

Powdered activated carbon and biofiltration improve MF performance: Part I

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This article shows how the use of high-dose powdered activated carbon and biofiltration are able to improve the performance of membrane-based microfiltration systems. The first part, which appears here, provides an overview of the study, materials and methods, and experimental design and operational conditions of the reactors. Part II will be published in the June 2007 issue of *Membrane Technology*.

A hybrid microfiltration (MF) system incorporating a high initial dose of 40 g/l powdered activated carbon (PAC) was operated for over one month. In a control reactor operated without PAC, transmembrane pressure (TMP) and backwash pressure (BWP) increased faster than the reactors operated with PAC.

A reactor with PAC that was fed water from a biofiltration unit fouled even more slowly. Protein and carbohydrate are major components of extracellular polymeric substances (EPS), often associated with the fouling of membranes. A protocol for EPS extraction and identifying target carbohydrates was developed and applied to both membrane-associated material and components in the bulk water. A protein assay was also adapted to this system. The reactor with PAC and biofiltration water as a feed could reduce the protein and carbohydrate fouling of the membrane as well as reduce the total quantity of carbohydrate and protein in the bulk water.

Membrane process

Larger pore membranes, including ultrafiltration (UF) and microfiltration (MF), are used for the separation of macromolecules and discrete particles from water. Non-porous membranes, including nanofiltration (NF) and

reverse osmosis (RO) membranes, can achieve separation of small molecules, dissolved organic material and inorganic ions.

In water with a high organic load, fouling of these membranes can occur necessitating cleaning or even replacement of the membrane. Pretreatment of feed waters with activated carbon can reduce this load,^[1] but often results in higher micro-organism counts in the feed to the high-pressure system with little net improvement in performance. Conversely, pretreatment with UF or MF can reduce the micro-organism load, but may not significantly impact the organic load.

Powdered activated carbon (PAC) is an important tool for maintaining the safety and aesthetic quality of drinking water. It can be combined with MF or UF to remove organic compounds as well as micro-organisms.^[2]

Fouling

The fouling is caused by sorption and trapping of organic substrates on the membrane surface and within the membrane matrix, often accompanied by microbial growth at the expense of these organic compounds.

The extent of membrane fouling is often quantified by a decrease in flux below a 'critical flux' value. However, the flux decline is

often only detected at the advanced stages of fouling after the membrane morphology is significantly altered and a significant fraction of the channels within the lattice structure of the membrane have lost their ability to transport water molecules.^[3]

Extracellular polymeric substances

The biofouling process initially starts with the deposition of substrates such as extracellular polymeric substances (EPS) which form a highly hydrated nanogel layer on the membrane surface.^[4]

EPS are large molecular weight compounds that are excreted by bacteria^[4-6] and play a significant role in bacterial adhesion onto solid surfaces by altering the physicochemical characteristics such as charge, hydrophobicity, and the polymeric properties.^[7-9]

EPS are composed of proteins, carbohydrates, humic substances, DNA and RNA.^[10, 11]

Interaction forces

When the EPS concentration increases, cell adhesion is enhanced by polymeric interactions.^[12] EPS also create scaffolds with suitable physical characteristics and interconnected pore structures that promote cell attachment, proliferation and differentiation.^[5, 13, 14]

The forces of interaction between the membrane surface and EPS may be physical (adsorption), chemical (covalent bonding) or electrostatic (van der Waals forces). The roughness characteristics of the membrane surface can change the surface forces by orders of magnitude.^[3]

The compatibility of the molecular dimensions of EPS and the membrane roughness define the distribution of asperities at points of contact and the adhesion strength. Recent studies show that there exists an optimal shape of the contact surface and an object which result into optimal adhesion to a substrate via molecular interaction.^[3]

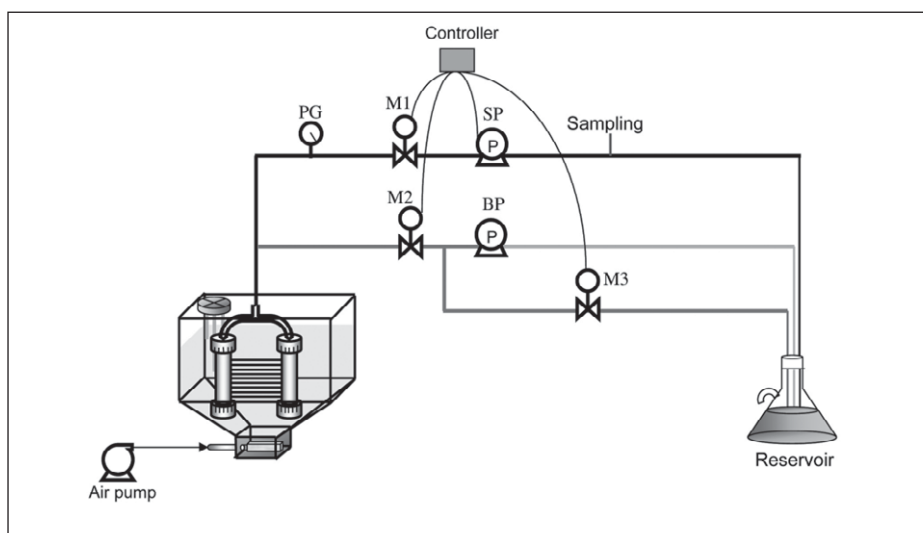


Figure 1. Schematic diagram of single powdered activated carbon microfiltration (PAC-MF) unit (PG, pressure gauge – connected to a computer; M1, electric valve for retardation of water during backwash; M2, electric valve for backwash; M3, electric valve for water circulation; SP, suction pump – connected to controller; and BP, backwash pump – NOT connected to controller).

Bonds

The presence of active groups within the membrane matrix determines the ability of the membrane material to form bonds with water and other substrates. The greater the tendency for a material to associate with water (that is, through hydrogen bonding) the more hydrophilic the membrane becomes.

Hydrophilicity influences the 'wettability' and adhesion characteristics of substrates to the membrane material.^[15] Hydrophilic membranes have higher water fluxes than hydrophobic membranes and are generally preferred for water treatment applications.

Surface water

Bench-scale experiments on a PAC-MF system were carried out using settled surface water (Tama River, Tokyo, Japan) either before or after treatment by a biofilter system during the summer in Japan.

More than 80% of the total flow of this river consists of the treated effluent from wastewater treatment plants located upstream. As a result, the dissolved organic matter (DOM) and other food sources for micro-organisms in the river water are much higher than a typical surface water source. Therefore, a greater degree of treatment may be introduced by implementing a PAC-MF process.

Different studies have been carried out on the fouling of different components of EPS, but little work has been done on carbohydrate fouling originating from surface water.

The objectives of this research were to:

- establish a standard method of EPS extraction from water treatment reactor samples;
- evaluate the effect of different types of common carbohydrates on MF fouling in

the presence and absence of a high dose of PAC;

- observe the effect of protein on membrane fouling in a PAC-MF system; and
- monitor the performance of the PAC-MF system fed with surface water.

Materials and methods

Site location

The Tokyo Metropolitan Authority has a water treatment plant using water from the Tama River, which is located in the south-west region of Tokyo, around 15 km from the main city.

The treated water is supplied only for industrial use. The bench-scale experiments on PAC-MF system were performed in this treatment plant. The river water was pumped from the intake point to a series of primary and secondary sedimentation ponds. Water was taken from the secondary ponds and split into three streams. Two of these were used directly as feed to reactors, while the third was used after treatment by the biofilter. The reactor and feed system are shown schematically in **Figure 1**.

Experimental design and operational conditions of the reactors

Each reactor consisted of a hollow-fibre MF membrane module operated in crossflow mode.

The membrane was made of polyethylene, and its surface was modified to be hydrophilic. The nominal pore size, the outer and inner diameter, the number of fibres, the length of fibres, and the surface area were 0.1 μm , 0.41 mm, 0.27 mm, 320 (16 \times 20), 120 mm, and 0.05 m^2 , respectively.

The membrane module was submersed in a reactor made of 5 mm polyvinyl chloride plates with an effective volume of 5 litres.

The TMP due to pure water flux of these used membranes was 2–3 kPa (0.02 to 0.03 bars), giving a flux of 0.5 m^3/day .

During this study, reactors 1 and 2 both received settled river water, while reactor 3 received effluent from the biofilter system. The biofilter consisted of a column packed with polyethylene cylinders, 5 mm in length, and with an inner diameter and outer diameter of 3 mm and 4 mm respectively. The filtration velocity was 320 m^3/d . Discharge from the biofilter was stored in a 100 litre reservoir prior to being fed to reactor 3.

Flux

Reactors 2 and 3 were initially dosed with 40 g/l of PAC (coconut shell origin, Type JWVA K 113–1985, Shirotsagi-C, Takeda Chemical Co, Japan). Although a few researchers^[16] found that PAC with additional surface treatment had much better adsorption quality, the PAC used in this research was used as received.

The flux during constant filtration was kept at 0.50 m^3/day , for a flow of 25 l/day and a residence time of 0.2 days. Aeration at 5 l/min was maintained underneath the fibre module to disturb the cake formation on the membrane surface and to prevent rapid flux decline. Level sensors were used to ensure a constant reactor volume, while suction through the membrane module maintained a constant flow rate.

All systems were equipped with a backwash mechanism, providing 2 minutes of backwash after every 20 minutes of filtration. The backwash was performed with stored filtrate. The backwash reservoirs were cleaned once a week and refilled with fresh filtrate.

TMP and BWP were automatically recorded using a data logger as part of the process control system. When TMP of any module increased by more than 50 kPa (0.5 bar), that unit was physically cleaned with a soft brush during the backwash step before the next filtration period; pure water flux was subsequently measured after membrane cleaning.

If membrane modules were operated at high pressure (above 60 kPa or 0.6 bar), physical cleaning alone was not sufficient for the next run cycle.^[17] The reactors were operated for 33 days continuously without discarding the backwash volume (that is, the backwash stayed in the reactor). Once the TMP of the membrane module inside reactor 1 (raw without PAC) exceeded 50 kPa (0.5 bar) after 32 days of operation, all reactors were stopped.

Analytical techniques

EPS was extracted from bulk fluid and membrane biofouling samples, and subsequently stained with lectins specific for particular carbohydrate moieties.

Zhang *et al.* (1999)^[18] extracted EPS from different activated sludge samples in various ways and proposed a method to extract EPS based on the highest recovery of carbohydrate, protein and DNA. The protocol used here is

modified from their best protocol. For example, the amount of settleable solid sample and also the volume of liquid sample were changed from the previous protocol.

Before such changes, several trials were done to obtain the maximum recovery of the target materials. To extract the EPS, 10 g of collected sediment were placed in a centrifuge tube and suspended in 25 ml of Milli-Q water, shaken and then centrifuged at 3500 rpm for 10 minutes. The supernatant was decanted and set aside. The pellet remaining in the centrifuge tube was re-suspended in 25 ml of 8.5% NaCl and 0.22% formaldehyde. The mixture was 'vortexed' at high speed for 1 minute to recover the capsule-bound material.

Following the vortex step, the previously retained supernatant was added, and 15 ml of this mixture (now 50 ml plus original sediment sample) was centrifuged at 12 000 rpm for 30 minutes. The supernatant was collected and filtered through a 0.2 µm cellulose acetate filter for treatment with the lectins. Activated sludge (2.0 g) from the Shinagawa wastewater treatment plant (Japan) was used as a positive control.

Target lectins

The list of selected lectins is shown in [Table 1](#) (Sigma-Aldrich Co, USA). Basically each lectin corresponds to the specific carbohydrate.

The types of lectins were selected based on the availability of those carbohydrates in the water and wastewater system. These lectins are from plant proteins that bind to specific carbohydrate groups on proteins or on cell membranes.

The lectin powders were diluted to 0.2% by 1 N poly-phosphate buffer (PBS) solution (8 g/l NaCl, 1.1 g/l Na₂HPO₄ — anhydrous, 0.2 g/l KCl, and 0.2 g/l KH₂PO₄). The dilute lectins were preserved at -20°C and covered by aluminium foil to protect them from light exposure.

Labelling of different lectins with extracted EPS samples

An extracted EPS sample (5 µl) was placed drop-wise on glass slides and oven-dried at 90°C to 95°C for 5 minutes. Labelled lectin solution (10 µl) was then placed on top of the dried droplet. The labelled lectin was allowed to react with the EPS components for 10 minutes in the dark, after which the slide was washed very gently with Milli-Q water, and then shaken to air-dry. One drop of slow fade was placed on top of the dried sample, and a cover slip was placed. Labelled samples were observed through an epifluorescence microscope (Microscope Series # Nikon, Eclipse E 800, Japan) using a 100X objective. Stored images were used with Photoshop software to compute the light intensity (green or red), and a mean value of light intensity for each lectin was estimated and averaged.

Table 1. Lectins used for labelling the extracted extracellular polymeric substances (EPS).

Common name	Fluorochrome	Specificity
Jack bean	FITC	D(+) glucose and D(+) mannose
Peanut	FITC	D(+) galactose
Coral tree	FITC	N-acetyl-D-galactosamine and D-galactose
Gorse or furze	TRITC	L(-) fucose
Red kidney bean	TRITC	Oligosaccharides

Extraction of total protein

The foulants from the membranes were removed with a soft brush and diluted into 100 ml of MilliQ water. A few portions (10 gm) of the foulants from each membrane module were used for the extraction of EPS and the rest were used for protein and other assays.

It was impossible to extract proteins from the membrane surfaces completely. Total protein of the samples inside the reactors and in the fouling layer on membrane modules were extracted using the Bicinchoninic Acid (BCA) protein assay reagent kit (Pierce, BCA protein assay reagent kit, 23225). Protein standards were prepared in the range of 0–50 mg/l with bovine serum albumin (BSA) from 2 mg/ml supplied albumin with this kit.

The enhanced protocol (Pierce, instructions) was followed with incubation at 60°C for 30 minutes to increase the sensitivity of the measurements. The absorbance of the cooled samples at 562 nm was compared against the standard curve to obtain the protein concentration and was subsequently converted to appropriate units for expression of biomass aerial density. A U-2010 spectrophotometer (Hitachi Co, Japan) was used to measure the absorbance of the samples.

Scanning electron microscopy image

During the preparation of scanning electron microscopy (SEM) images, the samples were dried at 35°C for 1 hour and then coated with gold (50 nm thickness) by an ion coater (IB-3, EIKO Company, Japan) within 2 minutes. The thickness of the gold coating depends on the magnification of the image. The SEM images were taken by an S 2400 SEM (Hitachi Company, Japan).

Second instalment

The second instalment of this article, which will be published in the June 2007 issue of *Membrane Technology*, will discuss the results of this study.

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(The full title of this paper, as submitted by the authors is: 'Effect of carbohydrates and protein on the biofouling formation of microfiltration membrane combined with a high-dose PAC.')

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Research Trends

Organic solvent NF and pervaporation

This study looks at large-scale organic solvent nanofiltration (OSN) and pervaporation processes. New membranes, modules and systems are under development for large-scale organic/organic separations. Practical applications are envisioned in the refining, chemical, pharmaceutical and polymer industries. A large-scale OSN process is Max-Dewax for solvent recovery in lube de-waxing. A commercial installation has been in operation since 1998 at a feed rate of 5800 m³/day (36 000 barrels/day). A pervaporation process, S-Brane, is also available for comparable large-scale operations. S-Brane selectively removes sulfur containing hydrocarbon molecules from fluidized catalytic cracking (FCC) and other naphtha streams. A 300 barrels/day demonstration plant has been run on-stream using FCC light and intermediate cat naphthas. S-Brane reduces the overall capital and operating cost for clean fuel compliance, and also provides a means for preserving octane value in technology based on hydro-treatment. There are several key steps in the development of a robust membrane process that can be moved from laboratory-scale to pilot-plant trials to a demonstration unit on-line at a refinery. These steps expand in complexity and size as process development moves forward. Both Max-Dewax and S-Brane are presented as examples of applications that have moved through this progression. Since these processes are large-scale and involve a relatively low capital cost compared with conventional technologies, gains in yield, quality, or energy savings are found to offer significant economic benefits. Experimentally, it appears that

high-pressure nanofiltration and low-pressure pervaporation are governed by the principles found in solution-diffusion models. Data taken in OSN mode is used to estimate pervaporation performance. The choice of membrane operating systems is dependent on the composition of the feed stream and the required product quality. In some cases, the high throughput for OSN outweighs the higher selectivities gained in pervaporation, since OSN is inherently a less expensive process to operate.

L.S. White: *J. of Membrane Science* **286**(1–2) 26–35 (15 December 2006).

DOI: 10.1016/j.memsci.2006.09.006

Transmembrane pressure in NF

Most studies to date of Donnan exclusion in membrane separation of mixed solutions of permeating and completely retained salts with shared mobile counter-ions have focused on its effect on negative salt rejection. In this study, a theoretical examination is presented of the effect of Donnan exclusion on flux in general and the threshold transmembrane pressure for non-zero flux in particular. These effects are expressed through the osmotic pressure of the different solutions in equilibrium with the membrane, which is directly affected by the value of the activity coefficient of the polyelectrolyte counter-ion ϕ_p . The osmotic pressure of polyelectrolyte solutions is determined by measuring the threshold transmembrane pressure for non-zero flux, and evaluating the coefficient from this. The activity of the permeating salt in a mixed solution can then be predicted and used to estimate the partition coefficient β of the permeating salt between the mixed and pure salt solution separated by a semipermeable membrane. This value is found to be in reasonable agreement with partition coefficients determined directly in dialysis experiments. Finally, the depression of the threshold transmembrane pressure for non-zero flux, on adding salt to a polyelectrolyte system, is estimated from values of the permeating salt partition coefficient β , previously determined in dialysis experiments.

J. Gilron, N. Daltrophe and O. Kedem: *J. of Membrane Science* **286**(1–2) 69–76 (15 December 2006).

DOI: 10.1016/j.memsci.2006.09.013

Influence of surface porosity on membrane distillation performance

Two kinds of polypropylene capillary membranes were used in this membrane distillation (MD) study. These membranes exhibited a similar morphology, but one of them has an additional low porosity layer on the internal surface of capillaries. The changes of membrane performance during the MD process of tap water were investigated. The presence of a low porosity layer (thickness below 1 μm) caused the air permeability to be reduced from 1.365 dm³/m² s kPa to 0.863 dm³/m² s kPa, whereas the MD permeate flux was decreased only by 15%. A significantly larger decline of the flux was caused by a CaCO₃ deposit, formed during distillation of the tap water. This deposit was removed every 30–70 hours by rinsing the modules with a 2–5 wt% HCl. Unfortunately, a repetition of this operation several times resulted in a gradual decline of the maximum permeate flux (distilled water as a feed). However, the module efficiency of the membranes covered by a surface layer of low porosity was found to decrease twice as slowly. The investigations revealed that a low surface porosity does not limit the possibility of surface wetting of polypropylene membranes, but hindered the scale formation inside the pores.

M. Gryta: *J. of Membrane Science* **287**(1) 67–78 (5 January 2007).

DOI: 10.1016/j.memsci.2006.10.011

Effect of inorganic scalants on NF membrane fouling

In this research the influence of inorganic scalants and natural organic matter (NOM) on nanofiltration (NF) membrane fouling was investigated by a crossflow bench-scale test cell. Mathematical fouling models were used to determine kinetics

DOI numbers

The Digital Object Identifier is a unique, permanent character string that links to electronic documents. To resolve a DOI, go to <http://dx.doi.org>, enter the DOI (for example, 10.1016/j.memsci.2006.09.006) in the box, and click 'Go'. Alternatively, type this website URL into your browser's address bar, followed by a slash then the DOI, and hit 'Return'.