# Fouling control in MBR systems: comparison of several commercially applied coagulants

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**Abstract**

Membrane bioreactors (MBRs) integrate biological degradation with membrane filtration in wastewater treatment. Membrane fouling, which is the main process drawback, results from the interaction between the membrane material and foulants, leading to membrane's efficiency deterioration. It is widely recognized that the mixed liquor colloidal and soluble microbial products (SMP) are principally responsible for membrane fouling. Appropriate feed wastewater pre-treatment is considered as necessary and the coagulation/flocculation (C/F) process is regarded as a relevant viable option for surface waters, or wastewaters treatment in order to remove suspended solids (SS), colloidal particles, natural organic matter (NOM) and other soluble materials. The objective of this study is the application of an alternative hybrid technique for fouling control using several commercially applied coagulants. For this purpose, a lab-scale MBR system has been constructed and various coagulants have been applied and tested, specifically the conventional Al and Fe based coagulants. Preliminary filterability tests were conducted in order to investigate the mixed liquor filterability characteristics and SMP concentration was determined both in mixed liquor and filtrate samples, in order to investigate reversible and permanent fouling. The most efficient coagulants are applied to the hybrid coagulation-MBR system, employing a fully automatic operation.

**Keywords:** membrane bioreactors; coagulants; fouling control; filterability tests; soluble microbial product.

## 1. Introduction

Membrane bioreactors (MBRs) have been widely used for municipal or industrial wastewater treatment [1, 2, 3], and recently for water reclamation as well [4]. The first reported application in MBR technology was in 1969, when an ultrafiltration membrane was used to separate activated sludge from the final effluent of a biological wastewater treatment system and the sludge was recycled back into the aeration tank [5]. Biomass separation membrane bioreactors, the most common type of MBRs are the combination of a suspended growth reactor and a membrane (usually micro- or ultra-) filtration unit into a single process [6]. Membrane bioreactors are more effective and advantageous when compared with the conventional wastewater treatment process [7] in terms of space requirement, effluent quality, high biomass concentration, footprint and reduced reactor volume. However, membrane fouling remains a bottleneck for the widespread application of MBR technology [8-10] and affects the efficiency of this process. Membrane fouling affects system performance, economic viability, high energy demand and high costs related with membrane material/replacement [11]. Experimental studies and practical operations have indicated that the biocake layer accumulated on the membrane surface is the main cause of membrane fouling in the MBRs process [12-14]. The biocake layer generally consists of a combination of precipitates of inorganic and organic materials, as well as extracellular polymeric substances (EPS) [15-19], which can be classified into soluble EPS (sEPS or SMP, soluble microbial product) and bound EPS (bEPS) and constitute a matrix of high molecular weight substances excreted from cells. Functions of the EPS matrix include mainly the aggregation of bacterial cells in flocs and biofilms, the formation of a protective barrier around the bacteria, the retention of water and adhesion to surfaces [20]. With its heterogeneous and changing nature, EPS can form a highly hydrated gel matrix, in which microbial cells are embedded [21] and thus, can help to create a significant barrier, resulting in the reduction of membrane permeability. This study is part of a research project which aims at the development of an integrated methodology for fouling control in MBRs using specific chemicals which will enhance the coagulation/flocculation process of the chemical species that are responsible for membrane fouling.

## 2. Materials and methods

### 2.1 Lab-scale MBR system

The experiments are conducted in a lab-scale MBR system which consists of five units: a wastewater feed unit, a bioreactor, a tank in which the coagulant is added, a membrane (side-stream) filtration unit and a permeate collection unit (Fig.1). By means of a peristaltic pump synthetic municipal sewage is led from the feed unit to the bioreactor, where the concentration of the dissolved oxygen is controlled by a dissolved oxygen meter in the range of 2-3 mg/L. The membrane used (ZW-1, a lab-scale model manufactured and supplied by the Canadian Zenon Environmental Inc.) is a PVDF ultrafiltration hollow fiber membrane with a surface area of 0.047 $m^2$ and a nominal pore size of 0.04 μm. The effluent of the aeration tank passes through the membrane system, while part of the activated sludge returns to the bioreactor by means of a peristaltic pump. The air needed for the bioreactor and the cleaning of the membrane is supplied by an air compressor, the pressure of which is appropriately reduced to the desired value by means of an air pressure reducer. The applied coagulants are added in the coagulant tank by means of a dosing pump. The permeate is withdrawn from the upper end of the membrane by means of a peristaltic pump, while an electronic high-resolution pressure transmitter is used for the recording of the transmembrane pressure and, thus, the extent of fouling during the process of filtration. The permeate collection unit is the final recipient of the produced permeate, a part of which is backwashed to the membrane filtration unit by means of a peristaltic pump. Membrane backflushing steps of 1 min were performed periodically after 10 min of filtration. This procedure is achieved by means of time switches. Transmembrane pressure, permeate mass and dissolved oxygen concentration values are recorded. The composition of the synthetic wastewater used is shown in Table 1.

**Figure 1** Lab-scale MBR system

**Table 1** Composition of synthetic municipal wastewater

| Synthetic wastewater composition | |
|---|---|
| **Substance** | **Concentration, g/L** |
| Peptone | 4.80 |
| Meat extract | 3.30 |
| $K_2HPO_4$ | 0.84 |
| NaCl | 0.21 |
| $CaCl_2·2H_2O$ | 0.12 |
| $MgSO_4·7H_2O$ | 0.06 |

### 2.2 Commercially applied coagulants

Various coagulants have been applied and tested, specifically a commercial available Al based pre-polymerized coagulant, such as the Polyaluminum Chloride PAC A9-M, supplied by *Loufakis Chemicals S.A.*and a conventional Fe based coagulant, such as the commercial available Fe salt, i.e. $FeCl_3 \cdot 6H_2O$ (Merck). For comparison reasons, beside the use of the aforementioned inorganic coagulants, a commercially available organic polyelectrolyte i.e. FO4350SSH 0.01% w/w, a cationic polyelectrolyte, was also tested (Table 2).

**Table 2** Indicative commercial available coagulants used

| Type | Description |
|---|---|
| **Inorganic** | |
| PAC A9-M | Pre-polymerized 0.1 M<br>4.5 Al% + polyamine |
| $FeCl_3 \cdot 6H_2O$ | Fe salt 0.1 M |
| **Organic** | |
| FO4350SSH | CPE-cationic polyelectrolyte<br>0.01% w/w |

### 2.3 Bench-scale experiments

Preliminary filterability tests were conducted in order to investigate mixed liquor filterability characteristics. For this purpose, the time to filter (TTF) test method was applied (Fig. 2): using a 90-mm Buchner funnel and Whatman #1 the time required to obtain 100 mL of filtrate was measured at the vacuum pressure of 510 mbar. The TTF tests were conducted before and after the addition of the commercial coagulants in the sample.

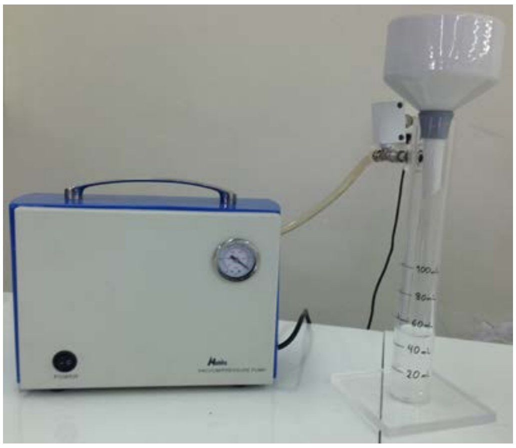

**Figure 2** Time to filter (TTF) a certain volume test equipment

The Phenol-Sulfuric Acid Method [22] is the most widely used colorimetric method for the determination of carbohydrate concentration in aqueous solutions. The basic principle of this method is that carbohydrates, when dehydrated by reaction with concentrated sulfuric acid, produce furfural derivatives. Further reaction between furfural derivatives and phenol develops detectible color. The standard procedure of this method is as follows: 1 mL aliquot of a carbohydrate solution is mixed with 1 mL of 5% aqueous solution of phenol in a test tube. Subsequently, 5 mL of concentrated sulfuric acid is added rapidly to the mixture. After allowing the test tubes to stand for 10 min, they are vortexed for 30 s and placed for 20 min in a water bath at room temperature for color development. Then, light absorption at 490 nm is recorded on a spectrophotometer. Reference solutions are prepared in identical manner as above, except that the 1 mL aliquot of carbohydrate is replaced by DDI water. A Hitachi UV/Vis spectrophotometer was used for this purpose.

## 3. Results and Discussion

### 3.1 Lab-scale MBR efficiency

The lab-scale MBR operated at a SRT of 33 days dealing with a medium-strength synthetic municipal wastewater in terms of organic content ($BOD_5$=300 mg/L). Permeate samples were analyzed for the following parameters: biochemical oxygen demand ($BOD_5$), chemical oxygen demand (COD), total nitrogen (TN), ammonium ($NH_4^+$-N), nitrate ($NO_3^-$-N), total phosphorous (TP), phosphate ($PO_4^{3-}$-P), total organic carbon (TOC), UV absorbance at 254 nm, electrical conductivity and turbidity. Effluent samples were collected at the same day of the week and the same time of the day to minimize the impact of weekly or daily variations, respectively. As shown in Fig. 3, 4 the lab-scale MBR supports high $BOD_5$, COD and $NH_4^+$-N (>95%) removal.

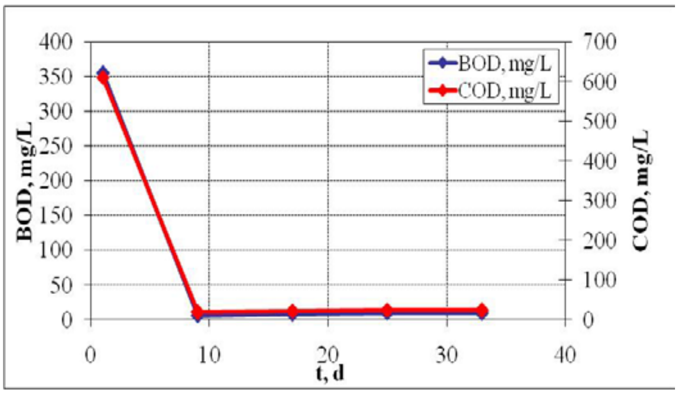


**Figure 3** Organic removal efficiency in the lab-scale MBR

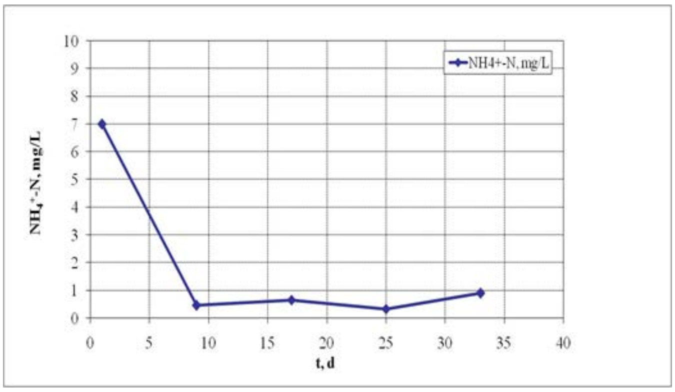


**Figure 4** Ammonium removal efficiency in the lab-scale MBR

### 3.2 Membrane fouling results

*3.2.1. Filterability tests*

Preliminary filterability tests conducted in a pilot-scale MBR unit [23], which operated under similar conditions (F/M ratio, DO etc), also showed that the addition of the aforementioned coagulants improved sludge filterability (Fig. 5). Thus, the application of these coagulants to the lab-scale MBR system is strongly suggested.

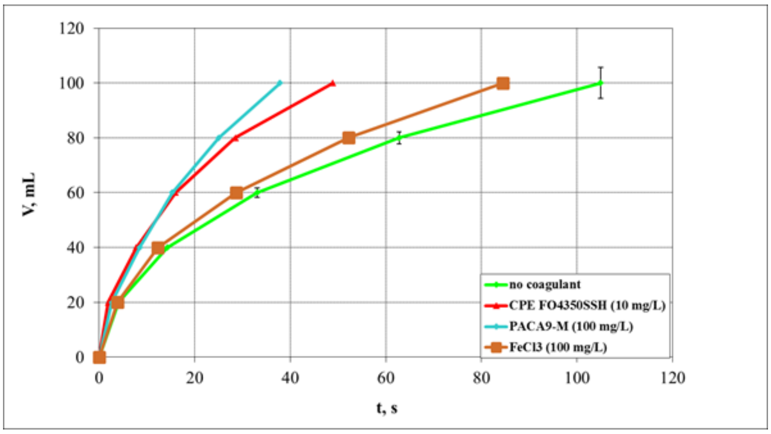


**Figure 5** Effect of different coagulants on sludge filterability

*3.2.2. TMP progress*

Results showed that the addition of polyaluminum chloride PAC-A9-M and CPE FO4350SSH was not effective, as the coagulant addition increased the rate of TMP (Fig. 6, 7).

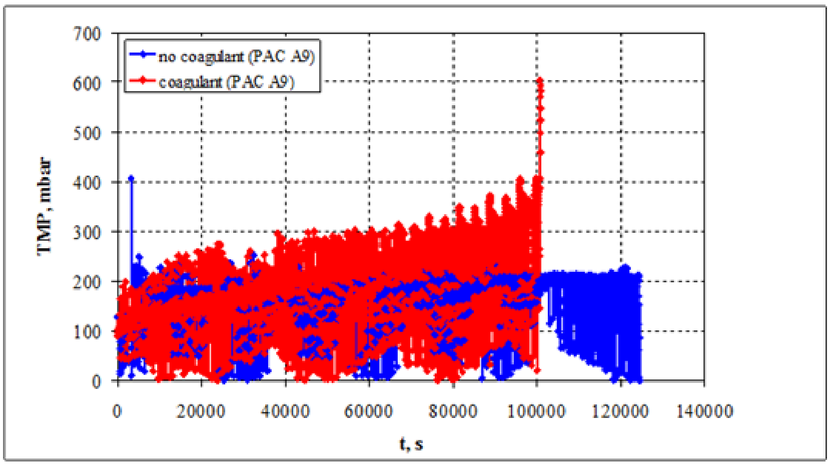


**Figure 6** TMP progress before and after the addition of PAC-A9-M (100 mg Al/L)

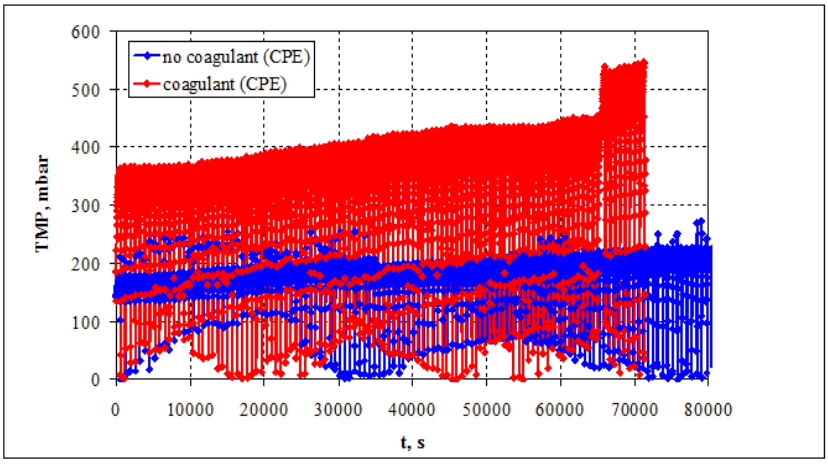


**Figure7** TMP progress before and after the addition of CPE FO4350SSH (10 mg/L)

On the contrary, Fig. 8 shows the changes of the TMP by the addition of $FeCl_3 \cdot 6H_2O$ which obviously reduced the increase rate of the TMP. It showed that $FeCl_3 \cdot 6H_2O$ had a significant effect on membrane fouling control. In terms of the different increase rate of TMP, it could be found that the membrane fouling control ability of coagulants was in the order of CPE>PAC>Blank>$FeCl_3 \cdot 6H_2O$.

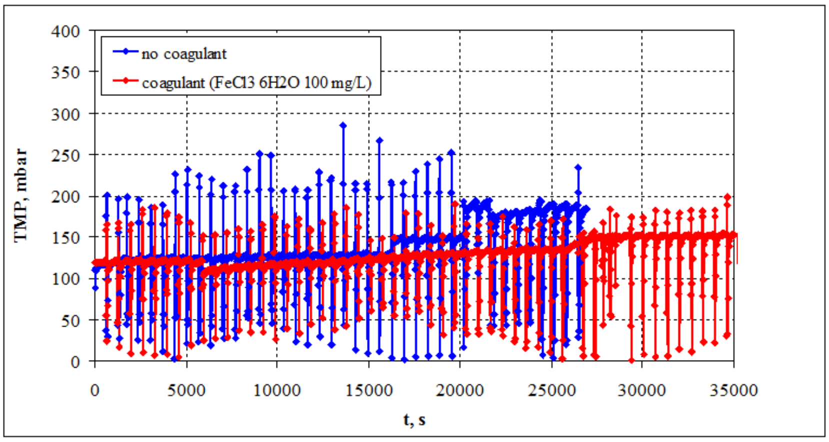


**Figure 8** Changes of TMP by $FeCl_3 \cdot 6H_2O$ addition100 mg Fe/L.

*3.2.3. SMP residual concentration*

SMP concentration measurements (indicative of irreversible or permanent fouling) conducted in mixed liquor samples before and after the inline coagulant addition in the -scale MBR system. Fig. 9 shows the results of the application of CPE FO4350SSH, PAC-A9-M and $FeCl_3 \cdot 6H_2O$ respectively. As exhibit, the addition of $FeCl_3 \cdot 6H_2O$ reduces SMP concentration aswell as the addition of cationic polyelectrolyte. Contrary to previous results, SMP concentration increased sharply by the addition of PAC-A9-M, at the third day of addition, creating gelatinous precipitation the membrane and therefore its application was stopped.

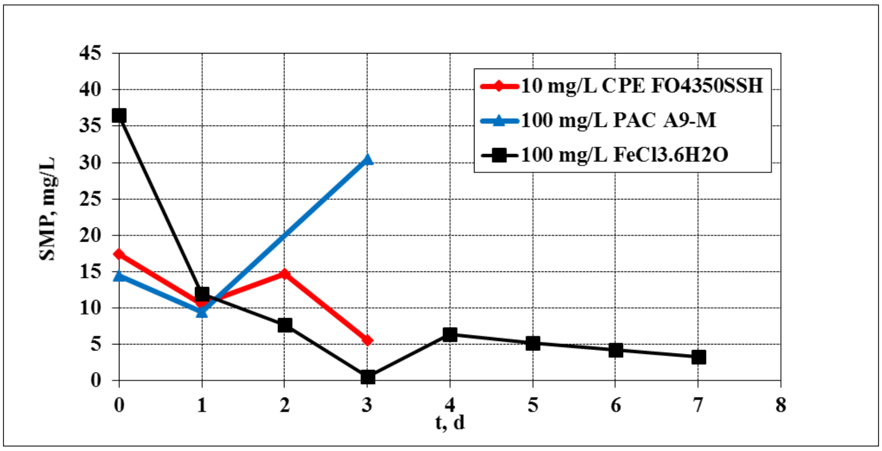


**Figure 9** SMP residual concentration after the addition of CPE FO4350SSH, PAC-A9-M and $FeCl_3 \cdot 6H_2O$, in the lab-scale MBR

## 4. Conclusions

The MBR technology is a novel method for treating municipal and industrial wastewater which offers multiple benefits, such as small space requirement, high effluent quality, etc. However, the most serious drawback in wastewater treatment using MBRs is membrane fouling, which gradually leads to membrane permeability decrease and efficiency deterioration. This results in increased treatment cost, due to high energy consumption and the need for frequent membrane cleaning and replacement. This study aims to develop an integrated methodology for fouling control in a MBR system, which will enhance coagulation/flocculation process, thus reducing biofilm formation on the membrane surface and limiting the fouling rate acting as a co-treatment step.

Due to the widespread application of MBR technology over the past few years, it becomes clear that the development of a methodology to mitigate membrane fouling is of paramount importance. The present work aims to develop an integrated technique for membrane fouling control in MBR systems and, thus, contribute to sustainable wastewater treatment.

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