Influence of PAC properties on membrane performance in a PAC-UF hybrid system
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ABSTRACT
The combination of ultrafiltration (UF) and powdered activated carbon (PAC) has gained in importance over the last 15 years. The aim of applying PAC-UF hybrid processes is to improve the rejection capacity and the performance of membrane processes. In this work the influence of PAC-addition on membrane flux decline and fouling formation was studied with a submerged module using different water matrices. The PACs used were characterized by measurements of the surface area, the particle size distribution and the surface charge to get a better understanding of the observed effects. Results showed that the membrane flux decline was dependent on the applied type of activated carbon. When adding Picachem 8P, the transmembrane pressure (TMP) increased very quickly and the membrane performance was even worse than that without PAC. However, when adding Norit SA-UF under identical filtration conditions, the TMP was stable and the membrane performance was better than that without PAC. The fouling layers of the two PACs applied showed entirely different structures. Therefore the selection of a suitable PAC is a main factor for the overall performance of PAC-UF hybrid systems with submerged membranes.

Key words | flux decline, fouling layer, powdered activated carbon (PAC)

INTRODUCTION
The combination of powdered activated carbon and ultrafiltration (or microfiltration) membranes (PAC-UF) has been suggested for the removal of organic substances since 1991 as an alternative to conventional water treatment by several authors (Adham et al. 1991; Jack & Clark 1998; Tomaszewska & Mozia 2002; Zhao et al. 2005; Lee & Walker 2006). The hybrid process effectively removes total organic carbon (TOC), dissolved organic carbon (DOC) and dissolved pollutants such as microcystins, pesticides and pharmaceuticals.

When combining PAC and UF, the PAC is added (continuously or in step-dose) to the raw water in a concentration typically between 10 and 20 mg/L. In exceptional cases concentrations of g/L have been applied (Adham et al. 1991; Konieczny & Klomfas 2002). In some cases activated carbon is added in a mixed tank before contacting the membrane. This procedure improves the adsorption of organic substances (Jack & Clark 1998). Either dead-end or cross-flow filtration can be used (Snoeyink et al. 2000; Baudin et al. 2001; Matsui et al. 2001; Ivancev-Tumbas et al. 2008). The advantage of dead-end filtration is the lower energy demand, since the capacity of the pump is primarily used to generate a TMP (transmembrane pressure) and not to create a cross-flow on the membrane surface. The principal disadvantage of dead-end filtration is the cake formation on the membrane surface and the necessity of cleaning procedures (e.g. backwash) in order to restore the permeability of the membrane. The use of submerged membranes as a pseudo-dead-end-filtration provides a good alternative for a PAC-UF hybrid system. The air bubbling on the membrane surface improves its cleaning by creating shear forces, and by this reduces the accumulation of PAC particles (Côté et al. 2001). Even higher shear forces and even better control of the cake formation can be achieved with cross-flow filtration but at the expense of high energy consumption (because of the recirculation of part of the feed) and lower module recovery.

The discussion on membrane performance and fouling formation under addition of PAC is associated with contradictions. Pirbazari et al. (1992), Campos et al. (1998), Tomaszewska & Mozia (2002) and many others reported a reduction of fouling formation when adding activated carbon to UF membranes. On the other hand, Jack & Clark (1998), Lee et al. (2000), Zhang et al. (2003), Saravia & Frimmel (2008) found that the addition of PAC can deteriorate membrane performance and reduce the membrane permeability. Jack & Clark (1998) suggested that the water composition plays an important role in the decline of permeability when using the PAC-UF process.

This work focuses on the influence of PAC-addition on flux decline and fouling formation in a submerged membrane module. The PACs used were characterized to gain a better understanding of the fouling formation.

**MATERIALS AND METHODS**

**Chemicals**

Two different activated carbons with similar mean particle size and different surface properties were chosen for the experiments: Norit SA-UF (Netherlands) and Picachem 8P (France). The general characteristics of both PAC materials are shown in Table 1.

**Membrane set-up**

Experiments were performed using a lab-scale system equipped with a flat sheet membrane (polyether sulfone (PES), 0.1 μm pore size, 0.00132 m² membrane surface, Membrana GmbH, Germany) at a constant flux of 32 L/(hm²) and a filtration/backwash interval of 30 min/30 s (Figure 1). Backwash (with permeate) was performed automatically using a combination of valves and a pressure tank. Details of the experimental set-up are reported elsewhere (Saravia et al. 2007).

During filtration, air bubbling was applied to the membrane surface to reduce fouling formation.

**Experiments**

Experiments were carried out with spiked pure water and natural waters: (a) demineralized water with a phosphate buffer (10 mM), solution pH = 7; (b) surface water from a bog lake with high NOM (natural organic matter) content with phosphate buffer, pH = 7 (Lake Hohloh, Black Forest, Germany; filtrated with 0.45 μm filter for elimination of particulate matter); (c) river water (River Neckar, Germany, settled for approx. 45 min). The major water chemical parameters are shown in Table 2.

Activated carbon samples were used as delivered, i.e. without washing before the experiments.

All experiments were performed under identical filtration conditions (membrane set-up) at room temperature (18–20 °C), with a hybrid system recovery of about 92% (permeate volume/raw water volume). According to the results of batch adsorption experiments (data not shown), 10 mg PAC per liter feed water was added.
The mean hydraulic residence time (HTR ≈ 5.5 h) in the process tank was calculated by dividing the volume of water in the process tank by the feed flow.

During the experiments, permeate flux, filtration and backwash pressure, air bubbling flow, temperature and PAC-concentration in raw water were measured.

**Analytical methods**

PAC-samples were characterized based on particle size (using a Mastersizer 2000-Particle Size Analyser, Malvern, UK), surface charge (Z-Sizer Nann ZS, Malvern, UK), specific surface (Nova 2200, Quantachrome Instruments, USA) and pore size distribution, by mercury porometry (Pascal mercury porosimeter 140 for low pressure, up to 350 kPa, and Pascal 440 for high pressure, up to 400 MPa, Thermo Electron Corporation, Italy). The structure of the PAC particles was characterized using scanning electron microscopy (SEM) (LEO 1530 Gemini with a Schottky field-emission electron source). The presence of acid and basic functional groups in the PAC particles was determined according to the method of Dastgheib et al. (2004).

The DOC concentrations in feed and permeate water were determined by a TOC-Analyser 820 (Sievers Instruments, USA). Cation concentrations were measured by ICP-OES (Inductively Coupled Plasma Optical Emission Spectroscopy) instrument (Varian Vista-Pro, CCD-Simultaneous OES).

The PAC concentration in the process tank was measured indirectly using a turbidimeter (Ratio/XR-Turbidimeter, Hach, Germany). The equipment was calibrated with PAC suspensions in different concentrations for the different water matrices.

Fouling layers and membranes were analysed by SEM (LEO 1530 Gemini with a Schottky field-emission electron source).

**RESULTS AND DISCUSSION**

**Characterization of PAC samples**

The particle size distribution of the activated carbons showed a narrow particle size distribution and an average particle size ($D_{50}$) of 8.5 and 9.5 μm for Norit SA-UF and Picachem 8P, respectively (Figure 2). Norit SA-UF has macropores and micropores, whereas Picachem 8P almost exclusively has micropores. The Norit SA-UF presented a fragile structure that collapsed during the measurement of the pore size distribution (Hg-porometry). SEM-pictures confirmed the results of pore size distribution (Figure 3).

The surface properties of both PACs were different: both were negatively charged at pH $= 7$, but Norit SA-UF had a lower Z-potential in all investigated water matrices. The difference between Z-potential of the PACs in the water matrices is due to the different ion concentration in waters. Neckar water had a much higher ion concentration than the NOM-rich brown water. The presence of ions in the solution led to a neutralization of the surface charge of the activated carbon.
The distribution of acidic and basic functional groups was also different for both PACs (Table 3).

**Filtration performance in different matrices**

**Experiments with demineralized water**

Filtration of the PAC in a demineralized water matrix showed that the presence of PAC has almost no influence on the filtration performance (Figure 4). After a permeate volume of approx. 50,000 L/m²² the permeability declined for about 6 and 10% for Norit SA-UF and Picachem 8P, respectively. During the filtration a PAC layer was built up on the membrane surface, but no PAC particles were found in the membrane pores (SEM-Analysis). Hence, PAC particles were big enough to avoid pore plugging. The PAC cake layer formed on the membrane surface could not be removed by backwashing or air bubbling. However, the cake layer structure was porous and did not contribute significantly to the permeability decline. Similar results were observed by Mozia et al. (2005), Saravia & Frimmel (2008) and others.

**Experiments with surface water rich in NOM**

Filtration experiments with a NOM-rich surface water matrix showed that different PAC materials had totally different effects on the membrane performance. With the addition of Picachem 8P the TMP increased very quickly and the membrane performance was even worse than that of the filtration without PAC (see Figure 5). When adding
Norit SA-UF under identical conditions, the TMP was stable and the membrane performance was better than that without PAC.

Since the experiments were carried out using the same water under identical filtration conditions, it can be deduced that different PAC properties were responsible for the different filtration performances.

The main differences between the PACs are the surface charge (Norit SA-UF presents a lower Z-potential), the particle structure (Norit SA-UF has macro-pores and is composed of agglomerated small particles, whereas the surface of Picachem 8P particles is even) and marginally the particle size distribution. It can be concluded that the surface properties of the activated carbons play a major role for the membrane performance.

Membranes used for water treatment have generally a negative surface charge in order to minimize the adsorption of negatively charged dissolved organic matter (DOM) on the membrane. The negative charge of PAC is beneficial, because of the repulsion between the PAC particles and the membrane surface which reduces particle-membrane interactions.

In the experiments with NOM-rich water, the cake layer became thicker than in the filtration with demineralized water. The thickness of the cake layer was between 20 and 40 μm after the experiments with Picachem 8P and demineralized water, whereas the cake layer after the experiments with NOM-rich water and Picachem 8P was uniformly at around 45 μm.

Additionally, Picachem 8P particles created thinner and denser cake layers than Norit SA-UF, which were strongly attached to the membrane surface. In contrast to the Picachem 8P cake layers, the Norit SA-UF cake layer detached from the membrane surface when the membrane was removed from the set-up after the experiments. Charge interactions between the PAC particles, NOM and the membrane surface can explain this behaviour.

The presence of NOM is an important factor for the PAC-UF performance. NOM can act as an adhesive between the PAC particles and the membrane surface building a compact fouling layer with high resistance to the water flow (Zhang et al. 2003; Saravia & Frimmel 2008). It can be concluded that cake layer properties and permeability will depend to a large extent on the initial PAC surface properties.

**Experiments with river water matrix**

Figure 6 shows the TMP as a function of the permeate volume for three experiments with river water: (a) filtration without PAC; (b) filtration with addition of Picachem 8P; and (c) filtration with addition of Norit SA-UF. The best filtration performance was achieved with Norit SA-UF, similar to the experiments with NOM-rich water. However, in the experiments with river water a higher flux decline (faster increase of TMP) and a TMP stabilization at higher TMP than those of the experiments with NOM-rich water was observed. Under identical filtration conditions but with Norit SA-UF a stable TMP was established at approximately 10 mbar with NOM-rich water and at approximately 40 mbar with river water.
The river water not only had higher concentrations of ions in comparison to NOM-rich water, but also contained suspended solids/particulate matter, mainly because of the different pre-treatment: NOM-rich water was filtered (0.45 μm) and river water was used after settling for 45 min.

The presence of ions can contribute to the neutralization of the PAC particles and the membrane surface. Additionally, ions can influence the size and the charge of NOM in water. At higher solution ionic strength, NOM generally tends to reduce its size due to compensation of negative charges (Swift 1989). For this reason the electrostatic repulsion between the membrane surface and NOM decreases. At the same time NOM molecules can adsorb easily at the membrane (pores and surface) and therefore can contribute to fouling formation (Saravia et al. 2006). Suspended particles build up a cake on the membrane surface, which can increase the resistance to the water flow.

The filtration of river water without PAC (Figure 6, in grey) showed a wide distribution of pressure values within the filtration interval. During the filtration interval, raw water particles build up a cake layer on the membrane surface, which can be only partially removed with backwashing. As a consequence the TMP data in Figure 6 appear as a wide curve.

The fouling layer after the filtration experiment with Picachem 8P was very dense (thickness about 30 μm), as demonstrated in SEM-pictures of the surface and cross-section of the fouling layer. In addition, the layer had a defined structure presenting an enrichment of small particles on the membrane surface (Figure 7, left). In submerged modules, the vacuum at the permeate side is responsible for the filtration. Small particles can be more easily carried by the flow to the membrane surface than bigger particles can. The mean particle size of Picachem 8P was 9.5 μm with a relatively narrow particle size distribution. The particles attached to the membrane surface had a size smaller than 2 μm. Fu & Dempsey (1998) and Meng et al. (2007) suggested that small particles can accumulate on the membrane surface, whereas big particles can be easily removed by the shear forces of air bubbling in membrane bioreactors. The structure of the fouling layer is influenced by both negative pressure (vacuum) and air bubbling.

The experiments with Norit SA-UF presented an entirely different structure of the fouling layer. The layer was much thicker (60 μm) but at the same time it was more porous and channels were observed within the fouling layer structure (Figure 7, right). There was no sign of a clear particle pattern.

**CONCLUSIONS**

The selection of the type of PAC is a main factor for the overall performance of PAC-UF hybrid systems with submerged membranes.
The addition of PAC can either contribute to fouling formation and permeability decline or improve membrane performance, depending on the PAC properties.

The application of Norit SA-UF improved the membrane performance independently of the water matrix. On the other hand, the use of Picachem 8P caused a clear deterioration of membrane performance. The permeate flux in the experiments with Picachem 8P declined much more than in the experiments without PAC.

It can be concluded that PAC particles influence membrane filtration in different possible ways:

(a) PAC abrasivity can partially remove the fouling layer.
(b) Organic substances (e.g. NOM, organic pollutants) absorb on PAC and hence reduce the fouling potential of the raw water. However, interactions between NOM and PAC particles can increase fouling and therefore counteract the positive effect of PAC-addition, if PAC particles contribute to fouling in the hybrid system as observed for Picachem 8P.
(c) PAC particles can form a more or less permeable fouling layer depending on water and carbon properties.

It is obvious that particle size and particle size distribution cannot be taken as the only parameters to explain the clear differences in the fouling layer structure and permeability of the PACs used, since both parameters were very similar. Other PAC properties such as particle charge and PAC structure play a fundamental role in the performance of PAC-UF hybrid systems.

In PAC-UF hybrid systems equipped with submerged membrane modules, the influence of particles on fouling formation can be reduced. The influence of NOM cannot be avoided. However, membrane fouling in hybrid systems can be reduced considerably by choosing suitable types of PACs. In the case of complex water matrices, systematic model experiments are still recommended to avoid major pitfalls in large-scale process design.

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