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ULTRAFILTRATION FOULING TREND SIMULATION OF A MUNICIPAL WASTEWATER TREATMENT PLANT EFFLUENT WITH MODEL WASTEWATER

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Abstract

Secondary treatment effluents from Municipal Wastewater Treatment Plants require tertiary treatments to be reused in agriculture. Among tertiary treatment technologies, ultrafiltration has been proven to be a reliable reclamation process. Nevertheless this technique has an important disadvantage: membrane fouling. This phenomenon causes decline in permeate flux with time and increases the operational costs. Due to the fact that secondary effluents from Municipal Wastewater Treatment Plants contain a large amount of different compounds and that there is certain variability in their composition, the use of a simplified model wastewater consisting of only few compounds may help to simulate better the ultrafiltration fouling trend. The main secondary treatment effluent components responsible for fouling membrane during ultrafiltration tests are extracellular polymeric substances. These substances are mainly composed of proteins and polysaccharides, thus they are commonly used to prepare model wastewaters. This work consisted in two parts. Firstly, a model wastewater was selected among different model solutions mimicking secondary treatment effluent. Secondly, ultrafiltration behaviour of the selected model solution was compared with the behaviour of the secondary effluent in the ultrafiltration tests at different cross-flow velocities and transmembrane pressures. The membrane used in the ultrafiltration tests was UFCM5 Norit X-flow® hollow-fiber. To prepare model wastewaters, three parameters (proteins and carbohydrates concentrations and chemical oxygen demand) were considered. The model wastewater that represented the best the fouling trend of the secondary treatment effluent had a composition of 15 mg/l of bovine serum albumin and 5.5 mg/l of dextran.

1. Introduction

In the last years many wastewater treatment plants (WWTPs) are being upgraded by implementation of tertiary treatments that improve the quality of the biologically treated wastewater.

The need for a tertiary treatment comes from the fact that high quality standards regarding suspended solids and pathogens are required for wastewater reuse. There are different techniques to carry out the wastewater reclamation. Among them, ultrafiltration (UF) has been proven to be a reliable process. In addition, UF has some advantages as high permeate quality, no by-product generation and high efficiency. Besides, it is easy to operate and economically feasible, due to low energy consumption and to the small footprint [1,2,3,4,5]. However, UF processes, as other membrane processes, have an important disadvantage: membrane fouling [6]. As a consequence of fouling, the permeate flux decreases[7] (lower productivity) and the process increases its operating costs [7] (due to the increase in energy costs [8] and the need of frequent membrane cleaning) and its maintenance costs [9] (due to lower membrane lifetime [10]).

Currently, studies show that the best UF membranes for secondary treatment effluent (STE) from a municipal wastewater treatment plant (MWWTP) are hollow-fiber membranes [11,12]. This kind of membranes are widely used for large-scale water and wastewater treatment plants due to their high active surface/volume ratio[13].

The characteristics of a STE from a MWWTP are very variable because they depend on the efficiency of the secondary treatment, which will be influenced by wastewater characteristics and the type of the implemented biological treatment and their operating conditions. Thus, a correct modelling of the UF process may be an appropriate step for selecting the best operational conditions to minimize membrane fouling.

Soluble microbial products as a part of extracellular polymeric substances (EPS) have been identified as the main membrane foulant [14]. They are released by the biomass in the biological process and polysaccharides and proteins are their main components[14]. Thus, these substances have been used by different authors in the literature to model STE. Nataraj et al.[15] studied the fouling mechanisms with solutions containing a polysaccharide and Nguyen et.al. [16] used proteins and polysaccharides since they seemed to be the main responsible molecules for the membrane fouling. These authors worked with xanthan, actigun CS11 and glucan. However, for the simulation of STEs, binary mixtures protein/polysaccharides have been more frequently used. Particularly, the behaviour of bovine serum albumin (BSA)/dextran mixtures was reported by different authors [14,17,18].

Other authors include in their simulated solutions humic acids [3], although this kind of substances is more often used when fouling phenomena of UF membranes processing surface

water are studied, since humic and fulvic acids are important components of the natural organic matter (NOM) [19].

In order to achieve a synthetic model wastewater composition that could mimic the UF fouling trend of the hollow-fiber membrane, different combinations and concentrations of model compounds were tested in this work. The model proteins used were Whey Protein Concentrate (WPC) 45% and BSA and the carbohydrates tested were dextran and xanthan. WPC has been also studied by other authors, but with the aim of studying the membrane fouling in applications of the UF to the dairy industry [20,21,22].

Besides, the UF fouling trend of the selected simulated wastewater was compared to that of the STE for different transmembrane pressures (TMP) and cross-flow velocities (CFV). The experimental conditions were selected according to previous literature. Thus, low transmembrane pressures (TMP) were selected according to [10] and cross flow velocities (CFV) between 0,59 and 2,96 m/s were chosen in the range proposed by Tasselli et al. [23] and M.C. Vincent et.al. [24].

2. Materials and Methods

2.1. Feed solutions

The feed solutions to UF module used were a STE from a Municipal Wastewater Treatment Plant located in Valencian Region (Spain) and different model solutions consisting of either a binary mixture polysaccharide/protein or WPC at different concentrations. The proteins used were: BSA from Sigma-Aldrich, and WPC (45% w/w). The carbohydrates used were dextran (250000 Da from VWR International Ltd) and xanthan gum (from xanthomonas campestris, provided by Sigma-Aldrich). All model solutions were prepared using tap water. Proteins and carbohydrates concentration were varied in the range of 10 – 18 mg/l and 5-9 mg/l respectively.

It is important to note that BSA and WPC may form aggregates. Therefore, their particle size may increase. The aggregates of BSA have a particle size of 6-12 nm [14].

WPC may contain a variety of other components apart of proteins. Some of them are phospholipids, lipids, minerals and sugars. The WPC can form aggregates which consist of proteins or a mixture of proteins with other components from whey [25].

Dextrans have hydrophilic properties and they have good water solubility, low toxicity and certain inactivity [14].

Xanthan gum is an anionic polysaccharide [26]. In addition, xanthan gum has a good water solubility [27].

Due to STE composition variability, different samples of STE were analyzed. The parameters measured were the concentration of proteins and carbohydrates and chemical oxygen demand (COD).

The COD was measured using the kits and a thermoreactor model "TR300" both from Merck. The proteins concentration was determined by a MicroBCA assay (Bicinchoninic acid protein assay micro) from Applichem. Carbohydrates concentration was determined by the *anthrone* (9, 10 dihydro-9-ketoanthracene) method (reagent from Panreac).

2.2. Particle size distribution (PSD)

Particle size of model foulants was measured. The equipment used to determine the particle size distribution was a Zetasizer nano-ZS 90 from Malvern. This equipment measures the particle size by laser diffraction.

2.3. Pilot plant

Figure 1 illustrates the scheme of the laboratory UF plant used in the experiments. The UF module was *Norit X-flow T/RX-300*:

Figure 1. UF Pilot plant scheme.

This plant allows the TMP and CFV to be fixed independently. Moreover, the temperature regulator ensures a constant temperature.

The hollow-fiber membrane used was a *UFCM5* from *Norit X-flow*. The properties of this membrane are shown in Table 1.

Table 1. Properties of the hollow-fiber membrane

2.4. UF tests

During the tests, the temperature regulator kept the temperature constant. Data were logged in a programmable logic controller (PLC).

During the UF tests, the feed tank was stirred, the retentate and the permeate were both returned to the tank and the permeate flux was monitored.

Two series of UF tests were performed. The aim of the first set of experiments was to select the wastewater composition that better represented the STE UF performance. This first set of experiments was performed at a TMP of 70 KPa, a CFV of 1 m/s [28] and a temperature of 21ºC.

Once the best model wastewater was selected, the second set of experiments was carried out. In this set of experiments TMP and CFV were varied to check whether the selected model solution represented the STE for different experimental conditions. These conditions are shown in Table 2.

Table 2. Second set of UF experiments.

2.5. Membrane cleaning

The cleaning protocol was performed at the lowest TMP and the highest CFV achieved in the pilot plant.

The cleaning protocol steps were:

1. A first rinsing of 30 minutes at 25ºC with deionized water.
2. A chemical cleaning with a cleaning solution consisting of 154 ppm of NaClO and 0.5 mol/l of NaOH (Panreac, Spain) in deionized water. The chemical cleaning was performed at 40ºC.
3. A second rinsing under the same conditions as the first rinsing.

3. Results and discussion

As explained above, several STE samples were analyzed for COD, protein and carbohydrate concentration. Their mean concentration values were 38.9 mg/l for COD, 16.5 mg/l for proteins and 7.3 mg/l for carbohydrates. Then, model wastewater solutions were prepared by combination of different proteins and carbohydrates. Their concentrations were selected in a way that the measured values of proteins, COD and carbohydrates of the simulated solutions were as similar as possible to those of the STE.

Membrane permeabilities before each UF test were not exactly the same because the cleaning efficiency could not reach 100% in all the tests. For this reason the permeate flux of the membrane was normalized according to Eq.1:

$$J_N = J \cdot \frac{R_0}{R_m} \qquad \text{Eq. 1}$$

In the Eq.1 "J" is the permeate flux obtained during the test, "J_N" is the normalized permeate flux, "R_0" is the resistance of the membrane before its first use and "R_m" is the membrane resistance before each test.

Figure 2 illustrates the evolution of the permeate flux with the time when the STE was ultrafiltered. As expected, a sharp flux decline occurred during the first minutes, meanwhile an almost constant flux was maintained in the rest of the experiment (approximately 24 L/(m^2h)).

Figure 2. Evolution of the normalized permeate flux of STE at 70 KPa and 1 m/s.

Table 3 shows the comparison between every simulated wastewater and the STE from the point of view of the flux evolution with the time. In order to compare the performance of the simulated wastewater in the prediction of the STE behavior, flux measurements have been divided into two groups: permeate fluxes in the initial part of the UF including the sharp flux diminution (initial decline) and the permeate fluxes measured when an almost constant flux was reached (steady state).

In this way, values of R-squared (R^2) and standard deviation (SD) calculated by comparing every simulated wastewater with STE can be observed in Table 3. R^2 total means the value of the regression coefficient calculated for all the measured fluxes in the UF tests, whereas R^2 initial decline and R^2 steady state were calculated for the fluxes of the initial decline and of the steady state, respectively. Identical nomenclature has been adopted for the calculated standard deviations.

Table 3. Values of R^2 and SD for UF tests (total, initial decline and steady-state)

The model solutions consisting only of WPC 45% at concentrations of 10 and 13 mg/L showed smaller values of total R^2 than the other solutions, which were prepared with a mixture of proteins and carbohydrates. R^2 slightly increased with the concentration of WPC 45%. However the addition of carbohydrates to the synthetic solutions led to a better fitness between flux data, what was due to the higher flux decline in the first part of the experiments.

On the contrary, the fitness of the steady sate fluxes became slightly worse for the solutions with carbohydrates addition. This led to similar global SD values for all the experiments with

WPC, although considerable differences were found in the SD values calculated in the steady state conditions for the different experiments.

The use of BSA instead of WPC improved the results since the highest total R^2 value was reached and the minimum SD value for the global data and especially for the steady state data were obtained. Zator et.al [14] concluded in their study that the fouling trend did not only depended on the composition but on the particle size too. They explained that smaller particles produce less fouling and the fouling mechanisms for these particles were internal and external pore blocking, but they considered the internal fouling as the predominant mechanism.

The particle size distribution measurement of WPC solutions (at different WPC concentrations) indicated that the mean diameter was slightly higher than 200 nm. Results have been expressed both in scattered by particles intensity (%), which is the magnitude measured by the equipment, and in particle number (%), which is calculated from intensity measurements. In this way, a particle with large diameter detected by the apparatus absorbs a high intensity but it loses its significance when the PSD in number is calculated. Figure 3 shows the PSD analysis for WPC both in intensity and in number in %. The high size of WPC in comparison with the membrane pore size (20 nm) leads to a higher external than internal pore blocking.

Figure 3. PSD analysis for WPC 45% a) In intensity (%) b) In number(%)

Although xanthan used also presented particles with diameter values higher than 200 nm, xanthan solutions were polydispersed from the point of view of the PSD. If data are converted to number-weighted PSD, their analysis yield a peak at 2.5 nm, what could be the reason why internal pore blocking increased for simulated solutions with xanthan entailing a high flux diminution in the initial part of the ultrafiltation tests. Figure 4 shows the PSD analysis for the xanthan solution both in intensity and in number in %.

Figure 4. PSD analysis for Xanthan a) In intensity (%) b) In number (%)

Concerning dextran, it should be commented that the fouling trend of the membrane with STE was mimicked with 7.3 mg/L better than with 5.5 mg/L when a same WPC concentration was used. The improvement in the fitting was due to the values obtained in the period of the initial flux decline. The effect of the dextran addition was very similar to that obtained with xanthan, though the particle diameter was higher (between 20 and 50 nm if particle number is considered. as shows Figure 5).

Figure 5. PSD analysis for dextran a) In intensity (%) b) In number (%)

The best model wastewater to simulate the STE behavior consisted of BSA (15 mg/l) and dextran (5.5 mg/l). BSA contributed to long term fouling as it was mainly deposited on the membrane surface. The addition of dextran contributed to a better fitting in the initial flux decline, contributing to internal and external pore blocking, since membrane pore and dextran have a similar size. This fact was also confirmed by the membrane retention to the dextran that was of 50.4 %. Thus, this model wastewater reached the highest value of R^2 and the lowest values of SD.

Therefore, the selected model wastewater was the binary mixture BSA (15 mg/L)/ dextran (5.5 mg/L). This solution was ultrafiltered under different conditions of CFV and TMP and compared with STE ultrafiltration at the same experimental conditions (Figures 6-9). Table 4 summarizes the R^2 and SD calculated values for the data of the three comparison experiments.

Figure 6. Comparison between STE and model wastewater UF performance (100 KPa of TMP and 1.2 m/s of CFV).

Figure 7. Comparison between STE and model wastewater UF performance (62 KPa of TMP and 1.2 m/s of CFV).

Figure 8. Comparison between STE and model wastewater UF performance (62 KPa of TMP and 0.8 m/s of CFV).

Figure 9. Comparison between STE and model wastewater UF performance (100 KPa of TMP and 0.8 m/s of CFV).

Table 4. Fitting accuracy of the selected model wastewater in front of the STE at different conditions

R^2 and SD values showed that model wastewater was capable of correctly representing STE in the UF fouling trend in the steady state flux data. With the exception of the test at the lowest values of TMP and CFV, the R^2 value in the steady state was above 0.96. Thus, it is confirmed that the selected simulated wastewater mimics STE at different operating conditions.

However, the behaviour in the initial part of the UF is more difficult to simulate. Initial flux decline with simulated wastewater was always a little sharper than initial flux decline for STE. It occurred independently of the operating conditions. It was observed that it was extremely difficult to obtain identical flux data in the tests with STE. The tests were carried out with the same STE samples in order not to vary wastewater composition, but slight changes in STE composition occurred due to organic matter deposition on the membrane or carbohydrates degradation. This did affect to the behaviour of the fouling trend in the initial part of the UF tests and it explains the differences observed, that led to R^2 values between 0.76 and 0.90.

4. Conclusions

UF experiments with simulated STEs from municipal wastewater treatment plants are of great importance for the study of the membrane fouling. The first goal to be achieved is the selection of a simulated wastewater mimicking STEs. After testing different protein and

carbohydrates solutions, a model wastewater consisting of BSA (15 mg/l) and dextran (5.5 mg/l) was selected to model STE UF performance. Selection was carried out according to the better fitness both in the initial flux decline and in the steady state parts of the experiments.

It has been proven that BSA formed aggregates whose particle size was higher than the membrane pore size; thereby the BSA presence in the simulated solution exerted a great influence on long term fouling. On the contrary, dextran had a similar particle size to the membrane pore size and this compound contributed to both long and short term fouling. PSD analysis helped to corroborate it.

It was very difficult to achieve high values of R^2 in the comparison of UF tests of simulated wastewater and STE for different operating conditions. Although fitness was high for the steady state fluxes, the initial flux decline was more difficult to fit. This was due to the small changes in the STE rather than to the change in the operating conditions.

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6. Nomenclature

Symbols

J	Permeate flux (L/m^{2}h)
J_N	Normalized permeate flux (L/m^{2}h)
R_0	Resistance of the membrane before the first use (m^{-1})
R_m	Resistance of the membrane before each test (m^{-1})
μ	Dynamic viscosity of the water (Pa·s)
s	Slope of the permeability test (L/m^{2}h·bar)
TMP	Transmembrane pressure (KPa)
CFV	Cross-flow velocity (m/s)
STE	Secondary treatment effluent
MWWTP	Municipal wastewater treatment plant
UF	Ultrafiltration
EPS	Extracellular polymeric substances
WPC	Whey protein concentrate
BSA	Bovine serum albumin
COD	Chemical oxygen demand (mg/L)
PSD	Particle size distribution (nm)
MWCO	Molecular weight cut-off (Da)
HF	Hollow-fiber

7. References

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