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Searching for a universal fouling indicator for membrane bioreactors

T. de la Torre[a,]*, V. Iversen[b], F. Meng[b], J. Stüber[a], A. Drews[b], B. Lesjean[a], M. Kraume[b]

[a]*Berlin Centre of Competence for Water, Cicerostr. 24, 10709 Berlin, Germany*
Now working with Acciona Water, Avenida de Europa 28108, Madrid, Spain;
Tel.: +493053653806; Fax: +493053653808; email: boris.lesjean@kompetenz-wasser.de
[b]*Chemical and Process Engineering, Technische Universität Berlin, Straße des 17. Juni 135, 10623 Berlin, Germany*
Tel.: +493031423701; fax: +493031421134; email: matthias.kraume@tu-berlin.de

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ABSTRACT

Numerous papers have been published studying the causes of fouling in membrane bioreactors (MBRs) and searching for a universal fouling indicator. Unfortunately, as these studies were performed using various set-ups and operating conditions (different membranes, sludge retention time (SRT), hydraulic conditions and diverse feed wastewaters, etc.), the results in terms of fouling rates and the influence of individual parameters rarely match up. In order to obtain a significant database of comparable results from different plants, an intensive monitoring campaign of four MBR systems started in 2007 in Berlin. In these units, 14 parameters were monitored on a weekly basis over 10 months to characterise the mixed liquor and the corresponding permeability, including the novel parameter transparent exopolymer particles (TEP), which represent a specially sticky fraction of the extracellular polymeric substances (EPS). By performing statistical analyses it was demonstrated that there is no unique fouling indicator, and origins of fouling must be searched in the combination of several parameters using multivariable analysis. Applying a multiple regression the critical flux values could be correlated with four parameters (temperature, nitrate, bound and soluble TEP) measured in the activated sludge for 95% of the data.

Keywords: Extracellular polymeric substances (EPS); Fouling; MBR; Statistical analysis, Transparent exopolymer particles (TEP)

1. Introduction

Numerous papers have been published studying the causes of fouling in membrane bioreactors (MBRs) (e.g., [1,2]) and searching for a universal fouling indicator (e.g., [3,4]). Unfortunately, as these studies were performed using various set-ups and operating conditions (different membranes, sludge retention time (SRT), hydraulic conditions and diverse feed wastewaters, etc.), the results in terms of fouling rates and the influence of individual parameters are rarely comparable. After the work of Rosenberger et al. [5], several posterior studies tried to replicate the relationship found by them between carbohydrates concentration in activated sludge supernatant and fouling rates in MBRs. In some cases, this linear relationship could be confirmed, whereas no relationship was found in other studies [6]. This illustrates the difficulty of evaluating MBR fouling in terms of commonly used parameters.

*Corresponding author.

Table 1
Operating conditions of the investigated MBR units (October 2007–October 2008).

	Volume (m^3)	SRT (d)	TS[a] (g/L)	COD filtrate* (mg/L)	COD influent (mg/L)	COD effluent (mg/L)	Temperature (°C)
MBR1	1.5	12	4–13	20–125	120–1600	14–72	16–28
MBR2	1.5	12	5–12	30–150	120–1600	13–45	16–26
MBR3	10	25	13–22	90–850	750–2500	40–50	10–26
MBR4	5	35[b]	5–13	48–440	750–2500	35–45	10–23

[a]In mixed liquor taken from the membrane tank.
[b]Since April 2008. No sludge withdrawal before (SRT>200 d).

The objective of this study was to evaluate the possibility of obtaining a universal parameter for different MBRs which could be used as a quick, easy indicator for fouling in MBR. Therefore, an intensive campaign was carried out in Berlin for 10 months monitoring four different MBRs on a weekly basis. For one side, the filterability of the activated sludge from the MBR units was measured using the Berlin filtration method (BFM), which uses a small membrane filtration aerated test cell which can be submerged directly in the biological tanks to determine the filterability of the activated sludge in situ. Filterability is expressed in terms of critical flux obtained by performing flux-stepping experiments. On the other side, 14 parameters were measured in the activated sludge and sludge supernatant. The resulting set of data was statistically analysed using multivariable analysis in order to investigate the relative influence of the studied parameters on activated sludge filterability.

2. Materials and methods

2.1. Membrane bioreactor systems investigated

The main characteristics of the investigated MBR units are presented in Table 1. MBR1 and MBR2 were identical and worked in parallel with pre-settled municipal waste water. In MBR2, a flocculant for permeability enhancement was added periodically [7]. MBR3 was designed for enhanced nutrient removal. An additional unit (MBR4) designed for chemical oxygen demand (COD) removal and nitrification was installed in January 2008 side by side to the MBR3 unit. Although both units were treating domestic waste water, rainwater infiltrations took place during the investigated period, which explains the broad range of the COD showed in Table 1.

2.2. Critical flux measurements—Berlin filtration method

Fouling propensity of mixed liquors in different MBRs was evaluated using the in situ BFM. Hereby the critical flux J_{crit} was measured directly inside the plant so that there is no alteration of the sludge. Geometry and aeration were set to mimic hydrodynamic conditions in a full scale technical module [8]. The measurement procedure of the BFM test cell was totally fixed so that the results from the different plants were comparable. The test cell (Fig. 1) used an ultrafiltration UF flat-sheet membrane (Poly Ether Sulphone PES, BioCel®) with an effective surface area of 0.025 m^2. The protocol for the measurement of J_{crit} shown in Fig. 2 was a modified flux-stepping method based on Ref. [9] which includes relaxation between steps, and a short period at a flux J = 10 L/(m^2 h) before every filtration step which enables the detection of possible irreversible fouling (which will not be discussed in this study). Additional measurements were carried out ex situ in an air-sparged cross-flow test cell [10].

The critical flux values were normalized to 20°C by correcting the TMP data with viscosity data of the permeate (η_p) as described in Ref. [8].

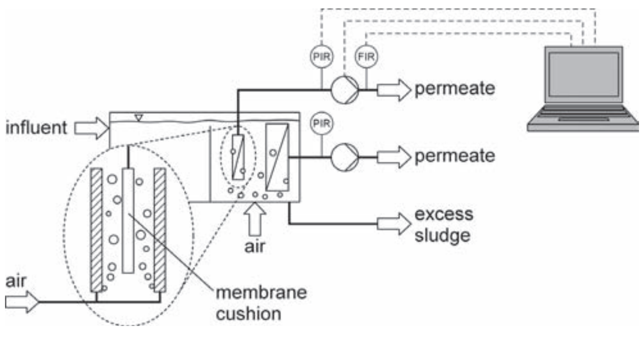

Fig. 1. Scheme of the in situ BFM test cell.

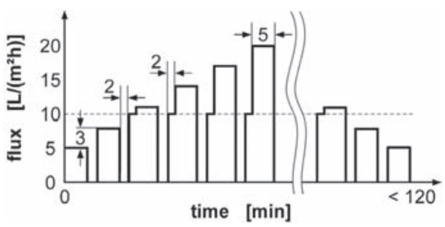

Fig. 2. Modified pre-step critical flux protocol.

2.3. Measured parameters in the activated sludge

The J_{crit} data obtained were correlated with the parameters measured during the monitoring campaign. These parameters were time to filter (TTF), capillary suction time (CST), diluted sludge volume index (dSVI), concentrations of bound and soluble extracellular polymeric substances (EPS), total solids (TS), organic total solids (oTS), total organic carbon (TOC), nitrate, nitrite and transparent exopolymer particles (TEP) (both bound and soluble). TEP represents a novel parameter which has been recently introduced into the investigation of MBR fouling [11]. They are mainly acid mucopolysaccharides and represent a sticky fraction of the EPS. Additionally, the sludge from each plant was fractionated by subsequently filtering through filters of different pore sizes. In every fraction, carbohydrates (CH), proteins, TEP and COD concentrations were measured in order to identify the most significant fraction for fouling and to obtain information about the size of the main foulants.

2.4. Chemical methods

Before performing the chemical analyses, mixed liquor filtrate and influent filtrate were obtained by paper filtration. For that purpose, filter papers (Schleicher and Schuell/Whatman, Black Ribbon Ø 90 mm, Germany) were rinsed with 200 mL deionized water. After that, 50 mL of sample were filtered. Duplicates of all analytical measurements were performed in order to minimize the random error.

To determine the concentrations of bound EPS (bEPS) and bound TEP (bTEP), an extraction process was performed using a cation ion exchange resin following Ref. [12]. After extraction, the measurement of the bound fractions followed the same procedure as that of the respective soluble fraction.

Alcian blue method. The analysis method described by de la Torre et al. [11] was used for the determination of the TEP concentrations.

Soluble COD. Commercial test kits were used for the determination of COD (Hach Lange, Germany) in the activated sludge filtrate and permeate.

EPS analysis. EPS concentration is determined as the sum of carbohydrates and protein concentrations. The method by Dubois et al. [13] was used to measure the concentrations of carbohydrates and the one by Frølund et al. [12] for that of proteins. To take cross-sensitivities into account, the carbohydrate concentrations were corrected for nitrate and nitrite concentrations [14]:

$$c_{\mathrm{CH\ corrected}} = c_{\mathrm{CH}} - 0.099c_{\mathrm{NO_3}} - 1.99c_{\mathrm{NO_2}}$$

2.5. Physical methods

CST, TS, oTS and dSVI were measured following standard methods [15]. TTF was measured under atmospheric pressure as the time required to obtain 25 mL of filtrate from 250 mL of activated sludge using a paper filter (Black Ribbon, Schleicher and Schuell, Germany).

2.6. Activated sludge fractionation

Apparent molecular weight distribution of soluble fractions was determined by fractionation using series of microfilters with nominal pore sizes of 50 µm and 10 µm (filter bags), 2 µm (paper filter, Blue Ribbon, Schleicher and Schuell, Germany) and 0.2 µm (cellulose acetate filters, Sartorius AG, Germany).

2.7. Statistical analysis

All results from the monitoring program were analysed with the statistical tool SPSS 17.0. First, the correlation matrix of two parameters was obtained with J_{crit} measured either in situ or ex situ being the dependent variable. For the evaluation of the correlation between the variables, the Pearson regression coefficient r ($-1 \leq r \leq 1$) was calculated which expresses the intensity of the correlation between the two variables. The higher the absolute value of r the stronger the relation between the two parameters. Not only the r value was taken into account but also the number of samples (N). The degree of significance taken into account the number of samples is given by the statistical analysis in terms of number of asterisks (*medium significance; **high significance).

Subsequently, a multiple linear regression was performed in which the significance of the parameters measured in the mixed liquor/sludge filtrate on the dependent variable critical flux J_{crit} was quantified. The standardized regression coefficients of the linear regression (β coefficients) are calculated by subtracting the mean value and dividing the standard deviation, so that they indicate the sensitivity of the dependent variable to each of the independent variables (predictors). Higher values of β indicate a greater impact of the influencing parameter on the dependent variable. The coefficient of determination R^2 represents the percentage of variance of J_{crit} that can be explained by the predictors. The significance of the model gives the probability that the fitting occurred just randomly.

As the measurement of the various parameters was often performed on different days, an interpolation of the data was necessary in order to achieve a representative group of data for the multiple linear regression (approx. 30 values). Temperature data were not interpolated as they were daily monitored.

Table 2
Correlations with J_{crit} measured in situ and ex situ (data from all MBR systems).

	J_{crit} in situ		J_{crit} ex situ	
	r	*N*	*r*	*N*
J_{crit} ex situ	0.050	6†	1	31
J_{crit} ex situ int.	0.452**	21	1	25
J_{crit} previous in situ	0.713**	15	–0.275	9+
J_{crit} previous in situ int.	0.927**	86	0.269	23
Temperature	0.566**	90	–0.207	18
pH	0.259	50	0.414	19
TEP coll.	–0.618**	30	0.035	13
TEP coll. int.	–0.558**	75	0.129	29
TEP rejection	–0.606**	30	–0.041	13
TEP rejection int.	–0.667**	75	–0.047	29
CH 2 µm	–0.694*	12	0.824	4+
CH 2 µm int.	–0.717**	33	–0.137	19
bTEP/TEP	0.845**	27	0.240	28
bTEP/TEP int.	0.773**	41	–0.139	13

*Medium significance and **significant.
†Less than 10 samples; int. = interpolated; *N* = number of samples; *r* = Pearson coefficient.

3. Results and discussion

3.1. Correlation matrix

Table 2 shows the statistical significance (expressed by the Pearson coefficient *r*) of individual parameters for the critical flux data from all four MBR systems together.

The considerable discrepancy between the correlations found with the interpolated data (int.) and those found with the raw data is caused by the different set of data gained by interpolation. The interpolation did not concern all parameters in the same way, as it affected more those which are more dynamic and also those which were less frequently measured.

Comparing the influence of the individual parameters on J_{crit} measured directly in the MBR (in situ) with the test cell results (ex situ), a more significant correlation was always found for the in situ measurement. This agrees with the correlation coefficient between these two parameters (J_{crit} in situ and J_{crit} ex situ), which is only 0.45.

The parameter "J_{crit} previous" was introduced to analyse the response time of the MBR systems. The critical flux showed a very high correlation with its last value measured, even if this was taken after more than one week. Therefore it was concluded that the parameter J_{crit} could be monitored on a weekly basis (which was done in this study). It also justifies the interpolation of J_{crit} data.

A direct influence of the temperature on critical flux is frequently mentioned in the literature. Although the critical flux values were temperature corrected to account for the temperature influence on viscosity, temperature also influences almost all the rest of the considered parameters from this study in a different way [4]. The linear relationship found is thus only "virtual", as much more complicated relationships probably would be found if a more detailed statistical analysis was performed. Such complex interactions also exist between several other parameters investigated here.

pH values did not significantly affect critical flux values. It must be stated that the influence of this parameter on J_{crit} is indirect, as it may affect other parameters like nitrate, carbohydrate and protein concentrations and properties, etc. When the correlation between pH and the other influencing parameters was considered, the highest Pearson coefficients (approx. 0.6) were found with CH filtered through 10-µm filter bags and with the rejection of proteins.

The highest significance for J_{crit} in situ was found for the ratio bTEP/TEP, with a regression coefficient of 0.845 (0.773 with interpolated data) for all MBR systems. The second most relevant parameter was the TEP rejection (difference between TEP concentrations in the sludge and in the permeate), which led to a Pearson coefficient of –0.667 with the interpolated data, and CH 2 µm to a coefficient of –0.694, which showed a higher *r* value but lower significance because of a low number of samples (*N* = 12).

Protein concentrations showed low correlations with the critical flux, represented by a maximum *r* of 0.45 for the rejection of proteins.

The bound parameters measured showed very low correlations as well as the TS (data not shown). However, TS and bTEP proved to be important parameters in the multiple linear regression.

Slightly higher significance was found when evaluating the retained fraction (subtracting the concentration in the permeate from the concentration in the mixed liquor sludge filtrate) of the carbohydrates, proteins and TEP than when using the values in the mixed liquor sludge filtrate.

The parameters typically used for the quick evaluation of activated sludge filterability or settleability TTF, CST and dSVI showed low Pearson coefficients of less than 0.6 in all cases (Table 3) and even lower coefficients when the parameters were standardized by dividing them to TS.

3.2. Multiple linear regression

Five variables were found to influence the critical flux the most: TEP in the filtrate, bTEP in the sludge, temperature, nitrate concentration in the filtrate and total

Table 3
Significance of parameters for quick filterability evaluation.

	J_{crit} in situ		J_{crit} ex situ	
	r	*N*	*r*	*N*
TTF	–0.542**	27	0.289	13
TTF int.	–0.396**	80	0.298	29
CST	–0.404	13	0.259	12
CST int.	–0.258	55	0.315	26
dSVI int.	–0.257	10	–0.580	10
dSVI	–0.135	36	–0.018	20
TTF/TS	–0.534	10	0.284	10
CST/TS	–0.418	23	0.120	12

**Significant.
int. = interpolated; *N* = number of samples; *r* = Pearson coefficient.

solids concentration. When the parameter bTEP/TEP was tested in the multiple linear regression, in all cases, lower coefficients of determination were found compared to regressions using bTEP and TEP individually. The reason why the ratio correlated so significantly with the filterability in the univariable analysis lies probably in the combination of two parameters that both influence J_{crit}. This results in better Pearson coefficients than taking only one of the variables (TEP or bTEP) into account.

The best fit for all MBR systems was found with the parameters listed in Table 4. The result is based on a number of samples between 34 and 90. The coefficient of determination R^2 equals 0.949. That means that the temperature and the concentrations of bTEP, TEP and nitrate in the sludge filtrate could explain 95% of the variance in the J_{crit} values. In this model, the best significance was obtained (0.000).

The relevance of nitrate concentrations on the filterability of sludge was already mentioned by Drews et al. [14] and Kim and Nakhla [16]. This study demonstrated that the nitrate influence on the filterability of activated sludge cannot be explained only by its influence on the soluble EPS concentration, as this parameter shows a lower relationship with filterability than the concentration of nitrate.

Table 4
β coefficients and significance of the model for the important parameters.

Parameter	β coefficient	Significance
NO_3 interpolated	0.488	0.000
TEP interpolated	–0.596	0.000
Temperature	0.566	0.000
bTEP interpolated	0.812	0.000

The TEP concentration was significantly more important for fouling than those of CH, proteins or total EPS, as the linear models obtained including these parameters always exhibited lower coefficients of determination.

4. Conclusions

It was demonstrated that there is no single universal fouling indicator and the causes of fouling must be searched in the combination of several parameters. Applying multivariable analyses, the critical flux values could be explained using four parameters measured in the activated sludge for 95% of the data.

The statistical univariable analysis identified the ratio bTEP/TEP as the most significant factor for J_{crit} having a positive effect on sludge filterability. Bound components (here bTEP) are known to have a beneficial effect on filterability probably as a consequence of a more porous cake layer. On the other hand, higher concentrated soluble components (here lower bTEP/TEP ratio) are commonly related to lower filterability, which agrees also with the results obtained in this study. However, when performing multivariable analysis, the parameters TEP and bTEP fitted better as individual predictors than as a combined independent variable. Although CH concentration showed high correlations when plotted against the J_{crit}, TEP which mainly covers the stickier polysaccharides fitted better in all cases when performing multiple variable analyses.

The third parameter that significantly influenced fouling was the temperature. Even though J_{crit} was temperature corrected, this parameter also influences several other factors like the membrane resistance itself, nitrification, floc sizes and the release of EPS.

Although nitrate concentration showed a low correlation with J_{crit} when considered as an individual parameter, it appeared to be of significant importance when incorporating additional variables in the multiple linear analysis. The mechanism by which this parameter influences filterability is not totally clear yet. It is known that soluble EPS concentration is affected by it but it is als known that there are further influences on filterability which was also demonstrated in this study.

The classical parameters for filterability and settleability taken from the CAS and commonly used for a quick evaluation of sludge filterability in MBR like TTF, CST and dSVI did not show any strong relationship with J_{crit} of the sludge. Only TTF showed a high correlation with the critical flux for the MBR system that had a relatively high TS concentration (MBR3).

Comparing the influence of the individual parameters on J_{crit} measured directly in the MBR (in situ) with test cell results (ex situ), a more significant correlation was always found for the in situ measurement. This indicates that ex situ test cell experiments are less representative for the fouling propensity of MBR-activated sludge.

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References

[1] P. Le-Clech, V. Chen and A.G. Fane, Fouling in membrane bioreactors used in wastewater treatment, J. Membr. Sci., 284, (2006) 17–53.

[2] F. Meng, S.-R. Chaeb, A. Drews, M. Kraume, H.-S. Shind and F. Yang, Recent advances in membrane bioreactors (MBRs): Membrane fouling and membrane material, Water Res., 43(6) (2009) 1489–1512.

[3] S. Rosenberger, H. Evenblij, S. te Poele, T. Wintgens and C. Laabs, The importance of liquid phase analyses to understand fouling in membrane assisted activated sludge processes—Six case studies of different European research groups, J. Membr. Sci., 296 (2005) 113–126.

[4] A. Drews, Membrane fouling in membrane bioreactors—Characterisation, contradictions, cause and innovative cures, J. Membr. Sci., (2009) (in press).

[5] S. Rosenberger, C. Laabs, B. Lesjean, R. Gnirss, G. Amy, M. Jekel and J.-C. Schrotter, Impact of colloidal and soluble organic material on membrane performance in membrane bioreactors for municipal wastewater treatment, Wat. Res., 40(4) (2006) 710–720.

[6] A. Drews, M. Vocks, U. Bracklow, V. Iversen and M. Kraume, Does fouling in MBRs depend on SMP?, Desalination, 231(1–3) (2008) 141–149.

[7] V. Iversen, H. Koseoglu, N.O. Yigit, A. Drews, M. Kitis, B. Lesjean and M. Kraume, Impact of membrane flux enhancers on respiration and nutrient removal in MBRs, Water Res., 43 (2009) 822–830.

[8] T. de la Torre, V. Iversen, A. Moreau and J. Stüber, Filtration charaterization methods in MBR systems: A practical comparison, Desalin. Water Treat., 9 (2009) 15–21.

[9] P. Le-Clech, B. Jefferson, I.S. Chang and S. Judd, Critical flux determination by the flux-step method in a submerged membrane bioreactor, J. Membr. Sci., 227 (2003) 81–93.

[10] S. Rosenberger and M. Kraume, Filterability of activated sludge in membrane bioreactors, Desalination, 151 (2002) 195–200.

[11] T. de la Torre, B. Lesjean, A. Drews and M. Kraume, Monitoring of transparent exopolymer particles (TEP) in a membrane bioreactor (MBR) and correlation with other fouling indicators, Water Sci. Tech., 58(10) (2008) 1903–1909.

[12] B. Frølund, R. Palmgren, K. Keiding and P.H. Nielsen, Extraction of extracellular polymers from activated sludge using a cation exchange resin. Water Res., 30 (1996) 1749–1758.

[13] M. Dubois, K.A. Gilles, J.K. Hamilton, P.A. Rebers and F. Smith, Calorimetric method for determination of sugars and related substances, Anal. Chem., 28 (1956) 350–356.

[14] A. Drews, J. Mante, V. Iversen, M. Vocks, B. Lesjean and M. Kraume, Impact of ambient conditions on SMP elimination and rejection in MBRs, Water Res., 41(17) (2007) 3850–3858.

[15] L.S. Clesceri, A.E. Greenberg and A.D. Eaton, Standard Methods for the Examination Water and Wastewater. American Public Health Association, Washington, DC, 1998.

[16] L. Kim and G. Nakhla, Comparative studies on membrane fouling between two membrane-based biological nutrient removal systems, J. Membr. Sci., 331(1–2) (2009) 91–99.