Membrane fouling during the filtration of swine manure pretreated by flocculation using cationic polymer

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Abstract
Swine wastewater (SW) treatment by reverse osmosis (RO) filtration requires the application of efficient manure pretreatments. Flocculation using cationic polymers improves suspended solids (SS) removal, but residual polymer in the liquid fraction may cause severe membrane fouling. This study investigated the effect of residual polymer in SW on the fouling of an RO membrane. The effects of residual SS, polymer charge density (CD) were investigated. Permeate flux tended to be lower when the SW contained both residual polymer and SS. Water flux recovery of the fouled membrane was lower for tests with than without polymer, and fouling tended to be higher with the low than the medium CD polymer. The fouling was reversible as chemical cleaning gave complete recovery of water flux. The RO membrane could thus be used in conjunction with a flocculation pretreatment without the polymer causing excessive fouling.

Introduction
The use of reverse osmosis (RO) filtration to concentrate manure nutrients in small volumes can improve the recycling of nutrients from livestock production as it facilitates the transport of the nutrients to agricultural areas with low livestock density. However, efficient pretreatment of the raw manure to remove most of the suspended solids (SS) is required prior to membrane filtration [1]. Manure flocculation using cationic polymers significantly increases the SS removal efficiency of solid-liquid separators, [2], making it a viable choice of pre-treatment for RO filtration. Polymer chains adhere to SS during flocculation and are removed with the solid fraction during the separation step. However, some free polymer chains and small particles coated with polymer may remain in the liquid fraction and cause excessive fouling of the membrane. Most membranes have a residual negative charge, which favours the attachment of cationic polymer to the membrane surface [3]. Masse et al. [4] reported a detrimental effect on nano filtration (NF) and RO membrane performance when a cationic polymer was used as a pretreatment for liquid swine manure. Previous studies concluded that the presence of residual polymer caused membrane fouling and stressed the importance of optimising polymer dose to the requirement of the effluent being treated as to minimize residual polymer in solution [4, 5]. The degree of membrane-polymer interaction, and thereby the severity of fouling, is expected to depend on the concentration of residual polymer as well as the characteristics of the membrane, the polymer and the liquid being treated. This study investigated the effects of residual SS and polymer concentration in solution as well as polymer charge density (CD) on the fouling of a RO membrane processing swine wastewater (SW).

Materials and Methods
Experimental procedures
Swine manure was first pretreated by a mechanically based solid-liquid separator, which yielded a liquid fraction (LF) containing 669 mg L^{-1} SS on average. Part of the LF was passed through an ultra filtration (UF) membrane to produce an UF permeate (UFP) without SS but with the same level of dissolved species and conductivity as the LF. Two polymers were evaluated, Superfloc-C492 (CD10) and Superfloc-C496 (CD35) (Kemira, Québec, Canada). The polymers were both high molecular weight, linear, cationic polyacrylamide polymers with CD of 10% and 35% for the CD10 and CD35 polymer, respectively. Optimum doses to flocculate swine manure having SS concentrations ranging from 29 to 106 g L^{-1} averaged 30 ±6.2 and 69 ±12 mg L^{-1} for CD10 and CD35, respectively [6]. In this study, CD10 and CD35 were added in doses of 0, 5, 10 and 20 mg L^{-1} to the LF effluent. The CD10 polymer was also added in doses of 0, 20 and 40 mg L^{-1} to the UFP effluent. Polymer was added to 500 L of LF or UFP. Spiked effluents were processed using a low fouling, spiral-wound RO

membrane (LCF3-LD Hydranautics) fitted to the semi commercial RO pilot described in [7]. Tang et al [8] measured a zeta potential between -5 to -4 mV at pH 5.5 to 10 for this membrane type. The feed was first concentrated by a factor of 2.5 by removing 300 L of permeate and then filtered continuously for a total processing time of 6 h. Transmembrane pressure was increased from 17.2 to 37.9 bar in the initial 40 min, and the SW was subsequently filtered at constant pressure and temperature (21.0°C ±0.3°C). The pH was kept at 7.5±0.1 by adding sulfuric acid (36 N). After each filtration cycle, the membrane was cleaned with an EDTA-STPP alkaline solution and a citric acid solution. During filtration, permeate flux across the membrane was continuously measured with an impeller flow meter (FPR301, Omega Engineering Inc.). Tap water flux through the membrane was measured before and after each filtration cycle as well after chemical cleaning. All water flux measurements were made at a pressure of 20.7 bar with tap water, with an average conductivity of 490 µS, adjusted to a temperature of 20.3°C.

Data Analysis

Fouling intensity was evaluated by comparing permeate flux during manure filtration and measuring water flux recoveries for the fouled and cleaned membrane. The initial 4 cycles performed were not included in the analysis of permeate and water flux because large losses in flux were partly due to membrane compression and fouling of vulnerable sites upon initial use of a new membrane. Permeate flux was compared by averaging the flux between 3 and 6 h of continuous filtration at constant conductivity.

Significant differences between the individual tests were determined using the General Linear Model and Tukey's HSD test modules in SPSS Statistics 20 for Windows (IBM 2012) ($p < 0.05$).

Results and Discussion

Permeate flux

With the LF effluents, containing an average of 669 mg SS L^{-1}, residual polymer in solution had no significant effect on permeate flux during filtration (Table 1). However, permeate flux was consistently lower for LF effluents with polymer than without polymer. There were no significant differences in average permeate flux between the low and medium CD polymers or between the three tested doses for each polymer. For the UFP effluent, containing no SS, adding 20 mg L^{-1} of CD10 polymer only yielded a reduction of 6.8% in permeate flux compared to filtration without polymer and the reduction was not significant. Furthermore, a single run at 40 mg L^{-1} resulted a permeate flux slightly higher than the average found for the UFP without polymer. Higher flux was measured with the UFP than the LF effluents, but the difference was not significant and was probably due to a lower conductivity of the UFP (43.6 mS) than LF (47.0 mS) concentrated effluent, resulting in a lower osmotic pressure.

With polymer added, the observed decreases in permeate flux for the LF effluents may be due to formation of a slightly denser fouling layer in the presence of residual cationic polymer as reported by [9]. However, very little effect was observed on permeate flux during filtration and an accelerated fouling of the membrane as observed by [4] was not found in this study. A liquid fraction containing residual SS and polymer constitutes the most likely on-farm scenario but the LFC3 membrane appeared to have been relatively resistant to fouling by cationic polymer, maybe because of its low residual charge at the surface. It should also be noted that the tested doses represented a severe overdosing of the polymer. The 20 mg L^{-1} dose represented 67% and 29% of optimum doses for the CD10 and CD35 polymer respectively [6]. As no effect of dose was found, it therefore appears that the LFC3 membrane, though to a certain extend affected by the polymer, would be resistant to overdosing.

Waterflux recovery

At all doses, water flux recovery of the fouled membrane was lower when CD10 was added to the feed than without polymer (Table 1). The reduction was significant for the 5 and 10 mg L^{-1} only. The addition of CD35, on the other hand, had no significant effect on flux recovery of the fouled membrane.

Table 1. Average permeate flux between 3 and 6 h of filtration and average tap water flux recovery (Standard deviations in brackets). Within rows, values with the same letter are not different at $p \leq 0.05$ using the Tukey's HSD test.

Feed	Polymer	Dose mg L^{-1}	n	Permeate flux L m^{-2} h^{-1}	Water flux (% of initial flux) fouled membrane	Water flux (% of initial flux) cleaned membrane
LF	-	0	2	9.9 (0.6)^{abc}	84.2 (2.1)^{cd}	100.7 (0.2)^{a}
	CD10	5	2	8.3 (0.4)^{a}	74.7 (0.7)^{ab}	99.9 (0.0)^{a}
	CD10	10	2	8.9 (0.1)^{a}	68.9 (4.9)^{a}	98.2 (1.0)^{a}
	CD10	20	2	8.8 (0.6)^{a}	76.4 (1.4)^{abc}	99.0 (4.5)^{a}
	CD35	5	2	8.6 (0.9)^{a}	84.3 (0.6)^{cd}	100.9 (1.9)^{a}
	CD35	10	2	8.8 (0.6)^{a}	81.1 (0.6)^{bcd}	99.4 (0.9)^{a}
	CD35	20	2	9.1 (0.0)^{ab}	82.6 (3.3)^{bcd}	100.0 (0.7)^{a}
UFP	-	0	2	12.0 (0.3)^{c}	84.7 (2.0)^{cd}	100.3 (0.4)^{a}
	CD10	20	2	11.2 (0.6)^{bc}	86.0 (0.6)^{d}	100.6 (0.2)^{a}
	CD10	40	1	12.3 (-)	87.0 (-)	100.3 (-)

Water flux recovery for the fouled membrane was consistently lower with CD10 than with CD35 polymer, but the difference was only significant at a dose 5 mg L^{-1} CD35. For the LFs, no difference was found between doses for either polymer. The average flux recovery of the fouled membrane was similar for UFP and LF when no polymer was added. The UFP was only tested with CD10 and the polymer did not affect water flux recovery for the fouled membrane.

Increased fouling only occurred with the LF effluents, again suggesting that the observed effect is due to the combination of polymer and SS rather than just residual polymer. Water flux recovery results suggested that the CD10 polymer had a higher fouling potential than the CD35. The CD35 polymer has more tightly spaced charges and is more likely to attach to multiple adsorption sites on one particle than CD10 [2]. In a low SS solution, this implies that CD10 polymer chains, though adhering in part to SS, may have more sections extended into solution than CD35. These may interact with residual negative charge on the membrane surface thereby attaching the fouling layer more firmly to the membrane. The low recovery of the fouled membrane water flux for CD10 supports the formation of a denser fouling layer during filtration of the LF. The fouling however was not irreversible. After chemical cleaning, water flux recovery ranged from 98.2 to 100.9% for all cycles (Table 1). The LF effluents containing CD10 tended to have lower recovery after cleaning, but the difference was not significant. Thus no significant differences were found between feed types, CD or dose implying that the fouling in all cases was reversible and the cleaning removed the polymer from the membrane surface.

Membrane aging

Water flux after chemical cleaning was compared to the initial flux measured with the virgin membrane for the LFC3 used in this study, $LFC3_{pol}$, and a LFC3, $LFC3_{nopol}$, used to process a similar effluent but without added polymer (Figure 1). Operating parameters were similar for both membranes, but the $LFC3_{nopol}$ filtered LF effluents continuously for 24 to 48 h before cleaning cycles. In the initial 6 days of SW filtration, water flux decreased to 86% of initial flux for both membranes. These 6 days only included two cycles with polymer for the $LFC3_{pol}$ and previous work suggested that the initial large flux losses may be due to membrane compression [10]. In the next 10 days of filtration, water flux decreased to 74% and 80% of initial flux for $LFC3_{pol}$ and $LFC3_{nopol}$, respectively, and remained at these levels for the next 10 and 14 days of filtration, respectively. These results suggested that residual polymer in SW accelerated the aging process of the LFC3 membrane. However, after an initial flux decline, the LFC3 membrane adjusted to residual polymer in solution. Thus long term polymer exposure may lead to a higher loss of membrane capacity but a stabilisation of membrane performance could occur over time.

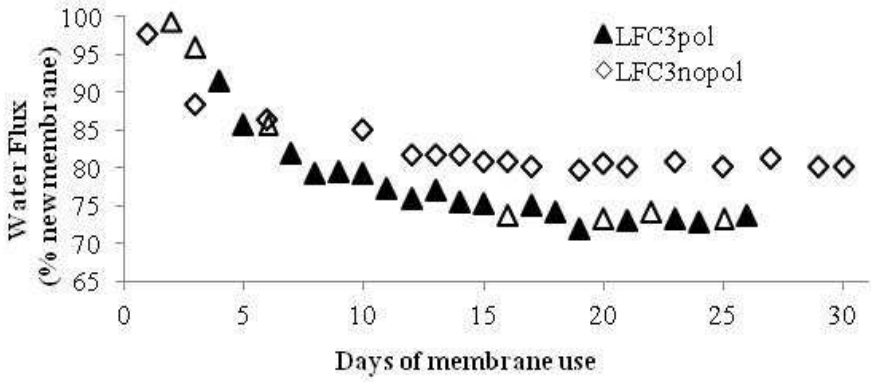

Figure 1. Water flux recovery after cleaning as percentage of the new membrane water flux for two LFC3 membranes: $LFC3_{pol}$ used in this study and $LFC3_{nopol}$ used to filter LF effluents similar to the effluent used in this study but without polymer. Empty bullets = no polymer added.

Conclusions and perspectives

Results from this study suggested that a polymeric flocculation pretreatment could be used to prepare manure for RO filtration with the LFC3 membrane. Furthermore, the system would be fairly resistant to overdosing of the flocculant. It should be noted, however, that filtration of liquids containing polymer may reduce permeate flux during filtration and appear to accelerate membrane aging.

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