were filtered through 0.45 μm membrane prior to the DOC measurement.

Molecular weight distribution (MWD)

High pressure size exclusion chromatography (HPSEC, Shimadzu Corp., Japan) with a SEC column (Protein-pak 125, Waters Milford, USA) was used to determine the MW distributions of rainwater. The mobile phase was made of pure water with phosphate (pH 6.8) and NaCl (0.1 M). Standards of MW of various polystyrene sulfonates (PSS: 210, 1,800, 4,600, 8,000, and 18,000 Da) were used to calibrate the equipment. The detection limit of UV was

Table 1 | Characteristics of PAC used in this study (James Cumming & Sons PTY Ltd.)

Specification	PAC-WB
Surface area (m^2/g)	882
Mean pore diameter (Å)	30.61
Micropore volumn (cm^3/g)	0.34
Mean diameter (μm)	19.71
Product code	MD3545WB powder

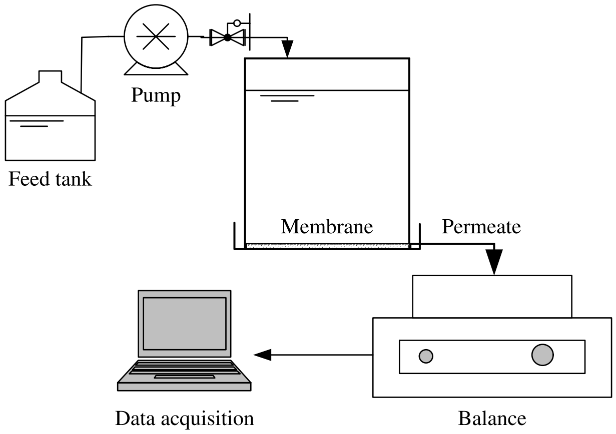

Figure 1 | Schematic diagram of dead-end cell unit for membrane fouling index experiment.

0.001 per cm. Since UV at 254 nm wavelength preferentially absorbs π-bonded organic matter, HPSEC with the UV detector is chiefly applied to MW estimations of humic and fulvic acids, and the aromatic hydrophobic portion of DOC. This has the limitation of detecting low UV-absorbing components, such as proteins and polysaccharides. Thus, fluorescence detectors were employed to interpret protein-like substances. Fluorescence detectors were used at two wavelengths, excitation (279 nm) and emission (353 nm). Before analysis with the HPSEC, all samples were filtered through a 0.45 μm pore size membrane and only the filtrate was used for analysis.

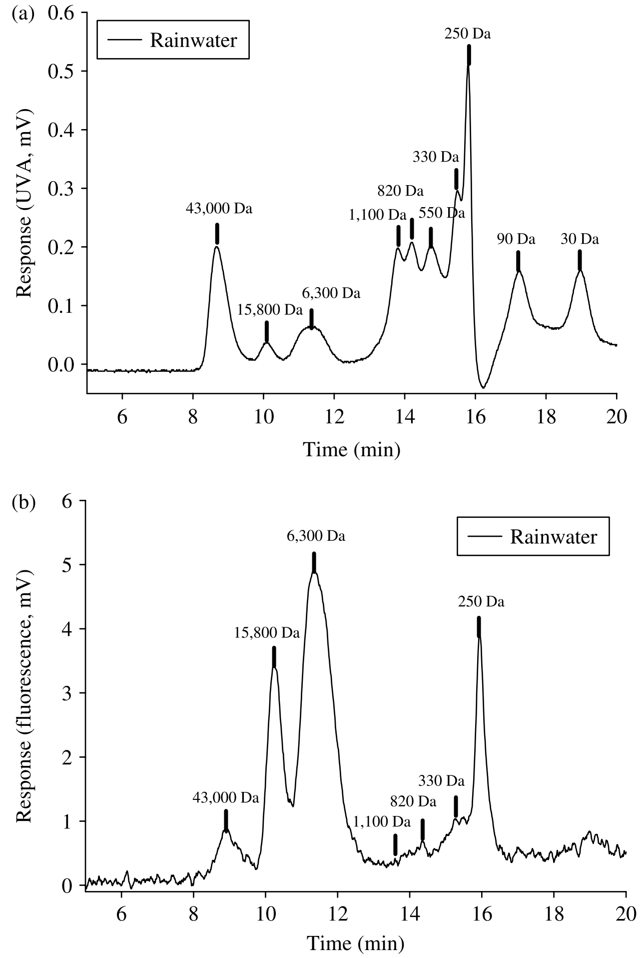

Figure 2 | MWD of organic matter in rainwater in terms of (a) UV and (b) fluorescence responses.

RESULTS AND DISCUSSION

MWD of organic matter in rainwater

Figure 2 shows MWD of dissolved organic matter in rainwater in terms of UV and fluorescence responses. Rainwater which initially had 1.8 mg/L of DOC included many different sizes of organic matter in the range of 43,000 Da–30 Da using the UV detector. Here, it should be noted that the rainwater characteristics and the MWD of organic matter vary from season to season and from place to place as well as ageing. According to Huber's study (2008), the major type of organic matter can be identified in terms of different retention times. The MW fraction of 43,000 Da, 1,100–550 Da, 330 Da, 250 Da and 90–30 Da found in this study represents biopolymers (polysaccharides and proteins), humic and fulvic acids, building blocks, low MW acids (hydrolysates of humic substances), low MW neutrals and amphiphilics, respectively (Huber 2008). Low MW neutrals and amphiphilic (slightly hydrophobic) compounds include sugars, alcohols, aldehydes, ketones and amino acids. The origin of DOC on polysaccharides and proteins may be from microbial activity for long storage of rainwater. Humic substances would be originated from a withered leaf on the roof surface. Building blocks, low MW acids, low MW neutrals and amphiphilics are probably from hydrolysates of humic substances and/or intermediates of microbial activity. Compared to wastewater, drinking water and seawater, the rainwater in the main consisted of MW of 15,800 Da and 6,300 Da. The MW of two organic molecules especially showed the highest intensity with the fluorescence response, suggesting that the MW included protein-like substances.

DOC and MWD after PAC adsorption

Figure 3 presents the DOC concentration of different fractions after PAC adsorption. The initial DOC concentration was 1.80 mg/L. The concentrations of the HP and HL fractions were 0.5 mg/L (28%) and 1.3 mg/L (72%), respectively. Compared with drinking water, wastewater effluent and groundwater, the rainwater used in this study contained more HL compounds. After PAC adsorption of 0.1 g/L, the DOC concentration decreased up to 1.2 mg/L (33% removal). The removal efficiencies of the HP and HL fractions were 50% and 27%, respectively. The PAC adsorption was found to show preferential removal of the HP fraction. This may be due to the HP nature of PAC.

Figure 4 shows the MWD of organic matter with and without PAC adsorption with rainwater. The smaller MW of 1,100 Da, 820 Da, 550 Da, 90 Da and 30 Da was significantly removed after PAC adsorption of 0.1 g/L, while the larger MW of 43,000 Da, 15,800 Da, 6,300 Da and 250 Da still remained. Humic substances (1,100–550 Da) were preferentially removed due to hydrophobic nature and the better removal of low MW neutrals and amphiphilics (90–30 Da) was probably due to pore entrapment into PAC. Shon *et al.* (2006) observed a similar removal trend of organic matter by PAC adsorption in biologically treated sewage effluent.

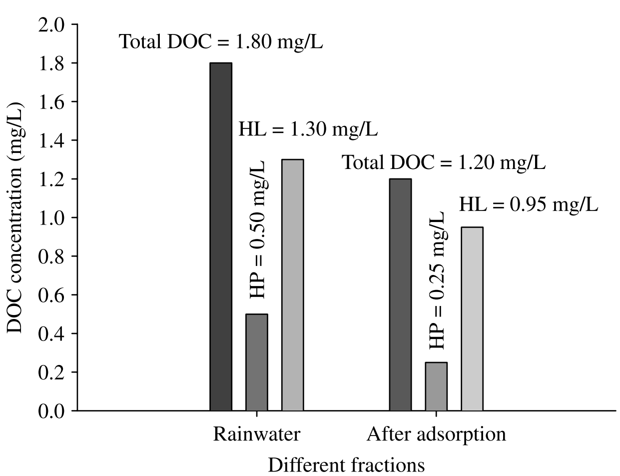

Figure 3 | DOC concentration of HP and HL fraction before and after PAC (PAC dose = 0.1 g/L).

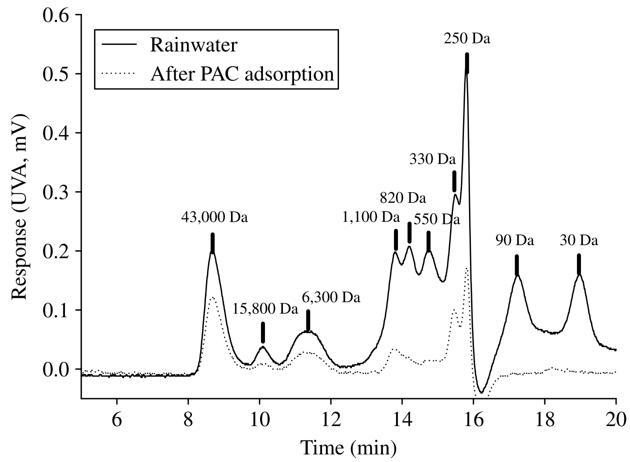

Figure 4 | MWD of organic matter after 0.1 g/L PAC adsorption in rainwater.

Fouling index after PAC adsorption

Figure 5 shows the temporal variation of permeate volume after PAC adsorption for rainwater. After 1 hour operation, the permeate volume with and without PAC adsorption was 2.15 L and 4.78 L, respectively. The permeate flux after PAC adsorption was 2.2 times higher than that without PAC adsorption. This suggests that PAC adsorption is also helpful in reducing particulate matter of more than 0.45 μm size.

Figure 6 shows the results of filtration time/permeate volume vs permeate volume after PAC adsorption. MFI was determined from the slope of the straight line obtained when plotting t/v versus v, in agreement with the

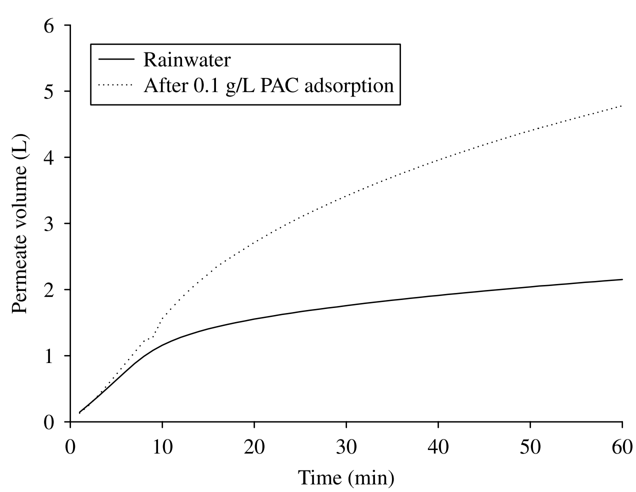

Figure 5 | Time vs permeate volume after PAC adsorption (pressure = 2 bar; temperature = 25°C; diameter of membrane used = 47 mm).

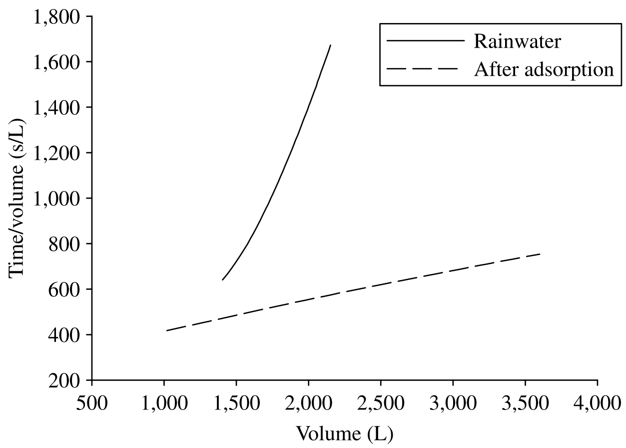

Figure 6 | Time (s)/permeate volume (L) vs permeate volume (L) after PAC adsorption (pressure = 2 bar; temperature = 25°C; diameter of membrane used = 47 mm).

Table 2 | SDI and MFI values of rainwater before and after PAC pretreatment

Rain water (RW)	SDI	MFI (s/l^2)
Rainwater	5.7	1,436
After 0.1 g/L PAC adsorption	3.0	147

general cake filtration equation for constant pressure (Boerlage *et al.* 1998).

$$\frac{t}{v} = \frac{\eta R_m}{\Delta P A} + \underbrace{\frac{\eta \alpha C_b}{2 \Delta P A^2}}_{\text{Slope(MFI)}} v, \quad (1)$$

where,

v	total permeate volume (L)
R_m	membrane resistance (1/m)
t	filtration time (s)
ΔP	applied trans-membrane pressure (Pa)
η	water viscosity at 20°C (N s/m^2)
α	the specific resistance of the cake deposited
C_b	the concentration of particles in a feed water (mg/L)
A	the membrane surface area (m^2)
MFI	cake fouling index (s/L^2)

The MFI values with and without PAC adsorption were 147 s/L^2 and 1436 s/L^2, respectively (Table 2). The SDI values were also investigated. The SDI value after PAC adsorption decreased from 5.7 to 3.0. This can be concluded that PAC adsorption as pretreatment to membrane filtration with rainwater is effective to reduce membrane fouling potential.

CONCLUSION

The MWD of organic matter with and without PAC adsorption in rainwater and the effect of PAC adsorption on SDI and MFI were investigated. The results led to the following conclusions.

1. The initial DOC concentration of rainwater was 1.8 mg/L and MW of organic matter ranged from about 43,000 Da to 30 Da. The organic matter in rainwater included biopolymers (polysaccharides and proteins), humic and fulvic acids, building blocks, low MW acids (hydrolysates of humic substances), low MW neutrals and amphiphilics.
2. The rainwater consisted of the majority of HL compounds (72%). PAC adsorption removed 33% of organic matter. The removal efficiencies of the HP and HL fractions after PAC adsorption were 50% and 27%, respectively. The PAC adsorption was found to show preferential removal of the HP fraction.
3. The smaller MW of 1,100 Da, 820 Da, 550 Da, 90 Da and 30 Da was significantly removed after PAC adsorption, while the larger MW of 43,000 Da, 15,800 Da, 6,300 Da and 250 Da still remained.
4. The MFI values decreased from 1,436 s/L^2 to 147 s/L^2 after PAC adsorption. The SDI values decreased from 5.7 to 3.0. This result implies that the PAC adsorption to membrane filtration with rainwater can be used as a pretreatment.

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