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Effect of addition of different additives on overall performance of bioflim-MBR (BF-MBR)

Igor Ivanovic*, TorOve Leiknes

NTNU - Norwegian University of Science and Technology, Trondheim, Norway
Email: igor.ivanovic@ntnu.no

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ABSTRACT

The effectiveness of five additives, two iron based and two alum based coagulants and one modified cationic polymer was investigated in relation to reduction of fouling rates in biofilm-MBR. Additionally, the amount of colloidal organic matter in terms of soluble microbial products (SMP), dissolved organic carbon (DOC) and filtered chemical oxygen demand (FCOD) removal, retained by membrane was related to measured membrane fouling rates. Optimal dosage was defined based on maximum values of coefficient additive utilization (CAU). Iron chloride at higher chosen dosage showed that fouling could be reduced up to seven times, where for polymerized alum chloride it was measured reduction of about 3 times. The iron chloride coagulant performed better than iron chloride sulfate, in terms of fouling reduction. Higher basicity of polymerized inorganic coagulant did not result in improved membrane performance. Modified cationic polymer showed good potential in instantaneous fouling reduction, however continuous dosing strategy was found difficult to use without thorough monitoring of the system performance. Reduction in fouling rates relates better to reduction of $SMP_{carbohydrates}$, than to $SMP_{protein}$ and DOC. Also FCOD was seen as good potential fouling predictor parameter. Synergetic effect of high total phosphorus removal rates and reduced fouling rates give advantage of iron chloride coagulant over the others tested additives in this study.

Keywords: Biofilm MBR; Fouling control; Colloidal organic matter; Coagulation

1. Introduction

The objective of this study is to investigate the effectiveness of different additives commonly reported as filterability enhancers and fouling reducers in the MBR technology on the overall performance in a biofilm-MBR (BF-MBR).

The BF-MBR is an alternative concept to conventional MBR, where a biofilm reactor is employed instead of an activated sludge reactor. Several advantages of this approach were previously reported; e.g., no need for biomass/sludge recirculation, significantly lower concentration of MLSS and low viscosity of biofilm effluent giving lower energy consumption for membrane aeration and less or no membrane module sludging/clogging problems [1–3]. However, membrane fouling caused by suspended and colloidal matter remains a major challenge in development of this concept, which is also common for conventional MBR and other membrane systems [4–5].

Commonly understood techniques for fouling reduction and control include optimization of air scouring and hydrodynamics [6], backwashing and relaxation [7], membrane reactor design [8], alternative filtration modes [9], etc. Recently a strategy of adding different additives has been explored in order to adsorb and/or coagulate (flocculate) and in that way reduce certain mixed liquid compounds which are suspected to cause membrane

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*Corresponding author.

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fouling. Different research groups investigated additions of inorganic coagulants [10–11], granular or powdered activated carbon [12–13], natural and synthetic polymers [10,14–16], or combinations [17]. Even though approaches in dosing strategies, MBR configurations and membrane materials applied differ significantly in mentioned studies, a similar response was observed in that addition of certain additives at optimum dosages results in reduction of SMP (EPS), enlarges floc sizes and reduces cake porosity. Therefore, improved membrane performance was observed giving lower fouling rates, longer operational cycles or higher (e.g., enhanced) fluxes. Polymerized metal coagulants were found to be more effective in terms of lager floc formations and better organic removal (i.e., COD and DOC removal) [11,18] then non-polymerized, which could result in improved filterability. Higher basicity of polymerized alum has been reported to result in better DOC removal in drinking water applications [18], however, observations of this effect in MBR applications have not been found reported in literature. In the last few years modified cationic polymers, specially designed for MBR applications, have gained popularity as studies by several authors have shown that at optimum dosages an increase in critical flux and concentration of MLSS, reduction of SMP's, increased cake porosity and overall improved performance of MBR systems can be achieved [14–15] .

Application of inorganic coagulants and/or cationic polymers should therefore also be beneficial in improving the performance of a BF-MBR since it can be applied on mixed liquors with lower amounts of suspended matter than activated sludge systems, and thus lower dosages could be expected. In addition, the ability of coagulants to flocculate and reduce the amount of submicron particles, which have been reported as one of the major foulants in BF-MBR [1], makes the addition of flux enhancers an interesting strategy to reduce fouling. A potential negative impact on the biological treatment stage [10] is not of concern in a BF-MBR as the membrane separation process is separated from the biological process with no feedback effect on the biological treatment. Furthermore, biological phosphorus removal in a biofilm reactor is only possible in SBR schemes [19] while for systems that are continuously operated, like in this study applying a moving-bed-biofilm reactor, only chemical precipitation by iron or alum is an available option.

2. Materials and methods

The pilot plant schematic used in this study is shown in Fig. 1 and bioreactor configuration is described in previous studies [1,8]. Two cylindrical shaped membrane reactors with volumes of 27.5 l were connected after the biofilm reactor. The membrane reactors were designed as completely mixed reactors, however, during experimental runs sedimentation under the membrane modules was observed and measured concentrations of MLSS in the retentate was on average two times higher than the concentrate around the membrane. Membranes were operated at constant flux of 25 l m^{-2} h^{-1} (without backwash or relaxation) and with constant aeration of SAD$_m$ ~ 1,8 Nm^3 m^{-2} h^{-1}. Recovery was set at 90% and HRT and SRT were 1 and 10.1 h, respectively. Membranes were operated until TMP increased up to 0.3 bar or 7 operational days, after which the membranes were chemically cleaned. To alleviate uncertainties on calculated mass balances for applied additives, the experimental approach was to apply continuous dosing with dosages slightly lower than optimal dose as determined by jar tests. Additives were diluted with tap water, and then continuously dosed using a computer controlled peristaltic pump (L/S® Easy-load® II, Masterflex). Proper flocculation after applied coagulant in water and wastewater systems is normally achieved by fast and slow mixing chambers, static mixers, pipe flocculators, etc., however in this study objective was to avoid additional process units and energy requirements for that purpose. Consequently, two possible dosing point were indentified and tested, point 1 (in Fig. 1) directly into the tubing connecting the distribution unit and membrane reactors (i.e., in-line), and point 2 (in Fig. 1) at the top of the membrane reactor. Based on the calculations given in [20], the G-value for point 1 was 4 s^{-1} (Re= 290 – laminar flow) whereas for point 2 it was estimated over 5000 s^{-1}. Point 2 was therefore chosen since very good mixing and dispersion of applied additive was secured by the high G value, compared to point 1.

All analyses were performed according to national standards or Standard methods. Mixed liquor suspended

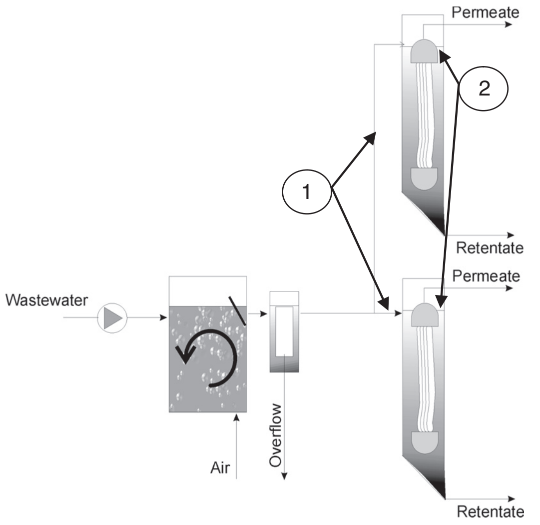


Fig. 1. Experimental set up (1 and 2 refer to possible dosing points).

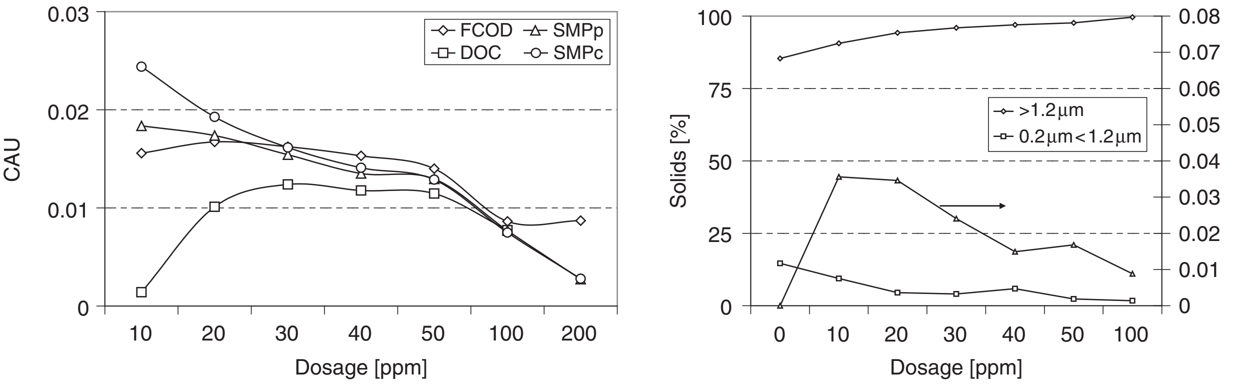
solids (MLSS) were analyzed by filtering through a Whatman GF/C 1.2 µm (55 mm) glass microfiber filter according to the Norwegian Standard NS 4733. In addition, during the jar tests a Whatman 0.2 µm (55mm) was also used in order to estimate the amount of solids in the water sample between 0.2 µm and 1.2 µm. Chemical Oxygen Demand (COD), ammonia (NH_4–N), total-N and total- P were measured with the Dr Lange LCK 114, 314, 303, 304, 238, 338, cuvette tests provided by HACH LANGE GmbH, and measured with a Lasa20 spectrophotometer. For the Filtered Chemical Oxygen Demand (FCOD), Soluble Microbial Products (SMP) and dissolved organic carbon (DOC), samples were first filtered with a Whatman GF/C 1.2 µm filter. SMP_p (soluble microbial products – as protein) and SMP_c (soluble microbial products – as carbohydrate) were measured according to the Lowry [21] and Dubois [22] methods. DOC was measured by a Tekmar Apollo 9000 TOC combustion analyzer (Teledyne Tekmar, Ohio). UV absorbance (UVA_{245}) and SMP were measured with a U 3000 spectrophotometer, Hitachi. The development of transmembrane pressure (TMP) was measured continuously using an online pressure transducer connected to a National Instruments, FieldPoint (FP1000 and FP-AI-110) unit, with the LabVIEW 8.2 data acquisition and analysis software. TMP and temperature were logged every second.

Four commercial metal based metal salt coagulants were chosen; two iron based using iron chloride ($FeCl_3$) and iron chloride sulfate ($FeClSO_4$), and two alum based coagulants using alum chloride and alum chloride with 50% higher basicity, both polymerized. One modified cationic polymer was used. Jar tests were conducted with iron chloride, alum chloride and cationic polymer for six different concentrations, chosen based on reported values found in the literature and preliminary jar tests with shaken flask. Prepared additives were added to mixed liquor taken from the membrane reactor in concentrations of 10, 20, 30, 40, 50 and 100 ppm metal, and polymer in 10, 30, 50, 70, 100 and 300 ppm. Jar tests were conducted in 800 ml beakers (d × h = 90 × 120 mm) aerated from the bottom with 7,5 l/min coarse bubble aeration in order to provide mixing conditions similar to that in the membrane reactor. For each sample were measured SMP_p, SMP_c, DOC, UVA_{254}, FCOD, and MLSS for two chosen filter pore sizes (i.e., ~ 1.2 µm and 0.2 µm). Time for reaction of the additives with the water was one hour, which is equivalent to the HRT of membrane reactors in the experimental design.

3. Results and discussion

3.1. Jar test results

Jar tests were designed to estimate optimum dosages that give the highest reduction of soluble organic matter (expressed as SMP_p and SMP_c, FCOD and DOC), and the highest reduction of solids fraction between 0.2 and 1.2 µm. All additives applied were observed to be able to reduce SMP's and FCOD for all dosages chosen. Thus, an optimal dose for highest organic removal was not found, suggesting that this is probably not within the range of dosages tested. The criteria for optimal dosage was therefore defined based on the highest coefficient of additive utilization CAU [mg of organic matter reduction/mg additive], Figs. 2a, 3a and 4a. Results differ for SMP's, DOC and FCOD which additionally made difficult to define what could be an optimal dosage. From Figs. 2–4 an optimum dosage not higher than 25 ppm for metal coagulants and not higher than 10 ppm for cationic polymer was defined, if all four parameters are to be taken into consideration with equal importance. Reduction of solids smaller then 1.2 µm was followed by enlargement of suspended matter (>1.2 µm), was observed for all applied dosages for both metal coagulants. This result indicates that



a) b)

Fig. 2. Removal efficiency - jar test for alum: a) soluble organic compounds, b) solids.

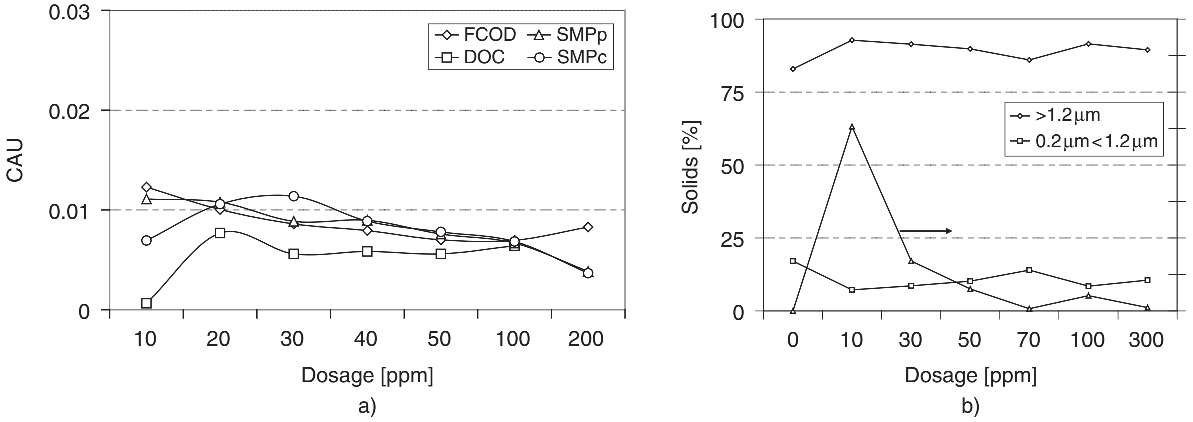


Fig. 3. Removal efficiency - jar test for iron: a) soluble organic compounds b) solids.

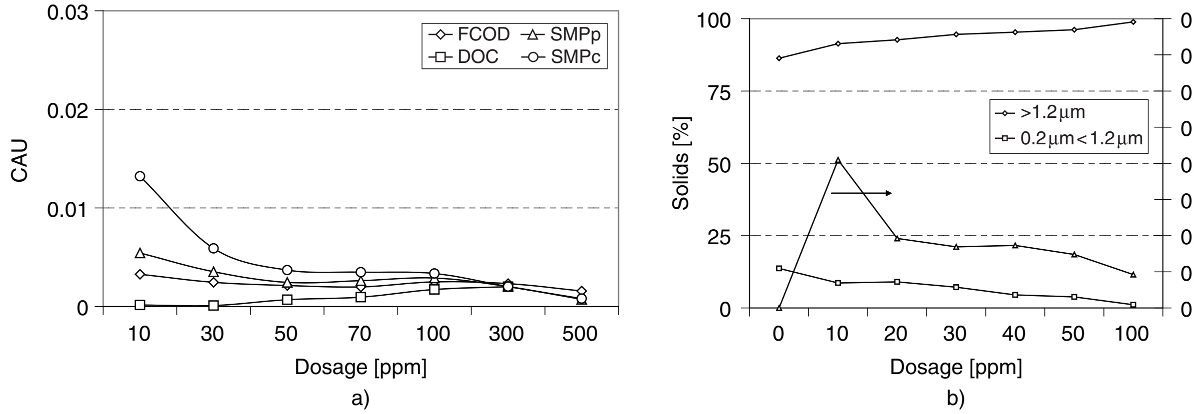


Fig. 4. Removal efficiency - jar test for polymer: a) soluble organic compounds b) solids.
*"**>1.2μm**" *refer to solids fraction higher than 1.2 μm and* "**0.2<1.2 μm**" *refer to solids fraction between 0.2 and 1.2 μm.*

colloidal matter, in general, is additionally reduced by flocculation and adsorption by suspended matter (i.e., fraction >1.2 μm), suggesting this is a significant mechanism for improved performance. Subsequently, the highest CAU [mg of submicron matter reduction/mg additive] value was again used as the criteria for optimal dosage. Dosages of 15 ppm for alum Fig. 2b, and 10 ppm for iron Fig. 3b were chosen as optimal and for the polymer was roughly estimated as 10 ppm since no significant changes in upper micron and submicron solids concentration were observed, Fig. 4b.

Based on the results and analysis of the jar tests, to test possible improvements in membrane performances experimental trials with the pilot plant were performed using dosages of 9 and 22.5 ppm for both metal coagulants, iron chloride and alum chloride, and 13.5 ppm for alternative iron chloride sulfate and alum chloride with high basicity. For the cationic polymer trials were conducted with 45 ppm, and then gradually decreasing the applied dose. Based on defined optimal dosages goal of pilot plant tests was to compare which coagulant type (iron or alum based) performs better at lower and higher dosages, (by comparing iron chloride and alum chloride), if there is a significant difference in membrane performances between two iron type of inorganic coagulant (by comparing iron chloride and iron chloride sulfate) and does higher basicity of polymerized inorganic coagulant effects filterability (by comparing alum chloride and alum chloride with high basicity). Also intention was to evaluate potential of modified cationic polymer in BF-MBR and to additionally compare its efficiency to inorganic coagulants. Reduction in fouling rates that refer to overall measured fouling was related to applied dosages and reduction in amount of colloidal organic matter.

3.2. Pilot plant results

The pilot plant was fed with municipal wastewater from a combined sewer system during the summer 2010. Inlet water characteristics were stable and average

Table 1
Characteristics of inlet water, biofilm reactor effluent and removal rates

	MLSS	COD	FCOD	SMP_p*	SMP_c*	DOC	UV_{245}**	NH_4–N	TN	tot-P
Inlet	176.48	614.50	316.80	66.80	10.25	91.78	0.69	46.29	52.04	22.30
[mg/l]	±41.22	±72.47	±54.48	±10.59	±1.66	±22.28	±0.15	±8.21	±11.03	±3.21
MBBR effluent	191.40	326.50	62.34	26.52	8.57	23.84	0.41	28.54	40.11	15.20
[mg/l]	±39.65	±39.60	±7.35	±4.54	±1.89	±3.30	±0.06	±15.81	±7.93	±2.67
R*** [%]	–8.45	46.87	80.32	60.31	16.42	74.03	–	38.34	22.92	31.82

*-refer to total amount of proteins and carbohydrates measured by colorimetric methods [21–22].

-unit **[cm^{-1}].

***-R refer to removal rates.

values were shown in Table 1. The bioreactors operated at HRT 4h had stable performance with respect to COD, FCOD, DOC, SMP's, NH–$N_{4,}$ TN and tot-P removal rates (Table 1). Water temperature was on average 20±1.5°C during the whole period.

Alum and iron at lower dosage (i.e., 9 ppm), showed similar performances giving average fouling rates of 1.65 and 1.70 mbar/h, respectively, which was three times better performance then during the control runs when average fouling rate was 4.11 mbar/h. The iron based coagulant showed better performance than the alum at higher dosages (i.e., 22.5 ppm), giving average fouling rates of 0.58 and 1.47 mbar/h, which was 7 and 3 times lower then in control reactor.

This was related to better SMP_c reduction of iron based coagulant, however not proportionally to observed reduction, again indicating complexity of membrane fouling in BF-MBR. Iron chloride sulfate at dosage of 13.5 ppm showed poorer performance in comparison to iron chloride at lower dosage (i.e., 9 ppm), with almost no improvement in membrane performance (i.e., fouling rate 3.92 mbar/h).

Alum chloride with higher basicity at dosage of 13.5 ppm resulted in almost the same fouling rates (i.e.,1.67 mbar/h) as regular alum chloride at lower dosage (i.e., 9 ppm), indicating that higher basicity not necessarily would improve filterability in BF-MBR. Alum chloride with higher basicity effected better MLSS aggregation which was measured as lower MLSS values around membrane for about 25% and in the same manner higher in retentate stream, but better DOC removal expressed thought CAU, due to this feature have not been seen as suggested in drinking water applications [18]. Results with cationic polymer indicated that only thoroughly controlled dosage of this polymer can give improvement. Continuous dosage in the beginning of the cycle gave improvement on performance since fouling rate was 1.71 mbar/h in first 24 h, however, later sharp increments in TMP development suggested that the membrane was fouled by the polymer itself. This was observed even at much lower dosages, bellow 9 ppm. Results suggested that continuous dosing is not an option, since eventually overdose of polymer occurs which results in membrane fouling by polymer. Therefore, the effect of intermittent dosing on membrane performance was further investigated. Both membranes were operated at a higher flux of 30 l.m^{-2}·h^{-1} , with higher recovery of 96% for 12 h, at which a dosage of 100 and 300 mg (per l of volume reactor) was instantaneously applied (Fig. 5). The sharp TMP rise was stabilized and after 3 h, when TMP started to rise a continuous dose of 2.7 ppm and 0.9 ppm was applied for the next 20 h. The strategy of 100 mg + 2.7 ppm reduced fouling rate by seven times for tested period, giving an indication that application of cationic polymer could be highly beneficial, however proper dosing strategy is crucial for successful use of this additive [14–15]. However, this finding has to be tested for longer period of time and further refinements of dosing strategies are required. This study was also used to estimate which of the parameters that represents organic colloidal matter (i.e., FCOD, SMP_p, SMP_c and DOC) could be the best with respect to predicting membrane fouling. Results from polymer were not taken in consideration, since a fouling potential by the polymer itself was observed.

Amount of compound retained by membrane was related to daily fouling rates (since chemical analysis

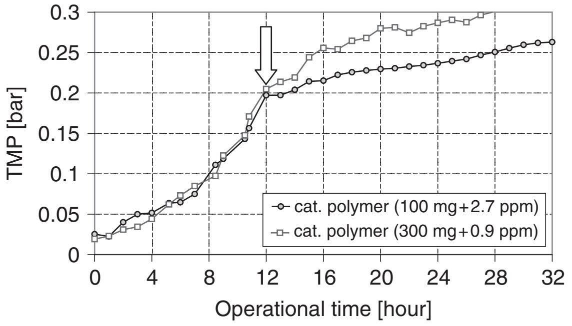


Fig. 5. Suggested strategy for polymer dosage for short term experiment.

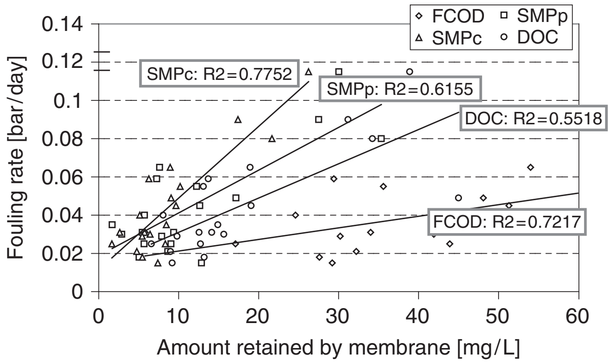


Fig. 6. Correlation between given parameters and membrane fouling.

was performed once a day from grab samples). Results suggest that SMP_c and FCOD could be used as a good fouling potential predictor, while SMP_p and DOC showed weaker correlations to fouling rates (Fig. 6). Both inorganic coagulants show a good ability to reduce total phosphorus, however, at lower dosages alum gave better removals per applied dosage compared to iron, i.e., 1.20 to 0.98 mg P removed/mg metal, while at higher dosages this ratio was almost the same 0.58 to 0.55, respectively. The polymer tested did not affect amount of tot-P.

4. Conclusions

Five different additives, iron chloride and iron chloride sulfate, two polymerized alum with different basicity and a modified cationic polymer, where chosen in order to investigated a possible filterability improvement in a BF-MBR process. After extensive jar tests three dosages were chosen, 9, 13.5 and 22.5 ppm, for pilot plant trials. The best improvement in membrane performance was observed for the higher chosen dosage of iron chloride, while alum chloride gave lower improvement at the same applied dosage. Higher basicity of the polymerized alum did not give an expected improvement in filterability due to higher CAU with respect to DOC removal. A cationic polymer was found difficult to use for continuous dosing application, though a fouling reduction potential was observed for an alternative dosing strategy tested. Amount of SMP_c retained by the membrane relative to the measured fouling rates was found to be the preferred parameter with respect to predicting membrane fouling potentials. Additionally, was confirmed that FCOD could be used as good fouling predictor in BF-MBR. Since, chemical precipitation of phosphorus by metal coagulants is common practice when applying moving-bed-biofilm reactors for wastewater treatment, a synergetic effect of phosphorus removal and improved membrane performance is foreseen when designing a BF-MBR using a moving-bed-biofilm reactor. Based on the testes conducted in this study the iron chloride coagulant in particular appears to be the additive of choice for a BF-MBR process.

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