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Impact of Chemical Oxidation on Sludge Properties and Membrane Flux in Membrane Separation Bioreactors

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ABSTRACT

The effects of sodium hypochlorite (NaOCl) on sludge properties and membrane permeate flux were studied using a pressurized stirred ultrafiltration cell. Oxidation with NaOCl resulted in sludge solubilization and decreased sludge floc sizes. The sludge dissolution constant was estimated at 0.3±0.1 mg sludge/mg free chlorine under testing conditions. The increases in soluble chemical oxygen demand and total carbohydrate concentration in centrifuged supernatant were less than proportional to chemical dosage. Membrane permeate fluxes were much lower as a result of oxidation. Soluble biopolymers accounted for more than 76 % of the total hydraulic resistance during ultrafiltration of oxidized sludge. By contrast, both the settleable sludge flocs and the soluble biopolymers were important contributors to the hydraulic resistance of sludge before oxidation. Given the benefits of NaOCl solution for membrane cleaning and its negative impact on sludge properties, the quantity of NaOCl solution used for maintenance cleaning of membranes should be optimized.

Keywords: Membrane Separation Bioreactors, Membrane Fouling, Chemical Oxidation, Sludge Properties, Membrane Flux

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Abstract

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Effets de l'oxydation chimique sur les propriétés des boues et sur le débit aux membranes dans les bioréacteurs à membranes

B.Q. Liao, J.J. Catalan, I.G. Droppo et S.N. Liss

Résumé

On a étudié les effets de l'hypochlorite de sodium (NaOCl) sur les propriétés des boues et le débit de perméation de membranes à l'aide d'un module d'ultrafiltration sous pression avec agitation. L'oxydation avec du NaOCl a entraîné la solubilisation des boues et la réduction de la taille du floc de boue. En conditions expérimentales, la constante de dissolution des boues a été estimée à 0,3 ! 0,1 mg de boue/mg de chlore libre. L'augmentation de la demande chimique d'oxygène soluble et de la concentration des glucides totaux dans le surnageant de centrifugation était inférieure à la valeur proportionnelle à la dose. Le débit de perméation des membranes était bien plus faible en raison de l'oxydation. Les biopolymères solubles étaient à l'origine de plus de 76 % de la résistance hydraulique totale au cours de l'ultrafiltration des boues oxydées. Par contre, avant l'oxydation, les flocs de boue décantables et les biopolymères solubles contribuaient de façon importante à la résistance hydraulique des boues. Étant donné les avantages d'une solution de NaOCl pour le nettoyage des membranes et son effet négatif sur les propriétés des boues, il y aurait lieu d'optimiser la quantité de cette solution à utiliser pour le nettoyage d'entretien des membranes.

NWRI RESEARCH SUMMARY

Plain language title

The influence of chemical oxidation on wastewater particle properties and membrane separation bioreactor performance.

What is the problem and what do scientists already know about it?

Membrane separation bioreactors are an effective way of treating wastewater. The performance of these systems is however dependent on the colloidal fraction and floc structure of the sludge. Membranes often require cleaning to maintain a high flow rate. NaOCl as an oxidant is often used as a cleaning agent.

Why did NWRI do this study?

The effects of NaOCl on sludge properties and membrane flux is not fully understood. This work was initiated to evaluate this common membrane cleaner's impact on reactor performance.

What were the results?

Membrane permeate fluxes were much lower as a result of oxidation, with soluble biopolymers accounting for more than 76% of the total hydraulic resistance during ultrafiltration of oxidized sludge. In contrast, the settleable sludge flocs and the soluble biopolymers were important contributors to the hydraulic resistance of sludge before oxidation. It was concluded that while NaOCl my effectively clean membranes, it will have a negative impact on sludge properties.

How will these results be used?

Results will be used to assist in the development of effective technologies for the treatment of wastewater.

Who were our main partners in the study?

This study is done in partnership with Lakehead University and Ryerson University.

Sommaire des recherches de l'INRE

Titre en langage clair

L'influence de l'oxydation chimique sur les propriétés des particules présentes dans les eaux usées et sur la performance d'un bioréacteur à membranes.

Quel est le problème et que savent les chercheurs à ce sujet?

Les bioréacteurs à membranes est un dispositif efficace pour l'épuration des eaux usées. La performance de ce système est toutefois tributaire de la fraction colloïdale et de la structure du floc des boues. Afin de maintenir un débit élevé, on doit fréquemment nettoyer les membranes. Le NaOCl, un oxydant, est souvent utilisé comme produit de nettoyage.

Pourquoi l'INRE a-t-il effectué cette étude?

Les effets du NaOCl sur les propriétés des boues et sur le débit aux membranes ne sont pas tous bien compris. On a entrepris la présente étude afin d'évaluer comment ce nettoyant couramment utilisé pour les membranes influe sur la performance du réacteur.

Quels sont les résultats?

En raison de l'oxydation, le débit de perméation aux membranes au cours de l'ultrafiltration des boues oxydées était bien plus faible, plus de 76 % de la résistance hydraulique totale étant causée par les biopolymères solubles. Par contre, les flocs de boue décantables et les biopolymères solubles contribuaient de façon importante à la résistance hydraulique des boues avant leur oxydation. On en a conclu que, s'il est vrai que le NaOCl peut en effet nettoyer les membranes, il a également un effet négatif sur les propriétés des boues.

Comment ces résultats seront-ils utilisés?

Les résultats de ces travaux seront utilisés pour la mise au point de méthodes efficaces d'épuration des eaux usées.

Quels étaient nos principaux partenaires dans cette étude?

La présente étude est réalisée en partenariat avec l'Université Lakehead et l'Université Ryerson.

NOMENCLATURE

A	Surface area of filtration (cm^2)
c	Solids concentration ($g\ cm^{-3}$)
J	Permeate flux ($g\ cm^{-2}\ s^{-1}$)
J_c	Permeate flux of supernatant ($g\ cm^{-2}\ s^{-1}$)
J_p	Permeate flux of soluble biopolymer solution ($g\ cm^{-2}\ s^{-1}$)
J_s	Permeate flux of activated sludge broth ($g\ cm^{-2}\ s^{-1}$)
ΔP	Trans-membrane pressure ($N\ m^{-2}$)
R_c	Hydraulic resistance caused by non-settleable colloidal particles (m^{-1})
R_m	Membrane resistance (m^{-1})
R_p	Hydraulic resistance caused by soluble biopolymers (m^{-1})
R_s	Hydraulic resistance caused by settleable sludge flocs (m^{-1})
R_t	Total filtration resistance (m^{-1})
t	Filtration time (s)
Vp	Permeate volume at time t (cm^3)
α	Average specific cake resistance ($cm\ g^{-1}$)
μ	Viscosity ($N\ s\ m^2$)

INTRODUCTION

In past decades, an important advancement in biological wastewater treatment has been the integration of membrane separation technology into the conventional activated sludge process for biomass separation. The application of membrane separation bioreactors (MSBRs) has completely eliminated the need for conventional secondary clarifiers. This novel process offers several advantages over the conventional activated sludge process, including compactness and smaller footprint, complete separation of hydraulic retention time and sludge retention time, lower sludge production, resistance to shock loading, and superior permeate quality.[1-3] However, the practical application of MSBRs has been limited by inherent membrane fouling problems, which lead to severe flux decline as well as frequent membrane cleaning and replacements.[1-7]

In MSBRs, fouling is the result of interactions between the membrane surface and components of the activated sludge broth, which consist of activated sludge flocs (settleable and non-settleable), soluble extracellular polymeric substances (EPS), and water.[8] During permeation, the mixed liquor and soluble components in water are transported to the membrane surface where concentration polarization occurs due to dewatering. The presence of soluble EPS leads to EPS accumulation on membrane and pore surfaces where both physical and chemical adsorption of EPS may occur. Because physical adsorption only involves weak interactions between EPS and membrane surfaces, physically adsorbed EPS can be partially removed by increasing the shear stress within the fluid. Chemical adsorption, however, involves stronger adhesion between the EPS and the membrane surface, and chemical agents are therefore required to clean the membrane surface. A second mechanism of membrane fouling is pore clogging, which is caused by cell debris and fine colloidal particles. During the permeation process, these fine particles with dimensions comparable to pore sizes accumulate in pores and thus reduce the membrane surface area for filtration. A third mechanism of membrane fouling is the deposition of sludge cake on the membrane surface. In

MSBRs, the concentration of mixed liquor suspended solids (MLSS) is maintained at 10-20 g/L. In regions close to the membrane surface, a concentration gradient occurs due to water suction, and the higher MLSS concentration leads to the formation of a sludge cake.[8]

While various strategies, including slug flow by aeration and backwashing, have been developed to minimize membrane fouling[8-11], periodical chemical cleaning with chlorine, acid, and base solutions is unavoidable to maintain a suitable membrane flux[12-14]. One concern associated with maintenance cleaning is the release of cleaning agents into the bioreactor, where they are in direct contact with biomass. It is anticipated that the released cleaning agents may affect the sludge properties and activities, which in turn may have an impact on the membrane flux. Furthermore, chemical oxidation (e.g., ozone treatment) has also been used in the MSBR process to minimize or reduce sludge production[15-18], but the potential impact of chemical oxidation on the performance of MSBRs is still unknown. The purpose of this study was to investigate the effects of chemical oxidation by NaOCl on sludge properties and membrane flux using a pressurized stirred ultrafiltration cell.

EXPERIMENTAL

Sludge Samples: Activated sludge samples were taken from the returning activated sludge line at the Main Treatment Plant in Toronto, Ontario, Canada. Prior to oxidation with NaOCl solutions at neutral pH, the MLSS concentration was adjusted to either 4.0±0.1 or 7.0±0.1 g/L using treated effluent from the plant to exclude the effect of concentration on the permeate flux.

Oxidation: Sludge samples were oxidized under gentle mixing with NaOCl solutions containing 0.1 and 0.3 wt % free chlorine. The required reaction time was determined at the beginning of this study, as shown in Figure 1. A 1-hour reaction time was allowed to complete oxidation.

Sludge Characterization: Sludge properties including particle size distribution, soluble chemical oxygen demand (COD), total carbohydrates, and proteins were measured before and after oxidation.

The particle size distribution of sludge flocs before and after oxidation was determined by image analysis. The measurement was based on a modified method originally developed for suspended sediments but applied to sludge flocs.[19-21] One drop (about 0.1 mL) of the sludge sample was taken using an eppendorf pipette with an open-mouth pipette tip (100-1000 μL) and mixed with 0.8 mL of low melting point agarose (0.75 % w/w) solution in a microcentrifuge tube (1.7 mL). The mixture was immediately poured into a plankton chamber. The agarose solidified in less than 1 minute. The stabilized samples were placed on a Zeiss Axiovert 100 microscope, which was interfaced with a Sony CCD video camera and a Northern Exposure (Empix Imaging, Inc.) image analysis system. Measurements were restricted to floc sizes greater than or equal to 4 μm, due to the limitation of the 50x magnification used. The floc size distribution (frequency) was calculated from a minimum of 1000 flocs in each sample.

Soluble COD before and after oxidation was determined according to Standard Water and Wastewater Analysis Methods.[22] Soluble total carbohydrates were measured using the Anthrone method and glucose as a standard.[23] Soluble proteins were determined using Lowery's method and bovine serum albumin as a standard.[24]

The MLSS and non-settleable effluent suspended solids were determined by Standard Methods.[22] The concentration of non-settleable effluent suspended solids in the supernatant was determined after the mixed liquor had settled for 1 hr.

Membrane Filtration: Batch membrane filtration experiments were conducted in a pressurized stirred ultrafiltration cell (Model 8200, Amicon, USA) at room temperature (23-25°C) with flat organic membranes (PM 30, Amicon, USA). The working volume of the ultrafiltration cell was 200 mL. The weight of permeate was recorded using a top-loading electronic balance. Trans-membrane pressure was regulated at 20 and 40 psi with nitrogen gas. The stirring speed in the ultrafiltration cell was controlled at about 250 rpm.

ANALYSIS OF RESULTS

Two different methods based on Darcy's Law and cake filtration theory, respectively, were used to calculate the filtration parameters from experimental filtration data. These two methods are presented below:

Darcy's Law: The membrane permeate flux can be described by a resistance-in-series model with the following form[7,25,26]:

$$J = \Delta P/(\mu R_t) \tag{1}$$

$$R_t = R_m + R_s + R_c + R_p \tag{2}$$

where ΔP is the transmembrane pressure, μ is the viscosity of permeate, R_t is the total hydraulic resistance, R_m is the intrinsic membrane resistance, R_s is the hydraulic resistance contributed by settleable sludge flocs, R_c is the hydraulic resistance contributed by non-settleable colloid particles, and R_p is the hydraulic resistance contributed by soluble biopolymers.

Series of batch filtration experiments were conducted with 1) the whole sludge (settleable sludge flocs + non-settleable colloids + soluble biopolymers + water), 2) the supernatant (non-settleable colloids + soluble biopolymers + water), and 3) the clean soluble biopolymer solution (soluble biopolymers + water), respectively. The supernatant was collected after the mixed liquor had settled for 1 hr. The soluble biopolymer solution was obtained by centrifugation of the supernatant at 4000 rpm for 15 minutes. Prior to the filtration experiments, the membrane was cleaned with NaOH (0.1N) and NaOCl (100 ppm) solutions. The intrinsic membrane resistance R_m was determined to be

1.6×10^{12} - 4.0×10^{12} m^{-1} by equation (1) using deionized distilled water. The other individual hydraulic resistances were then calculated from the following set of equations:

$$R_P = \Delta P/(\mu J_p) - R_m \quad (3)$$

$$R_c = \Delta P/(\mu J_c) - R_p - R_m \quad (4)$$

$$R_s = \Delta P/(\mu J_s) - R_c - R_p - R_m \quad (5)$$

where J_p, J_c, and J_s are the stable permeate fluxes of soluble biopolymer solution, supernatant, and whole sludge, respectively. Practically, J_p, J_c and J_s were determined by averaging the last 4-5 data points of each permeation experiment.

Cake Filtration Theory: In a dead-end batch filtration experiment at constant pressure drop, the relationship between the total permeate volume and time is given by[27,28]:

$$t/Vp = [\mu c\alpha/(2\Delta P\ A^2)]Vp + \mu R_m/(\Delta P\ A) \quad (6)$$

where t is time, Vp is the total permeate volume at time t, A is the membrane surface area, c is the mass of solids deposited per unit volume of filtrate, and α is the average specific cake resistance. Therefore, a plot of t/Vp versus Vp is expected to yield a straight line. The values of the parameters α and R_m can then be found from the slope and intercept of the line, respectively.

RESULTS AND DISCUSSION

Effects of NaOCl Oxidation on Sludge Properties

As shown in Figure 1, the sludge concentration decreased rapidly with the addition of NaOCl, indicating that solid sludge was oxidized into soluble biopolymers. The sludge dissolution constant was found to be 0.3±0.1 mg sludge/mg free chlorine under testing conditions. Therefore, the addition of NaOCl solution for membrane cleaning also results in sludge dissolution in MSBRs. This finding provides a partial explanation as to why the sludge yield or sludge production in MSBRs is usually lower than that in conventional activated sludge systems[3].

The impact of NaOCl oxidation on the sludge floc size distribution is shown in Figure 2. Before oxidation, more than 20% of the sludge flocs were larger than 50 μm. After oxidation, the percentage of sludge flocs larger than 50 μm decreased to 10% and 7% at free chlorine dosages of 0.1wt % and 0.3wt %, respectively. This reduction in sludge floc size with NaOCl oxidation resulted in a larger quantity of non-settleable colloids. The non-settleable colloids concentration in the supernatant increased from 20 mg/L before oxidation to 260 and 320 mg/L after addition of 0.1wt % and 0.3wt% free chlorine, respectively. Hence, chemical oxidation not only solubilizes some of the sludge, but also reduces the size of the remaining sludge flocs. These results are consistent with previously reported observations for ozone treated sludge.[17]

Figure 3 shows the impact of NaOCl oxidation on soluble COD, total carbohydrate, and protein concentrations in the centrifuged supernatant. The soluble COD and total carbohydrate concentrations increased with an increase in NaOCl dosage. However, their increase was less than proportional to the NaOCl dosage. The soluble protein concentration increased for a NaOCl dosage of 0.1wt% free chlorine, but no further increase in protein concentration was observed when the NaOCl dosage was augmented to 0.3wt% free chlorine. If all of the NaOCl had been used for sludge solubilization, a proportional relationship between the NaOCl dosage and the concentration of soluble species would be expected. Hence, the experimental results suggest that only part of the NaOCl dosage was used for sludge solubilization. The remainder of the NaOCl may have reacted with dissolved biopolymers, including carbohydrates and proteins, to convert them into mineral products, thus accounting for the fact that their concentration in solution increased less than proportionally to the NaOCl dosage. However, the percentage of free chlorine used for the oxidation of soluble biopolymers could not be reliably estimated from the available data. The results suggest that mechanisms of membrane cleaning with NaOCl involve not only the oxidation of accumulated EPS on membranes but also the dissolution of cell debris accumulated in pores and sludge cake on membrane surfaces.

Effects of NaOCl Oxidation on Membrane Flux

The permeate fluxes measured with the whole sludge, supernatant, and soluble biopolymer solution at a transmembrane pressure of 20 psi are shown in Figures 4, 5, and 6, respectively. The oxidized sludge, supernatant, and soluble biopolymer solution had a much poorer filterability than their counter parts before oxidation. These observations are likely explained by the conversion of part of the solid sludge into soluble biopolymers and the reduction in sludge floc size due to oxidation. It is well known that a reduction in sludge floc size and/or an increase in soluble biopolymer concentration result in a poorer sludge filterability. The relative contributions of each component of the activated sludge broth to the total hydraulic resistance of the broth are shown in Table 1. Before oxidation, the hydraulic resistances attributable to the settleable sludge flocs and to the soluble biopolymers accounted for 44% and 52% of the total hydraulic resistance of the broth, respectively. After oxidation, the hydraulic resistance contributed by the soluble biopolymers accounted for more than 76% of the total hydraulic resistance of the broth, while the hydraulic resistance contributed by the settleable sludge flocs was only 5-11% of the total hydraulic resistance of the broth under testing conditions. These results are consistent with the findings of Hodgson *et al.*[29], Nagaoka *et al.*[4], Ongier *et al.*[27], and Mukai *et al.*[30] in that soluble extracellular polymers play an important role in membrane fouling.

Only slight decreases in permeate fluxes were observed for oxidized sludge, supernatant, and soluble biopolymer solutions when the NaOCl dosage increased from 0.1 to 0.3 wt % free chlorine (Figures 4, 5 and 6). The corresponding increase in total hydraulic resistance of the broth from 20.7

x 10^{12} to 25.6 x 10^{12} m^{-1} (Table 1) was moderate, even though the soluble COD concentration (which is the main contributor to total hydraulic resistance) almost doubled from 790 to 1390 mg L^{-1} (Figure 2). The smaller relative increase in total hydraulic resistance compared to soluble COD concentration with NaOCl dosage is consistent with previous findings[31]. It has been suggested that the rapid increase in resistance at low biopolymer concentrations may be due to pore plugging and closure, whereas the slower increase in resistance at higher biopolymer concentrations may be due to surface (cake) accumulation[31].

Although the long-term impact of NaOCl oxidation on membrane flux remains unknown, the results of this study indicate that oxidation has a significant effect on the initial stage of membrane fouling. The presence of a larger quantity of soluble biopolymers and smaller floc sizes after maintenance cleaning accelerates the initial stage of membrane fouling and therefore shortens the cleaning interval. Consequently, the quantity of NaOCl solution released to the bioreactor during maintenance cleaning should be minimized to reduce membrane fouling.

As shown in Figures 7 and 8, the membrane permeate flux increased with an increase in trans-membrane pressure and decreased with an increase in sludge concentration. Moreover, the effect of sludge concentration on the membrane permeate flux was much stronger before oxidation than after oxidation (Figure 7). This is because the contribution of the settleable solids concentration to the total hydraulic resistance of the broth was much larger before oxidation (44%) than that after oxidation (5-11%).

Analysis of the filtration data according to cake filtration theory yielded Figures 9 and 10. The plots of t/Vp vs. Vp for sludge are not linear, which is not consistent with the observations of Ongier *et al.* (2002). The deviation from linearity is more significant for oxidized sludge (Figure 9) and clean soluble biopolymer solutions (Figure 10) than that for sludge before oxidation (Figure 9). The non-linear relationship suggests that some or all of the parameters α, c, and Rm in equation (6) are not constant during filtration. The reasons for this may be related to the presence of a large amount of soluble biopolymers in the oxidized sludge, significant cake compression, and/or membrane compaction. Hence, the results suggest that conventional cake filtration theory may not be appropriate for describing the filtration behavior of the activated sludge broth and soluble biopolymer solution under testing conditions.

CONCLUSIONS

The effects of NaOCl oxidation on sludge properties and membrane permeate flux were assessed experimentally. The following conclusions can be made.

1.) NaOCl oxidation led to the solubilization of solid sludge. The sludge dissolution constant was estimated to be 0.3±0.1 mg sludge/mg free chlorine under testing conditions.

2.) The oxidized sludge had smaller floc sizes and a larger quantity of non-settleable suspended colloids when compared to sludge before oxidation.

3.) Only part of the NaOCl dosage was used for sludge solubilization; the remainder may have been used to oxidize dissolved biopolymers.

4.) The oxidized sludge had a lower filterability than unoxidized sludge because of the presence of significant amounts of soluble biopolymers (including carbohydrates and proteins) and smaller sludge floc sizes.

5.) Soluble biopolymers contributed the majority of the total hydraulic resistance of the broth (> 76%) during filtration of oxidized sludge. The resistance contributed by the settleable solids accounted for only 5-11% of the total hydraulic resistance of the oxidized broth.

6.) An increase in sludge concentration resulted in a decrease in membrane permeate flux. In contrast, an increase in the trans-membrane pressure led to an increase in membrane permeate flux.

7.) Conventional cake filtration theory was not directly applicable to describe the filtration behavior of both the sludge flocs and soluble biopolymers under tested conditions.

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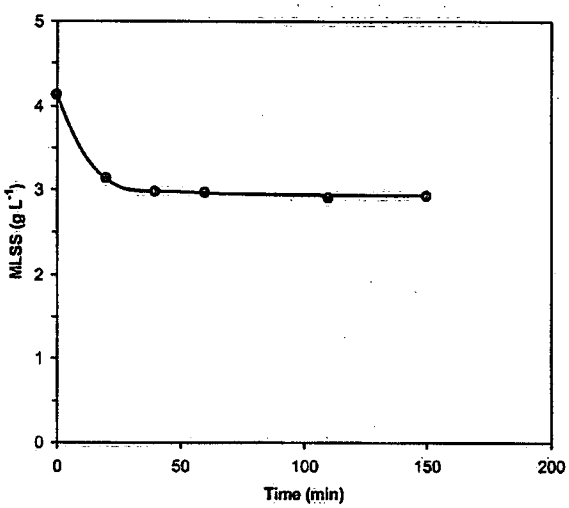

Figure 1 Liao *et al.*

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