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Cake layers and long filtration times protect ceramic micro-filtration membranes for fouling



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Introduction

The objective of this research was to decrease membrane fouling of a ceramic microfiltration system and at the same time increase the recovery. A conventional operation in micro- and ultrafiltration is an in-line coagulation and a frequent hydraulic backwash. The idea about these frequent backwashes is to limit the accumulation of fouling on the membrane. But the cake layer of iron or alum flocks can also protect the membrane for pore blocking and a frequent backwash can expose the membrane for particles that cause pore blocking. The frequent backwash is also using a lot of permeate. In this way the net flux is lower than the actual flux and the recovery can be as low as 60 to 70%. In this research it was hypothesized that this cake layer worked as a membrane protecting layer and was accumulating on the top of membrane by long filtration backwash intervals (>6 hours). Also a layer of powdered activated carbon was put on the membrane at the start of a filtration cycle (pre-coat) and combined with an iron coagulation.

Numerous research show that coagulation was one of efficient pre-treatment for low pressure membrane. Coagulation has two positive contribution aspects for the downstream membrane filtration. 1. Remove some part of dissolved compounds which low pressure membrane can't remove by itself. 2. Decreasing membrane fouling by aggregating the small particles into big particles to avoid membrane pore blocking. Coagulation effectively removes hydrophobic organics and high molecular weight of hydrophobic compounds.

The main membrane fouling related particle after coagulation pre-treatment colloids with the size between 100kDa and 1um. The particles which are larger than 1um after coagulation were not contributing to the hydraulic irreversible fouling of the membrane. Oppositely, the "large" flocks formed during coagulation were decreasing membrane fouling.

Nevertheless, all positive effects of coagulation were investigated under operating conditions with frequently back wash. The possible positive effect of a cake layer in the long filtration intervals still a question need to be answered. The long filtration intervals could lead to thicker cake layer, which could reinforce



the neutral hydrophilic colloids removal. The long filtration intervals could also increase membrane permeability recovery during an hydraulic backwash. However, the membrane cake layer fouling can also increase the trans membrane pressure because of the resistance in the cake layer itself.

In this research, the membrane filtration was carried out to investigate the combination of cake layer and membrane, instead of only the membrane. The coagulation was optimized with the focus of limiting cake layer resistance and enhance the cake layer protection effect. Also the combination with a powdered activated carbon (PAC) pre-coat layer was tested. The PAC-precoat has a multiple purpose: It protects the membrane for fouling but also organic substances like DOC and organic micropollutants are removed.

Material and method

Canal water (Schie canal, Delft, The Netherlands) was used as the feed water in this research. To make the same water quality in each experiment, 1000L canal water was stored and used during the experiment. Under-pressure membrane filtration was used at a constant flux (60 l/(m^2.h)) . Kubota ceramic membranes with 0,1 micron pore size were used. Proper coagulation/flocculation (fast mixing slow mixing) was used prior to the membranes. The flocks were not removed before membrane filtration. The coagulation-unit was composed of coagulant injection point part, static mixing part, tubing fast coagulation part and tubing flocculation part (Fig 1.). $FeCl_3 \bullet 6H_2O$ was used as coagulant with 8mg/l Fe^{3+} concentration in the coagulation process. The PAC was pre-coated on the surface of membrane before filtration test. A flocks cake-layer was accululating on the PAC-precoat layer during the filtration process.

Results and discussions

Coagulation conditions are affecting the hydraulic cake layer resistance. From coagulation theory we distinguish different coagulation zones which are depending on pH and coagulant dose. The hydraulic cake layer made in the sweep coagulation zone (pH=4) has the lowest cake layer resitance (figure 2). The TMP reached -0.6 bar after 15 hours membrane

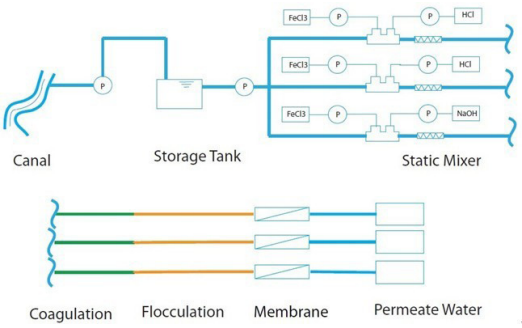


Figure 1 - Experimental setup.

filtration. The cake layer made in the adsorption destabilization zone (pH=8) has probably also an open structure which resulted in a TMP of -0.6 bar after 11 hours. The most dence cake layer occurred in the restabilization coagulation zone (pH=6). The TMP reached -0.6 bar already after 4 hours. With the same canal water quality, the same membrane materials, the same coagulant, the difference in performance was notable. In the sweep coagulation zone, the hydraulic cake layer help ceramic micro membrane filtrated about four times more canal water than with the cake layer protection from restabilization zone.

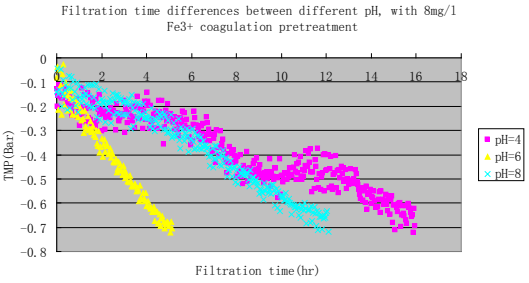


Figure 2 - Different membrane fouling performance in different coagulation mechanism conditions.

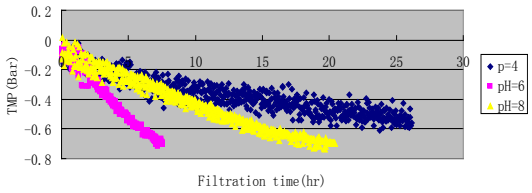


Figure 3 - Filtration time differences at different pH, with PAC precoating and 8mg/l Fe-coagulant dose.

With a PAC pre-coating combined with iron coagulation the total resistance increase was even less than with only iron coagulation (figure 3). The resistance increase in the combined cake layer was in a similar way influenced by coagulation mechanism conditions. The TMP reached -0.6 bar after 25 hours, 15 hours and 5 hours, within restabilization coagulation zone (pH 4), sweep coagulation zone(pH 8), and adsorption destabilization zone (pH 6).

The PAC was pre-coated on the top of the membrane at the start of a filtration cycle. This pre-coated PAC layer combined with Fe-coagulant dose had the best performance with respect to increase in cake layer resistance. During the first three hours the TMP-increase was showing some charactewristics of pore blocking: a fast increase of the TMP. After 3 hours the resistance increase was relatively slow at pH 4 and 6 indicating that only cake filtration occurred.

DOC was removed by coagulation and by the PAC-layer. The removal by the coagulation was constant during the experiment. The PAC was saturated rather fast: the additional DOC removal is only limited after three hours of filtration (see figure 4).

In figure 5 the influence of the different process conditions on the maximum filtration time is summarized.

PAC is widely used in full scale plants while continuously dosed to an underpressure microfiltration system. In our research PAC was used as a precoating layer. These two different dosing operations were compared in one experiment (figure 7). In both cases the same amount of PAC was used. In the case of a pre-coat the amount for 6 hours was precoated on the membrane at the start of the filtration cycle. In the case of the continuous dosing the PAC was dosed at the same place as the iron coagulant. The iron dose was 8 mg/l.

It is clear that the pre-coat is protecting the membrane for foulants because the backwash after 6 hours is almost 100% effective while the backwash of the continuous mode is nopt effective at all. The TMP is not recovering in the continuous mode.

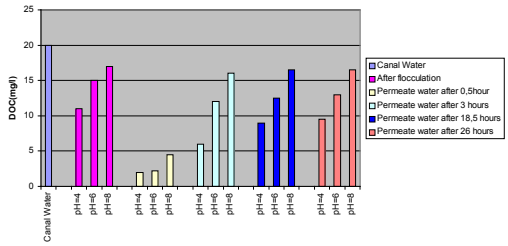


Figure 4 - DOC concentration during the different treatment areas and process time, with 20mg/l PAC precoating and 8m/l Fe^{3+} coagulation-flocculation pretreatment.

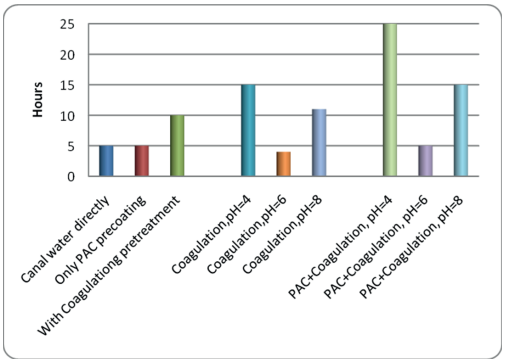


Figure 5 - Filtration time until the TMP reached -0.6 bar with different operation conditions.

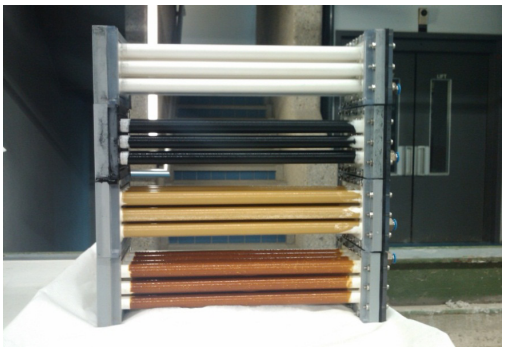


Figure 6 - Blank membrane, precoated PAC membrane, fouled membrane without coagulation pretreatment, Fe-coagulation cake layer. (From the top).

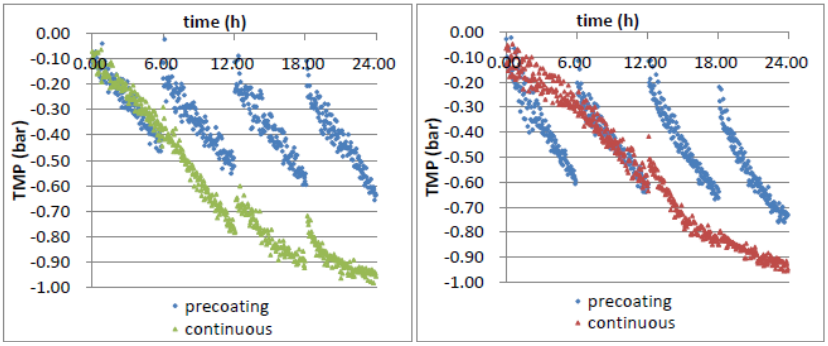
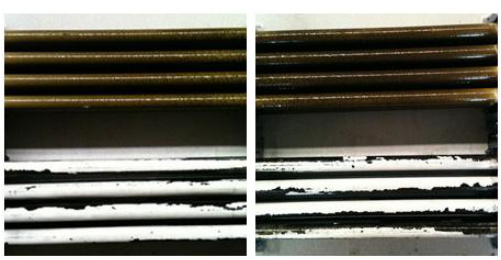


Figure 7 - Filtration/backwash cycles comparing PAC precoating and PAC continuously dosing.

According to the above figures, it is observed that precoating PAC operation got a stable TMP increasing every membrane filtration cycle. There is no hydraulicaly irreversibable fouling observed. The cake layer formed with continuously dosing of the PAC was difficult to backwash. This layer resulted in a continuous TMP increasing and very large hydraulically irreversible fouling. The explanation is that the mixed layer of PAC/ironhydroxide/foulants is attached stronger to the membrane wall than the PAC layer in the case of a precoat. The pictures after backwashing show that in the case of a precoat the membrane is much cleaner than in the case of the continuous dosing (figure 8). The combined PAC/coagulant/foulants layer is a slimy layer on the membrane which is not coming of during a hydraulic backwash.



Backwash after 18 hours Backwash after 24 hours

Figure 8 - Membrane surfaces after a hydraulic backwash. PAC precoating dosing (below) and PAC continuously dosing (top).

Conclusion

- By controlling the coagulation conditions the filtration time can be extended to 15 hours (pH4) and 12 hours (pH8)
- Coagulation zones highly determine cake layer resistance. At pH 6 the cake layer is very dense. Whereas at pH 4 and pH 8 results in permeable cake layers.
- If a precoat of PAC is used the same mechanisms occur.
- The advantage of a PAC-precoat is a more effective hydraulic backwash.
- The combined PAC/coagulant/foulants layer is a slimy layer on the membrane which is not coming of during a hydraulic backwash.