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Submicron powdered activated carbon used as a pre-coat in ceramic micro-filtration

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ABSTRACT

The aim of the research is to show the benefits of the use of submicron powdered activated carbon (SPAC) in combination with ceramic microfiltration. The SPAC is applied to the surface as a pre-coat layer. The goals are to improve the removal of NOM and organic micro-pollutants. The SPAC pre-coat layer is also used to reduce fouling of the microfiltration membrane (without the use of a coagulant). Additionally, virus removal might be increased by the SPAC-layer. The results are presented from laboratory scale experiments with flat sheets membranes and from pilot experiments with a ceramic membrane module. The laboratory scale experiments show good results for NOM-removal and atrazine removal. Although the empty bed contact time is very short (<1 s), actual breakthrough curves are observed for these two components. The small particle size is beneficial for the adsorption kinetics of the components. In laboratorys' experiment, the SPAC also contributed to physical removal (straining) of biopolymers during the filtration of surface water. Because these biopolymers are removed before they can reach the membrane surface, we expect that the fouling of the ceramic membrane will decrease. However, we could not confirm this in pilot experiment because the SPAC layer did not evenly coated the membrane surface or the SPAC was already flocculated before being dosed to the membrane.

Keywords: Ceramic membranes; Powdered activated carbon; Micro-pollutants; Pre-coat

1. Introduction

Ceramic membrane filtration is promising technique to treat raw surface water [1]. Microfiltration membranes are very robust, have a low fouling tendency, and their chemical resistance is very high so chemically cleaning is not a problem. The backwash velocity can be very high (pressure during backwash about 5 bar). The porosity of the membrane is very high so the specific flux (permeability) of a clean microfiltration membrane is between 1000 and 2000 $l/(m^2 .\ bar)$. The operating flux is in most cases at least twice as high as the operational flux of polymeric UF and MF systems [1]. With the decreasing costs of ceramic membrane manufacturing the technique becomes more and more feasible for drinking water production. For instance, there have been 76 full scale plants installed in Japan with a total capacity of 158,000 m^3/d by Metawater Co., Ltd. (former NGK).

Because of the very high-backwash velocity it is possible to combine ceramic membrane filtration with powdered activated carbon filtration. Matsui [2] first investigated the use of submicron powdered activated carbon. Submicron powdered activated carbon (SPAC) is well retained by the microfiltration membrane (0.1 micron pore size). In a batch experiment Matsui found that the submicron PAC (average size 0.8 micron) removed more NOM compared to the normal PAC (average size 33 micron). The advantage of SPAC is probably the faster

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adsorption kinetics due to the smaller grain size. But also the adsorption capacity can be increased due to decreased pore blocking [3]. In this study the SPAC is also used as a pre-coat to protect the membranes from fouling. Galjaard [4] used diatomeus earth in order to improve the backwash of ultafiltration. The mechanism is probably that the foulant is adsorbed or attached to the pre-coat before it can reach the membrane. This study investigates the application of submicron-powdered activated carbon (SPAC) as a pre-coat on a ceramic membrane. An additional advantage from a pre-coat application is that the thin layer can act as an adsorption column and in this way the disadvantage of a batch adsorption process is avoided. In a batch process the effluent concentration is always the equilibrium concentration of the batch. Lower concentrations are only possible by dosing more powered activated carbon to the batch process. In a column process, very low concentrations are possible depending on the breakthrough curve an adsorbate (NOM or micro-pollutant). A large part of the column is loaded to equilibrium with the influent concentration, so the loading of the activated carbon is higher than in a batch process. Although the contact times are very short in the thin layer on the membrane surface we expect real breakthrough behaviour of adsorbates because the adsorption kinetics in submicron PAC is very fast.

To summarise we expect to establish a number of goals with the dosing of SPAC as a pre-coat on ceramic membranes:

- A better removal of natural organic matter (NOM)
- A better removal of organic micro-pollutants
- A better removal of viruses
- A fouling protection of the membrane by the pre-coat

In this paper we present the results of the experiments investigating the first two goals. The removal of NOM and micro-pollutants was investigated at lab-scale with a flat sheet membrane and the removal of NOM also in a pilot experiment with a monolith ceramic membrane.

2. Materials and methods

The normal powdered activated carbon (NPAC) used for these experiments was NORIT SX ultra, a PAC with already small particle size ($d_{10} = 5$; $d_{50} = 25$ and $d_{90} = 100$ um). This PAC was pulverized during 15 hours in a flow-through ball mill in order to produce the sub micron powdered activated carbon ($d_{10} = 0.3$; $d_{50} = 0.8$ and $d_{90} = 1.7$ micron measured with a Coulter LS 230). Both samples were stored as a concentrated suspension. The pH of the suspension was about 7.

Delft Canal water was used for all the experiments, with a TSS of 25 mg/l, a TOC of 15 mg/l, a UV_{254} absorbance of 0.5 cm^{-1}, and a SUVA of 3.3 L/mg-m. The water was pre-filtered through a 0.45 micron cellulose filter to remove the largest particles. All experiments shown in one graph are measured with the same batch of surface water. An Amicon unstirred cell was used to conduct the batch experiments. A PVDF 0.1 micrometer flat sheet membrane filter with a diameter of 58 mm was used in this cell. All filters were soaked for 24 hours in Milli-Q water before the experiment. The flux was measured with an electronic balance and the flux was maintained constant by increasing the pressure manually. The SPAC or NPAC is dosed in milli-Q at the start of the experiment. After the PAC layer is filtered on the membrane surface the addition of pre-filtered surface water starts. The transmembrane pressure is measured as a function of time Samples are taken from the permeate for analyses of DOC, UV and atrazine.

In Fig. 1, a schematic drawing of the pilot plant is shown. The plant is operated at a constant flux of 150 l/m^2.h. The membrane module used was a monolithic ceramic membrane provided by Metawater with 55 channels per module. The total membrane surface area is 0.4 m^2 and the pore size 0.1 μm. The pilot plant is operated in a dead-end mode. The PAC is dosed before the feed pump during the first 4 minutes of the filtration cycle. The trans membrane pressure (TMP) was measured as a function of time. Samples were taken from the permeate.

3. Results and discussion

In Fig. 2 the DOC concentration in the permeate is shown in time, relatively to the DOC concentration in the feed water for the two powdered activated carbons. In both cases a flux of 150 l/m^2.h was used and the PAC-dosing was 70 mg/L produced permeate but dosed as a pre-coat at the beginning of the filtration. The SPAC performed a little bit better probably because of the faster adsorption kinetics.

With the same operational conditions the removal of atrazine was measured (Fig. 3). The feed concentration of atrazine was 100 μg/L. It is clear that the atrazine removal in the layer with SPAC is much better. Although the contact time is very short (<1s) we observe an actual breakthrough curve of the atrazine in the SPAC layer. In surface water the concentration of micro-pollutants is most of the time 100 times lowerand we expect that micro-pollutants like atrazine are removed to the full extent during a filtration cycle of 60 minutes even at a lower SPAC dosing.

If we compare the NOM-removal in the flat sheet laboratory set-up with the NOM-removal in the pilot installation (Fig. 4) we observe that the NOM-removal with the flat sheet membrane is much better compared to the NOM-removal in the pilot equipment. We can regard the experiment with the flat sheet membrane as

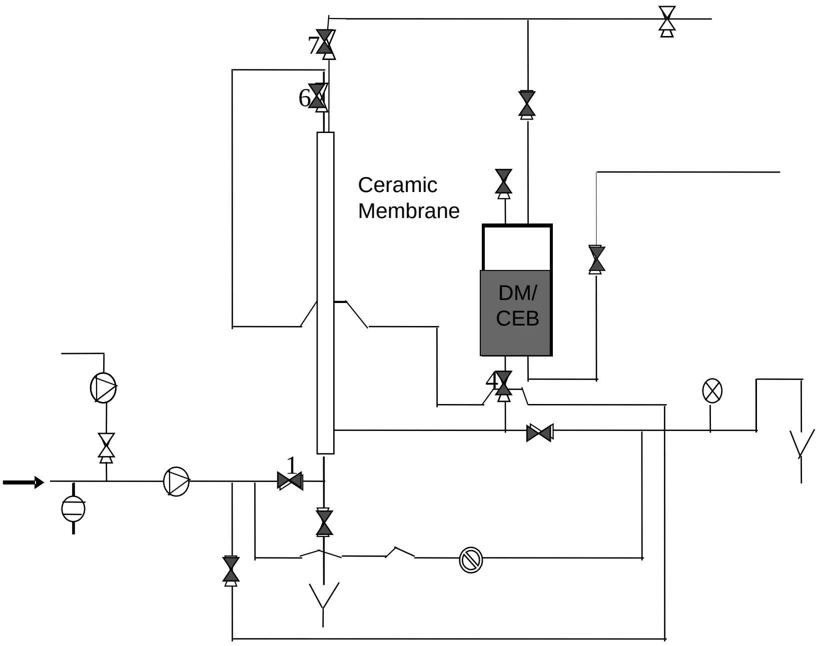

Fig. 1. Pilot plant set-up with a ceramic membrane microfiltration membrane of 0.4 m^2.

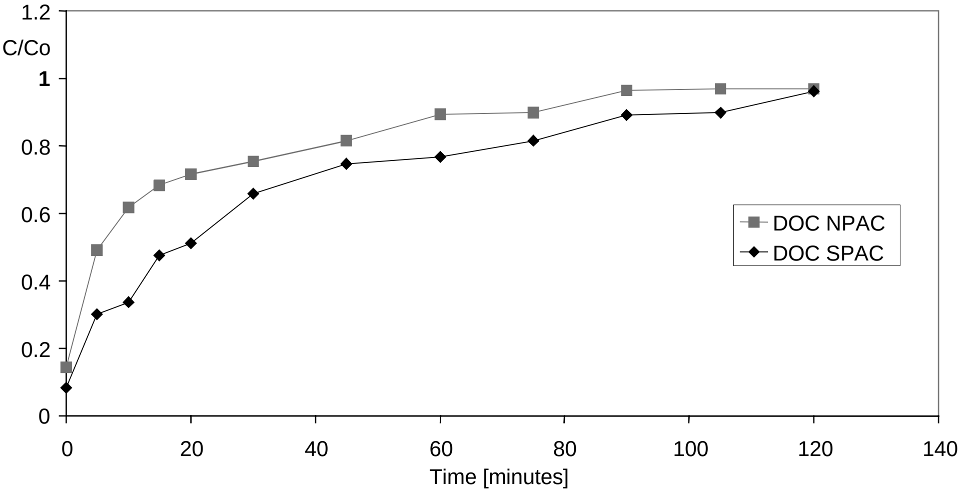

Fig. 2. DOC breakthrough curve with normal powdered activated carbon (NPAC) and sub micron powdered activated carbon (SPAC).

the most ideal situation: the SPAC is dispersed well just before dosing and the SPAC is evenly distributed over the membrane surface. The situation in the pilot plant is less ideal: The SPAC may be flocculated to larger aggregates and/or the SPAC is not evenly distributed over the membrane surface.

Because of the problems with the application of the pre-coat in the pilot plant we were not able to perform fouling experiments. In a flat sheet system we cannot observe fouling because there is no backwash and no conclusions are allowed about the irreversible fouling (i.e., the fouling that is not removed by the hydraulic backwash). Nevertheless the results in the flat sheet system indicate that some foulants are removed in the SPAC layer. In Fig. 5, we see a large increase in resistance during filtration of the PVDF-membrane with an SPAC layer on top of it. The resistance increase does not increase in the case of no PAC-layer and is very limited in the case of the NPAC layer. The explanation is probably that the NOM-colloids or NOM-biopolymers are well removed in the SPAC-layer, blocking the pores in the SPAC layer and increasing the resistance in the

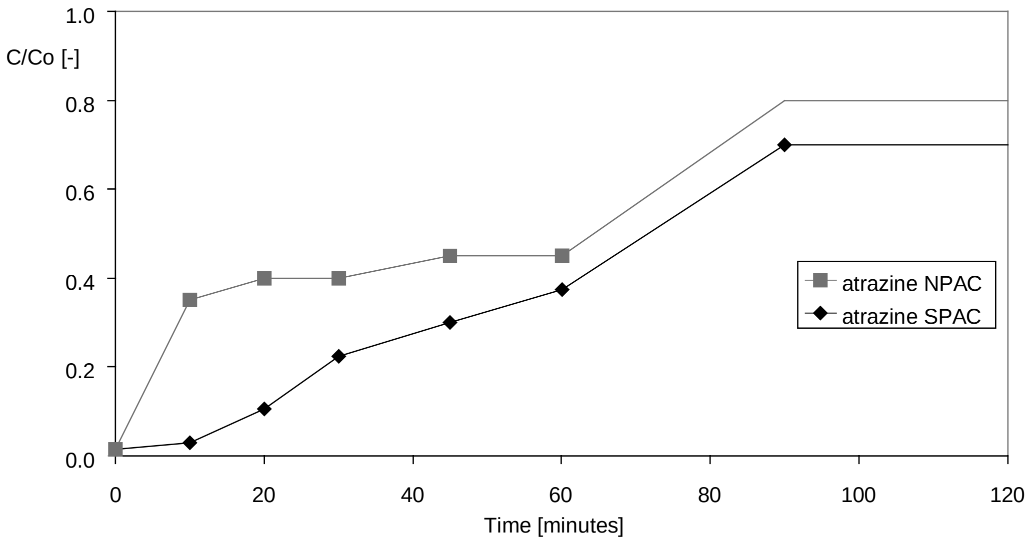

Fig. 3. Atrazine breakthrough curve with normal powdered activated carbon (NPAC) and sub micron powdered activated carbon (SPAC).

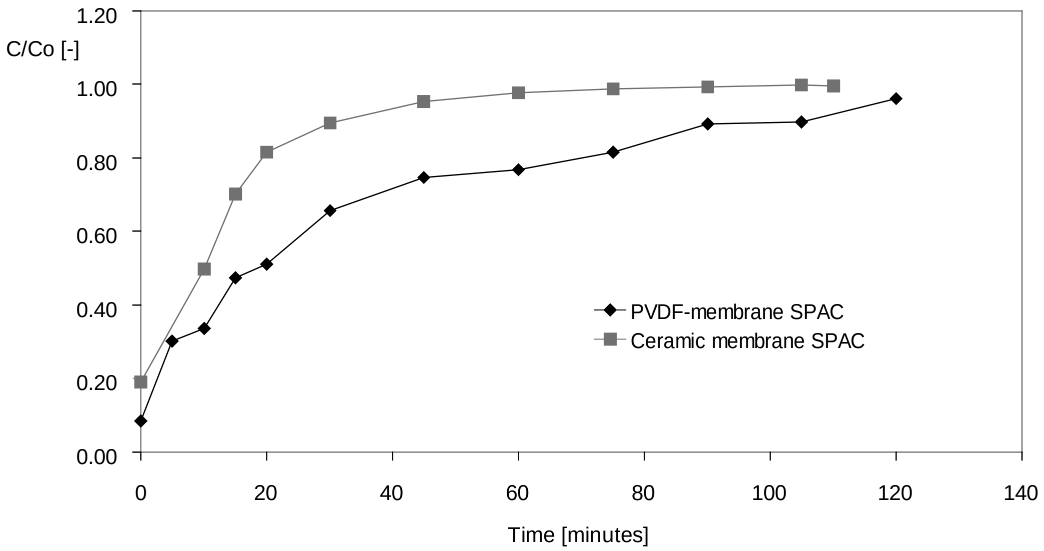

Fig. 4. NOM breakthrough curve with SPAC in the flat sheet laboratory experiment and the pilot experiment with ceramic membranes. SPAC-dose is 70 mg/L produced water (but dosed as a pre-coat).

SPAC layer. These fouling components are removed with every backwash and are probably not fouling the membrane itself. Also with LC-OCD analysis, the breakthrough of different NOM-fractions is measured. It appeared that the biopolymers (MW>20000 Dalton) were removed very well by the SPAC-layer and not by the NPAC layer. These biopolymers are regarded as the most important fouling compounds of MF/UF membranes fed with natural waters[5]. Removing biopolymers will decrease the fouling in ceramic membranes systems only when SPAC is evenly distributed over the membrane surface and the SPAC is well dispersed.

4. Conclusions

The application of submicron powdered activated carbon (SPAC) is investigated in some preliminary experiments. Submicron powdered activated carbon is dosed as a pre-coat to the membrane in the first minutes of the filtration cycle. A layer of SPAC on a microfiltration membrane acts as an adsorption column. Although the

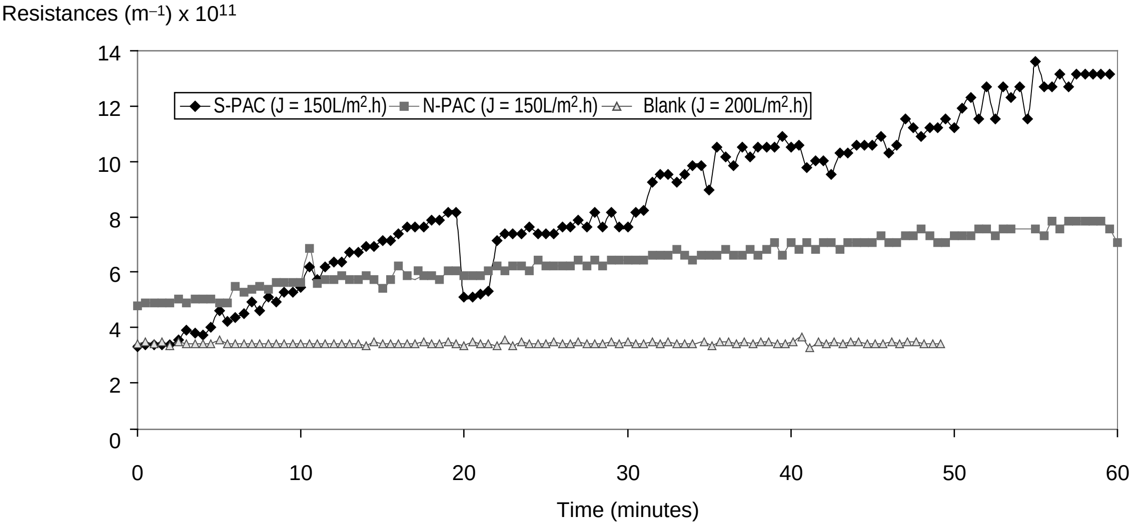

Fig. 5. Constant flux experiments (without PAC layer; with NPAC-layer and with SPAC-layer).

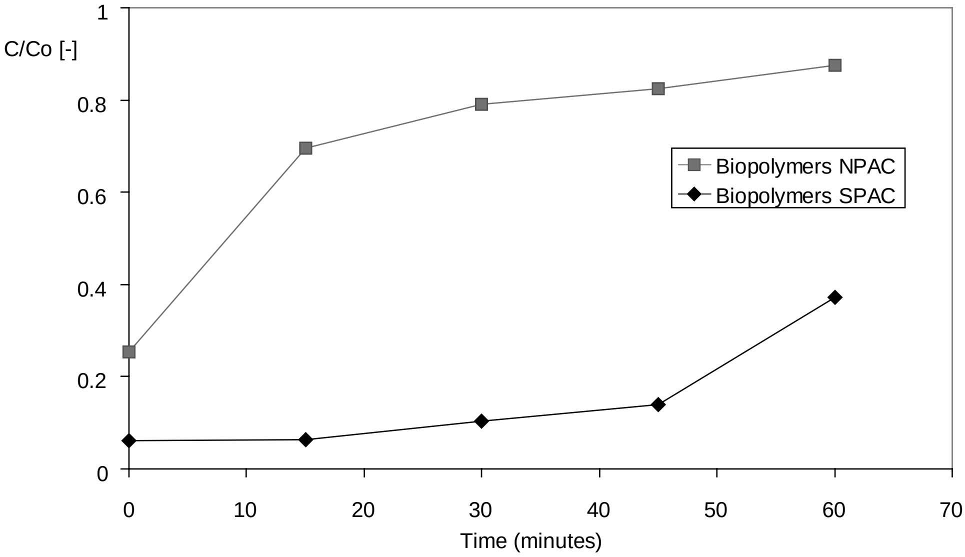

Fig. 6. Breakthrough of biopolymers (measured with LC-OCD).

empty bed contact time is very small (<1 sec) a breakthrough curve is observed for both the removal of natural organic matter and atrazine. The adsorption kinetics in the layer are very fast and the pre-loading with natural organic matter is not a problem because the layer is removed with every backwash (e.g. every hour). SPAC shows better adsorption properties compared to normal powdered activated carbon. The removal of NOM slightly increased. But the removal of atrazine is substantially improved with SPAC.

In the pilot plant the removal of NOM is less efficient with the same SPAC dosing. This can be explained by either an uneven distribution of the SPAC layer on the membrane surface or the formation of aggregated PAC in the dosing vessel of SPAC. The application of the precoat on the membrane surface must be improved before fouling experiments with the pilot plant can start.

With a flat sheet membrane the SPAC layer showed an increase of the resistance during filtration of surface water. Also biopolymers were removed to a large extent in the SPAC layer. Because biopolymers are regarded as the main fouling component in micro- and ultra-filtration we expect that a proper SPAC layer in the pilot plant will reduce fouling in the ceramic membrane installation.

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