Estimation of long-term resistance changes in a submerged MBR system using theoretical and empirical methods

Master's Thesis

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Abstract:

This project investigates different models used and possibly usable for modelling of resistance changes from sorption in MBR systems. The goal was to create a model for prediction of time needed to reach predetermined resistance values. Data was taken from a constant pressure submerged MBR setup, logging was done every 30 seconds over one year. Data filtering was based on standard deviation from a moving average. All models had only a subset of the full data available for fitting, whose size increased one by one after each fit.

The widely used first order exponential model failed to produce any result. A modified version, the stretched exponential model had a better outcome, but it was still prone to produce errors. It was found that these models presume the existance of only one steady-state resistance value while in practice that may be not a valid assumption. A more sophisticated model was developed to overcome this difficulty, but lack of necessary data type prevented its use. Finally, an empirical model based on rate of resistance increase was able to predict cycle endtimes with greater accuracy.

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Table of abbreviations and nomenclature

α .... Porosity of membrane on unit surface [1/m^2]

β .... Fitted variable of stretched exponential model; value depends on rate of diffusion

μ .... Dynamic viscosity [Pa$*$s]

ρ ....Density of contaminated water [kg/dm^3]

a ....Ratio of adsorbed and maximal capacity of adsorbed material

a_{lim} ....Value of a at R_{lim}

A_m ....Surface of membrane [m^2]

c .... Concentration of foulants in water [mg/dm^3]

c_{in} ....Concentration of foulants entering the membrane [mg/dm^3]

c_{out} .... Concentration of foulants leaving the membrane [mg/dm^3]

C ....Membrane dependent constant [1/μm^4]

$\langle D_{cs} \rangle$ .... Average cross-sectional diameter of pore [μm]

$\langle D \rangle$ ....Cross-sectional diameter of pore [μm]

f_D .... Darcy-Weisbach factor

g ....Gravitational constant [m/s^2]

h ....Height of water column in tank [cm]

J ....Flux through membrane [dm^3/s]

L ....Length of pore [μm]

m_{ad} ....Mass of adsorbed material into membrane [mg]

m_{cap} .... Maximal mass of adsorbed material into membrane [mg]

MBR..Membrane bioreactor

Δp_p .... Pressure drop on a single pore [Pa]

r_{ads}..Rate of adsorption [mg/s]

r_f ....Rate of membrane fouling [1/s]

r_{inc} .... Rate of resistance increase [1/(dm^3∗s)]

R .... Resistance to flow in an MBR system [1/dm^3]

R_a ....Resistance from sorption onto the membrane [1/dm^3]

$R_{a,ss}$ ....Maximal resistance from sorption onto the membrane [1/dm^3]

R_{irrec} ....Irrecoverable resistance of the mebrane [1/dm^3]

R_{irrev} .... Irreversible resistance of the membrane [1/dm^3]

R_{lim} .... Resistance where the operation of MBR turns cost-inefficient [1/dm^3]

R_m ....Virgin membrane resistance [1/dm^3]

R_{rev} .... Reversible membrane resistance [1/dm^3]

R_{tot} .... Overall resistance of MBR system to flow [1/dm^3]

RMSE ....Root mean squared error

SSE .... Sum of squares due to error

t ....Time [s]

t_{lim} .... Time at which R_{lim} reached [s]

t_{pr} .... Predicted time by model or method [s]

T .... Temperature [°C]

TMP .... Transmembrane pressure [Pa]

$\langle v_p \rangle$ ....Mean flow velocity in a pore [m/s]

V_{ad} ....Volume of adsorbed material [µm^3]

V_{lim} ....Maximal volume of adsorbed material [µm^3]

Preface

This thesis has been written by Mátyás Tóth during the 9th-10th semester of Chemistry at Aalborg university. The thesis was written from 01.09.2016 to 10.06.2017 with the purpose of developing a better model for prediction of long-term resistance changes in membrane bioreactors. For the patience, helpfulness in explanation of basic disciplines of membrane bioreactor systems, and data to work with, I would like to thank Morten Lykkegaard Christensen, and Mads Koustrup Jørgensen.

References are given according to the Havard method (Author, year) and abbreviations are placed in parenthesis the first time mentioned and used afterwards throughout the report.

Aalborg University, June 10, 2017

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Introduction

On 28th of July 2010, the United Nations General Assembly accepted Resolution 64/292 (United Nations 2010), whereas the basic right to clean and accessible water and sanitation is not arguable in the fulfillment of the other human rights. Therefore they called upon the member states and international organizations to provide sufficial funds, capacity building and technology to all, but mainly developing, countries to cover regions where these are not accessible. This resolution was made bearing in mind the United Nations Millennium Declaration (2000) whereas the ratio of population suffering the inaccessity of clean water and sanitation is to be halved by 2015.

Although the Declaration reached its goal as reported in the Progress on sanitation and drinking water (WHO/UNICEF 2015), new problems have surfaced. As of 2015, the poor people have the least access to clean water and sanitary facilities, while they were the target of the Resolution. That neccessitates cheaper and more widely accessible methods of wastewater cleaning and sanitation techniques while utilising environmentally sustainable solutions.

As for the wastewater technologies, many different methods are known and commercialized. The most widely used is the conventional activated sludge process (CAS) (Frost & Sullivan 2016), which is able to function with relatively small operational costs. Despite its big share in wastewater treatment, new methods are raising to take its place, with the membrane bioreactors (briefly, MBR systems) showing the biggest growth (Research and Markets 2015, Frost & Sullivan 2016). MBR systems offer higher quality effluent with smaller reactor volume, smaller environmental burden, and less sludge production without the need of secondary clarification or tertiary steps (as sand filtration) but at elevated installation and operational costs (Melin et al. 2006). These systems also offer removal of bacteria in the case of microfiltration (MF), and most viruses in case of ultrafiltration (UF) by size exclusion (Melin et al. 2006).

The MBR configuration can either consist of submerged membranes or membranes outside of the bioreactor, on an external circulation as seen on Fig. 1.1. In both cases, influent must be pre-treated in order to prevent damages and clogging of membranes by non-soluble solids. That may be done by sedimentation and by meshes with small grid distance, consequently. The membranes are installed within the bioreactor (submerged MBR) or are placed externally (side-stream MBR configuration). Pressure difference makes the contaminated water flow through the membranes and produce permeate. Another important factor in an MBR sys-

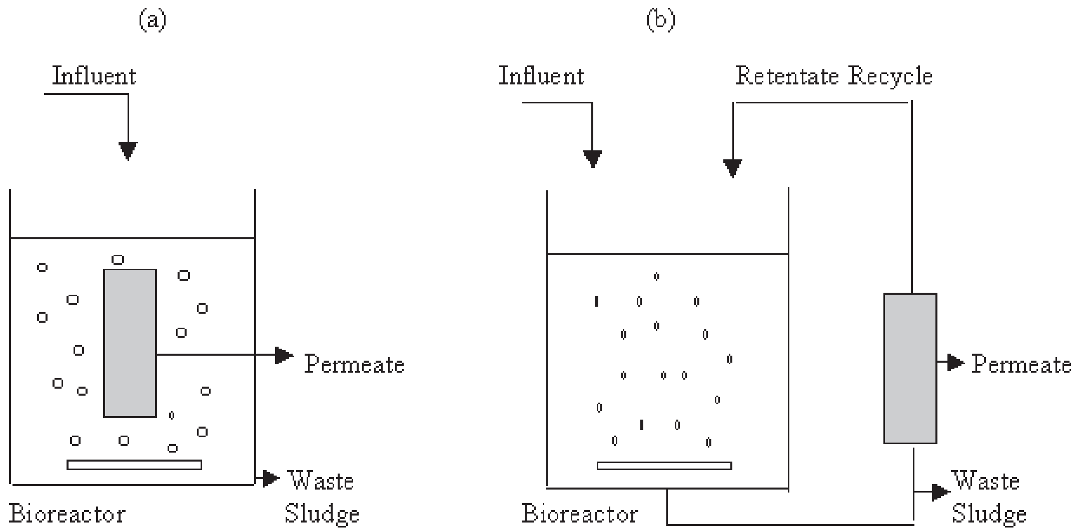

Figure 1.1: The two possible configuration of MBR systems: a) submerged MBR, b) side-stream MBR configuration. (Melin et al. 2006)

tem is the aeration which is done to provide oxygen to the biomass inside the bioreactor. In submerged MBR configuration it also scours the membrane surfaces thus preventing build-up of dense cake. Based on the membrane setup, further classification is possible to dead-end and cross-flow filtration. In dead-end filtration, water flow is orthogonal to the membrane surface, while in cross-flow it is tangential.The latter gained popularity primarily because of the slower cake formation as solids collected on membrane surface are washed away with unfiltered water (Melin et al. 2006). In dead-end filtration, the cake can be removed by other physical means, mostly by backflushing.

Fouling of the MBR system is one of the main causes of its elevated operational and maintenance costs (Drews 2010). Resistance originating from cake formation is often referred to as reversible resistance. On a longer term, materials adsorbed into the membrane pores increase the system's resistance to flow, thus maintenance cleanings are inevitable. That kind of fouling is coined as residual fouling which can be removed by chemically enhanced backflushing (maintenance cleanings). Of the same origin, some adsorbed materials remain even after maintenance cleanings, but can be removed by various types of chemical cleanings. This type of fouling is referred to as irreversible fouling. Finally, some contaminants can not be removed by any means from the system, increasing its resistance to flow permanently. This is referred to as irrecoverable fouling, and determines the overall lifetime of the membrane.

Materials causing fouling in the MBR system can be classified into three main categories: inorganic, organic, and biological contaminants (Wang et al. 2014). Inorganic fouling is caused by metal oxides and salts. Organic fouling consists of many kinds of carbon-based substances without regard of origin. Organic contaminants of antropogenic origin can be for example grease, oil, and surfactants, but also residues of medicaments' active ingredients. Organic contaminants of biological origin can be proteins, polysaccharides, and humic substances. Biofouling is based on the formation of compounds (biofilms) and metabolysm of microorganisms on the membrane surface.

In spite of the ongoing heavy research on membrane bioreactors and the amount of experimental data collected, complete understanding and control of processes inside an MBR system remain elusive. Currently, plant design and operation is mainly based on empirical methods rather than theoretical models (Drews 2010). Application of such methods prevents direct comparison between different setups, and makes improvements hard to extend to other configurations. Therefore improvements on the current theoretical view are in great demand. Better understanding of short-term and long-term processes is crucial in reduction of installation, maintenance, and operational costs.

While reversible fouling is being actively researched (Hu et al. 2017, Yang et al. 2017, Zouboulis et al. 2017), irreversible and irrecoverable fouling is a less preferred topic of articles. That may be attributed due to their slow increase over time overshadowed by reversible fouling, thus data about their value at a given time is not readily available for analysis(Huyskens et al. 2008). More accurate understanding of how the resistance increases over time, especially due to irreversible resistance is therefore could prove essential in further development.

This thesis tackles the problem of prediction of irreversible resistance over time in MBR systems, aiming for a better theoretical understanding of such facilities with support of practical data. This is done by analysis of data from a pilot-scale submerged MBR setup with constant pressure applied.

Data processing

2.1 Data source

Data have been collected by the contribution of Renseanlaeg Vest, Aalborg, which utilized a submerged MBR setup with constant pressure. The original file consisted of the following data columns: time (Unix time, seconds), flow rate (J) [l/h], concentration of foulants in contaminated water (c) [mg/dm^3], temperature of contaminated water (T) [°C], oxygen concentration [mg/l], denitrification tank level [cm], and water column height level [cm]. Using this data, the density (Tanaka et al. 2001) and dynamic viscosity (Kestin et al. 1978) of contaminated water have been calculated, disregarding the effect of dissolved contaminants. The transmembrane pressure (TMP) [Pa] was determined from the water column height level as seen in eq. 2.1.

$$TMP = h * g * \rho \tag{2.1}$$

The total resistance to flow (R_{tot}) was also calculated for each data point, using the Darcy law [source], as seen in eq. 2.2.

$$R_{\text{tot}} = \frac{\text{TMP}}{\mu * J} \tag{2.2}$$

2.2 Analysis and filtering of acquired data

In order to examine the irreversible and irrecoverable resistance changes, data must be collected from a long time interval as their absolute value changes slowly over time (Huyskens et al. 2008). Thus the monitoring of the total resistance is required for successful modeling. As seen on Fig. 2.1, the R_{tot}(t) function on a big scale shows no apprehensible change on long term, the data looks fuzzy and random.

That prevents the direct usage of data in further analysis as fitting of any model on this data set would either show really wide error intervals or would not even converge. Looking into detail on Fig. 2.2, the individual filtering-flushing cycles appear where resistance changes periodically which highlights part of the problem: the backflush and the initial part of a cycle is not part of the current investigation as they do not depend on the fouling of the membrane.

A self-made analytical program was utilized in order to filter out these intervals and the statistical noise of data. The theoretical background used in the program

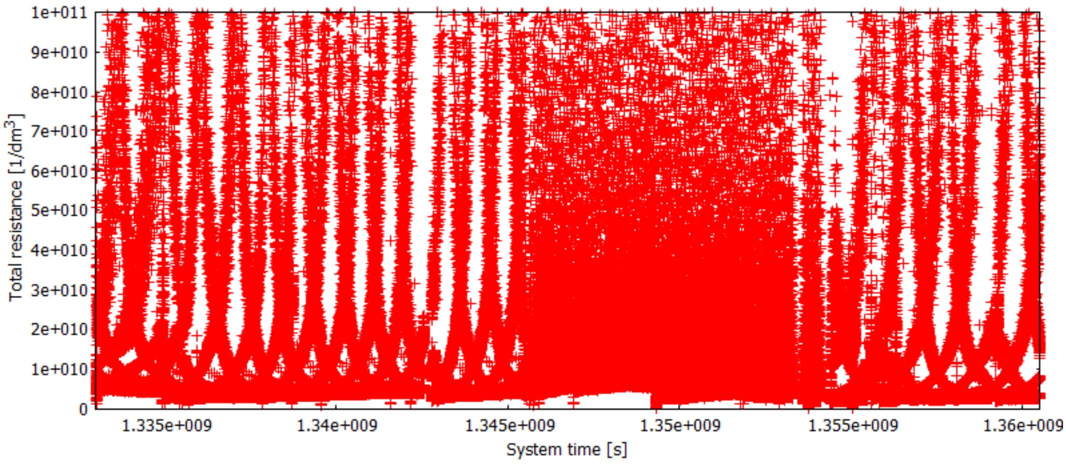

Figure 2.1: The entirety of data, approximately 1 year's worth of data points.

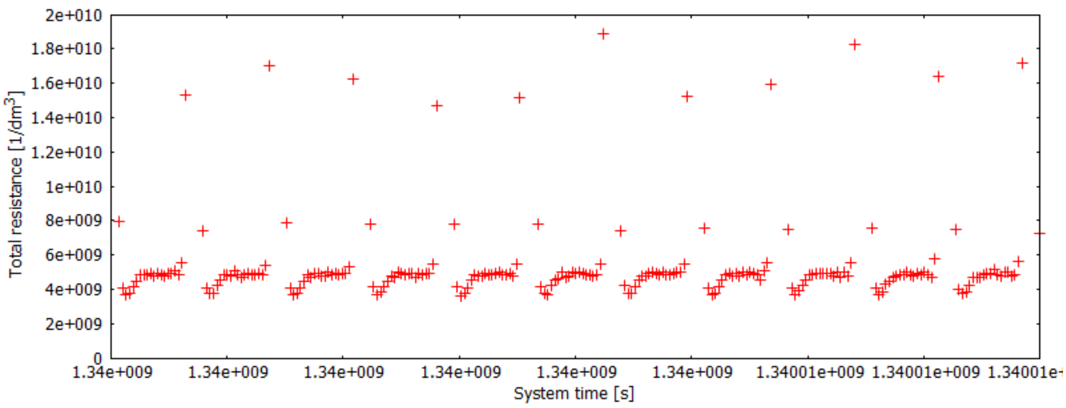

Figure 2.2: The total resistance of the MBR system over time, a small chunk (2 hours 10 minutes) of raw data.

is detailed in section 2.3. Finally, data of interest have been narrowed down to smaller segments where the resistance of the membrane increased more or less steadily. Unfortunately, in certain cases, long intervals of data had to be discarded because of possible instrumental failure or interventions. The remaining parts have also been separated as dictated by the dates of chemical cleaning of filters. These are handled as separate data sets during the analysis.

2.3 The statistical-analytical program

The main purpose of the current program was to reduce noise, and to remove irrevelant data like backflush from the main data body. The properties of this data set had to be taken into account while developing the statistical method: the average increases or decreases as time passes, and a single MBR cycle has considerable changes in flow rate (and this way, resistance) but it does not possess many data points. While the first problem can be addressed by a moving average of 'n' values, the latter one requires this moving average to not use too high 'n'. This problem is unique, and required special application of statistical tools. It was solved by using '$n+1$' moving averages, where each average was calculated using 'n' values around the investigated one without including it as shown in the following example. That was done to prevent shifting of average towards the examined value.

First, 'n' data values was taken, before and after the investigated value:

$$d_1,\ d_2,\ d_3, \ldots d_n, D, d_{n+1}, d_{n+2}, \ldots d_{2n}$$

where d_x denotes a data value, and D denotes the investigated value. Then '$n+1$' number of averages was defined:

$$\langle d_{1,\ n} \rangle = \frac{d_1 + d_2 + d_3 + \ldots + d_n}{n},$$

$$\langle d_{2,\ n} \rangle = \frac{d_2 + d_3 + d_4 + \ldots + d_n + d_{n+1}}{n},$$

and so on until $\langle d_{n+1,\ n} \rangle$:

$$\langle d_{n+1,\ n} \rangle = \frac{d_{n+1} + d_{n+2} + d_{n+3} + \ldots + d_{2n}}{n}$$

The respective standard deviations for each average were calculated:

$$\mathrm{SD}_{k,n+1} = \sqrt{\frac{\sum_{i=k}^{i\ <\ k+n} \left(d_i - \langle d_{i,n} \rangle\right)^2}{n-1}}$$

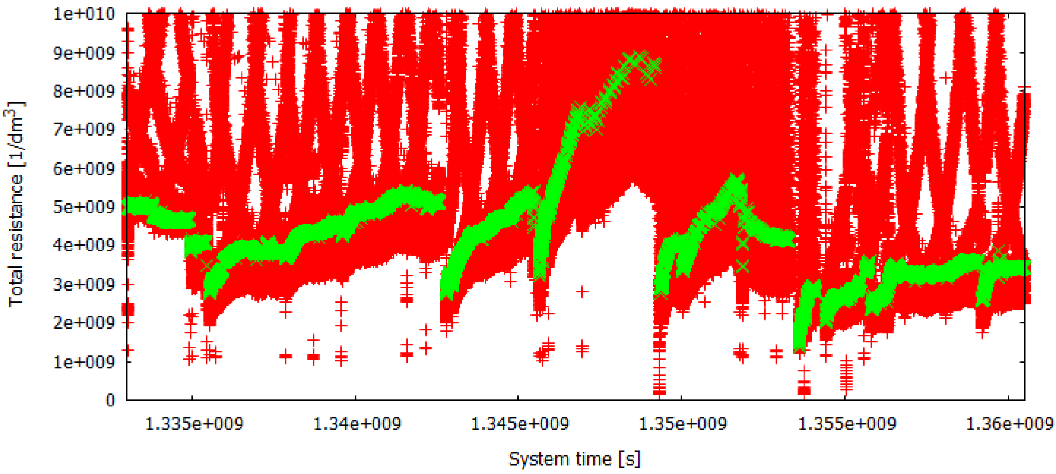

Figure 2.3: Comparison of raw (red) and filtered data (green). Most of raw data was cropped.

where $k \in \mathbb{R} \mid 0 < k < n+1$.

In case the value of interest was within a certain $'m'$ ($m \in \mathbb{R} \mid m > 0$) times standard deviation of at least one of the respective averages, and that average does not include any negative value, it was be regarded as a representative value of the cycle. Filtering was done based on the total resistance values. The value $'m = 0.0001'$ and $'n = 6'$ was chosen to leave about 0.02% of the original data, thus cutting off outliers but leaving enough for statistical purposes and fitting. As seen on Fig. 2.3, with these settings, the data is considerably smoother and contain a negligible amount of outliers. The effect of changing the $'m'$ while keeping the $'n'$ constant, and vica versa, can be seen on Fig. 2.4.

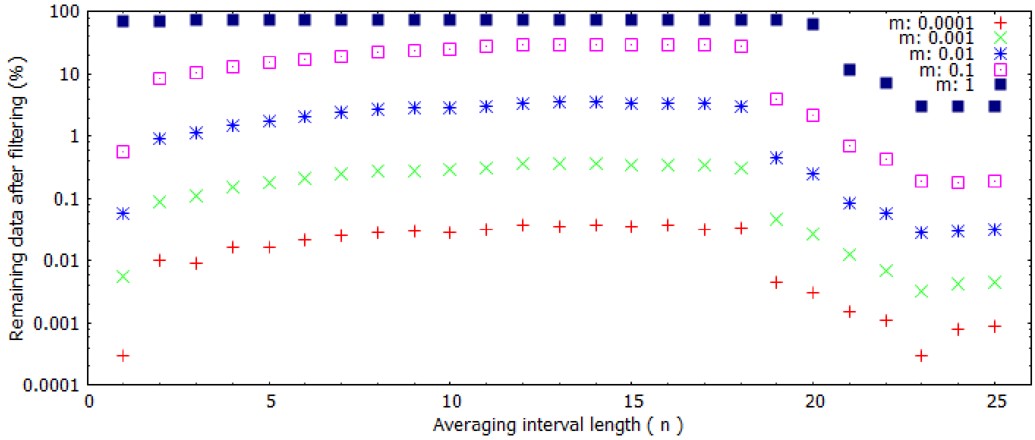

Figure 2.4: Filtering based on total membrane resistance using different filtering parameters. The *'n'* length of the averaging interval can be varied but the filtering efficiency does not show significant change while $1 < n < 19$. Meanwhile, *'m'* is roughly linearly proportional to amount of filtered data.

Exponential models

3.1 First order exponential model

The need for modeling of resistance from adsorbed material in an MBR system was present since Darcy's law was established. Early examples (Aimar 1987, Carrère et al. 2001) utilized an exponential function to simulate the base resistance change over time. That method is also applied in later articles (Juang et al. 2008*a*,*b*). Therefore using this model is a natural choice as a first approach.

Based on the Darcy's law, the resistance to flow can be expressed:

$$R = \frac{\text{TMP}}{\mu * J} \tag{3.1}$$

and according to (Huyskens et al. 2008), R can be further expressed as:

$$R = R_m + R_{\text{rev}} + R_{\text{irrev}} + R_{\text{irrec}} \ldots \tag{3.2}$$

As detailed by (Huyskens et al. 2008), the different resistance types may be regarded as independent from eachother. That allows the development of different models for each of the different resistance types.

Irreversible and irrecoverable fouling is based on adsorption of foulants to membrane pores (Judd & Simon 2015). Resistance from adsorption onto the membrane surface was found to be time dependant (Aimar 1987). The same can be concluded about resistance originating from absorption of contaminants into the membrane volume if the particle size is negligible compared to the diameter of pores. In either case, the resulting resistance decrease from foulants was described by the following equation (based on the Langmuir model):

$$R_a = R_{a,ss} * (1 - exp\,(-b * t)) \tag{3.3}$$

where $R_{a,ss}$ (maximal resistance from adsorption) and b (membrane and feed solution dependent constant) are fitted parameters. In the following section, the fitting is based on that equation, disregarding other parameters (like temperature, concentration of foulants, etc).

3.2 Fitting of first order exponential model to available data

Based on eq. 3.3, fitting was done on three different sections of data. Transforming the equation to a better suited form for fitting:

$$y = R_{a,ss} * (1 - exp(-b * x)) \tag{3.4}$$

where y denotes the resistance of the system at a given time, and x is the time stamp for a given resistance. To reduce error of fitting, the resistance and time values were reduced both to start from zero and to not reach excessively high values.

In order to model the ability to predict the date where a certain resistance value is reached in a real MBR setup, the model based on eq. 3.4 was fitted (using Matlab) to the first resistance values available in the data set. In each step, a new data point, following the previous ones in terms of time, was added to the initial cluster of data points, and a new model was fitted. Repeating this procedure led to a set of fitted parameters which were logged in a file. At the same time, a limiting resistance value was chosen by hand (R_{lim}), whose time stamp (t_{lim}) was also noted. That resistance value was regarded as the maximal resistance that very MBR system can reach (from this type of fouling) before turning inefficient in terms of operational costs. Using the previously fitted parameters and eq. 3.3, the time needed to reach the given resistance value was calculated (t_{pr}). Comparing this procedurally predicted time and the t_R can give a feedback on usefulness of this model. Unfortunately, despite fitting this function successfully on data in each and every case, actual value for t_{pr} was returned by the fitted functions only in exceptional cases (0-7 in different data sets). Despite this, the goodness of fit indicators do not show particularly bad fitting; the R-square varies between 0.8 and 0.99 throughout all data sets as seen on Fig. 3.1. Other goodness of fit statistics were also calculated for later comparison (see section 3.6).

As the exponential model is far from being able to predict future resistance values reliably in an industrial setup, the necessity of another, better model was realized.

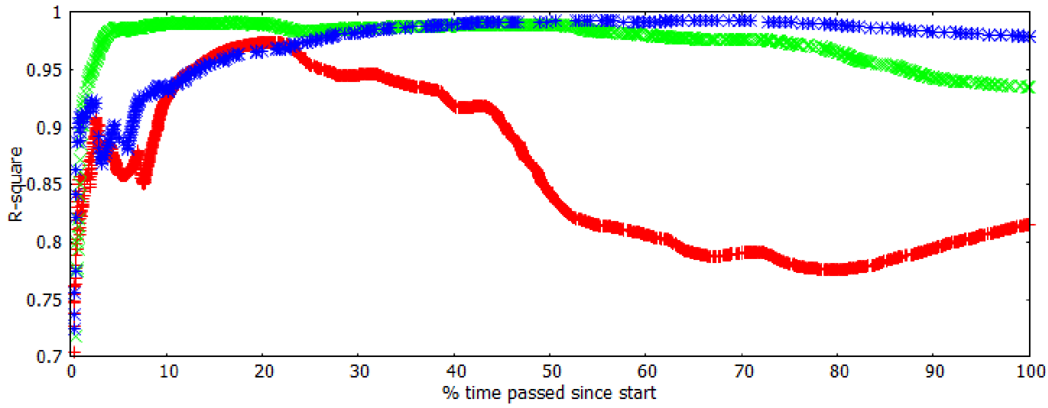

Figure 3.1: R-square values gathered from fitting of first order exponential model to growing data sets. Differently colored dots denominate different data sets.

3.3 Stretched exponential model

As known from colloidics and nanoscience, all liquids and solids seek to minimize their own surface energy. In the case of liquids, this is done by spontaneously changing their shape while solids are unable to do so. That leads to adsorption of other materials on the surface of the latter. In equilibrial conditions, Langmuir model is a reliable description of this process, but as seen in the previous section, it can not be utilized in this case. As detailed in (Snopok 2014), when something other than the actual adsorption of the material on a surface is the time-determining step, non-exponential kinetics may occur. Based on his model, eq. 3.3 must be corrected by addition of another fitted variable: an exponent inside the exponential function.

$$R_a = R_{a,ss} * \left(1 - exp\left(-(b * t)^{\beta}\right)\right) \tag{3.5}$$

The notations are the same as in 3.3. The value of β may change according to the diffusion speed of adsorbeants; at $\beta = 1$, the diffusion remains normal, while lower values show an anomalous case of subdiffusion (Ramsden 1992, Snopok 2014). Higher values of β give feedback about superdiffusion, but this is the rarer case (Snopok 2014).

3.4 Fitting of stretched exponential model

Similarly to section 3.2, eq. 3.5 is written up with the notations used for fitting:

$$y = R_{a,ss} * \left(1 - exp\left(-(b * x)^{\beta}\right)\right) \tag{3.6}$$

where y denotes the resistance from sorption, x denotes time since the start of the cycle, and $R_{a,ss}$, b, β denotes fitted parameters. The procedure was the

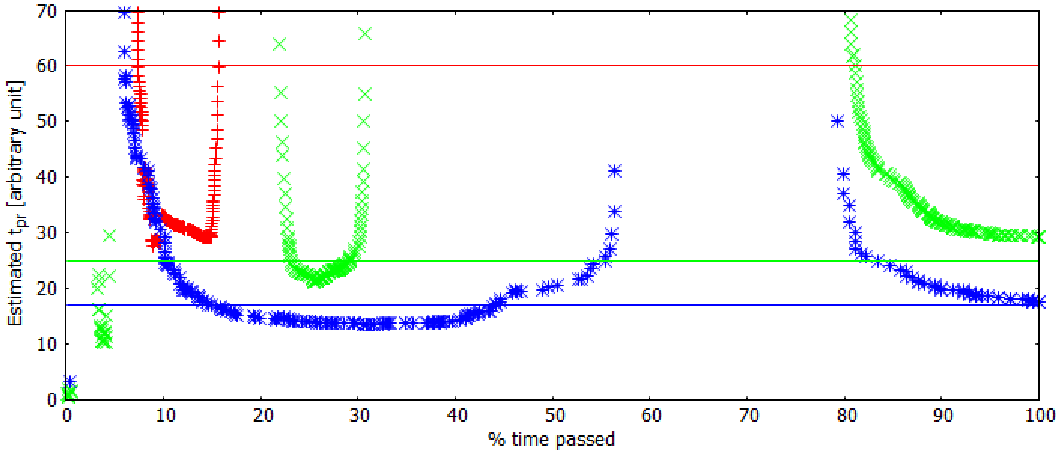

Figure 3.2: Comparison of predictive accuracy of the stretched exponential model with three different data sets (different colors). The three differently colored horizontal lines denote the corresponding t_{pr} that should be approached by the estimation values of the same color.

same as in section 3.2; numerous models were fitted to model a real MBR setup. Constriction of beginning values of parameters for fitting was inevitable in this session as certain value pairs of b and d are not apprehensible and the fitting of the function stops prematurely.

This time, the functions fitted did return values for t_{pr}, although often long time intervals are missing. Comparison of t_{lim} and t_{pr} can be seen on Fig. 3.2.

Values returned form this function still do not allow early prediction of the end of the filtering process, but tend towards the actual t_{lim}. Comparing the goodness of fit statistics with those from the fitting of first order exponential, this model gives a better description of data over time as expected. Typical R-square values are above 0.97, with the exception of the first data set where they are between 0.85 – 0.90. Degrees of freedom adjusted R-square shows that introduction of a new fitted parameter is justifiable, as seen on Fig. 3.3.

Furthermore, the sum of squares due to error (SSE) and the root mean squared error (RMSE) values from this model are also lower on a long term than those from the first order exponential model confirming the better adaptibility of the model on the current MBR setup's changing environment. Despite a better fit, that model is also unable to properly model the resistance changes to help prediction of future trends; also it is not able to accurately predict the end time point of a cycle even when getting close to it, rendering this model also of limited use. On another note, both exponential models assume the existance of one single $R_{a,ss}$ value, while this is subject to environmental changes. These models may be good for modeling of resistance from sorption in small or laboratory scale where the temperature, concentration of foulants, quality of foulants, TMP, etc. is controlled carefully, but lose their efficiency in an industrial setup. A model is needed where

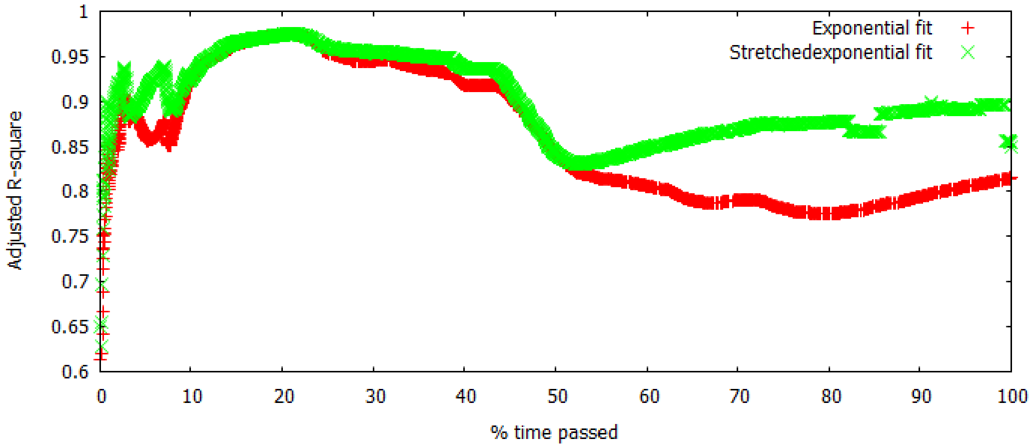

Figure 3.3: Comparison of the two exponential models using degrees of freedom adjusted R-square values. At start, almost no difference can be observed between the two functions, but later the stretched exponential model clearly has a better performance.

these parameters are also taken into account, thus negating this problem.

The adsorption-based non-exponential model

Although the first order exponential and the stretched exponential model for the resistance from sorption offers a certain degree of versatility, it is subject to changes in environmental values in the MBR system thus losing its capability to predict resistance changes accurately. These models also do not give much hindsight as to what is happening during membrane fouling.

Based on the Darcy-Weisbach (Sharp et al. 2002) and Darcy's law (Jørgensen et al. 2012), development of a new model was attempted to predict the changes in membrane resistance over time. This model, based on adsorption inside pores, takes into account multiple parameters possibly varying over time, such as temperature, flow rate, transmembrane pressure, and concentration of foulants. It is presumed that the diameter of particles fouling the membrane is neglegible compared to the pore diameter (which severly limits applications). Complete and partial pore blocking is dismissed.

First of all, the adsorbed mass of foulants over time can be defined as:

$$m_{\text{ad}} = \int_0^t r_{\text{ads}} \, \text{dt} \tag{4.1}$$

where a possible definition for r_{ads}:

$$r_{\text{ads}} = J * (c_{\text{in}} - c_{\text{out}}) \tag{4.2}$$

Adsorption of foulants results in decreased pore diameter; if the adsorption is consistent throughout the pore walls and pores tend to have the same approximate diameter:

$$\langle D_{\text{cs}} \rangle = \left(1 - \frac{m_{\text{ad}}}{m_{\text{cap}}}\right)^{1/2} * \langle D \rangle \tag{4.3}$$

The latter assumption was based on the phenomenon of the balanced fouling of pores described Yoon (2015). Pore shapes were presumed to be roughly round. A direct link between adsorbed mass of foulants and pore diameter was presumed by the assumption of homogeneous adsorption of contaminants of different quality on the pore walls, their negligible size compared to the pore diameter, and the density of adsorbed foulants being constant. In this case, the volume of the adsorbed layer is linearly proportional to the mass of it, without partial or complete blocking of the pore by any particle. If the pore is regarded as a cylinder, the sludge inside it will be shaped as a coaxial cylinder. The volume of such hollow shape can be described as the following:

$$V_{\text{ad}} = \frac{L * \pi}{4} * \left(\langle D \rangle^2 - \langle D_{\text{cs}} \rangle^2 \right) \tag{4.4}$$

The overall volume of the pore:

$$V_{\text{lim}} = \frac{L * \pi}{4} * \langle D \rangle^2 \tag{4.5}$$

Their ratio:

$$\frac{V_{\text{ad}}}{V_{\text{lim}}} = \frac{\left(\langle D \rangle^2 - \langle D_{\text{cs}} \rangle^2 \right)}{\langle D \rangle^2} = 1 - \frac{\langle D_{\text{cs}} \rangle^2}{\langle D \rangle^2} \tag{4.6}$$

Rearranging to express D_{cs}:

$$\langle D_{\text{cs}} \rangle = \left(1 - \frac{V_{\text{ad}}}{V_{\text{cap}}} \right)^{1/2} * \langle D \rangle \tag{4.7}$$

As the density of the of the adsorbed foulants remain constant, eq. 4.7 and eq. 4.3 is equivalent.

According to the Darcy-Weisbach law, the following pressure loss appears for each pore as the contaminated water flows through it:

$$\frac{p_p}{L} = f_D * \frac{\rho}{2} * \frac{\langle v_p \rangle^2}{\langle D_{\text{cs}} \rangle} \tag{4.8}$$

or, as in the current notations:

$$\frac{\text{TMP}}{A_m * \alpha * L} = f_D * \frac{\rho}{2} * \frac{J^2}{(A_m * \alpha)^2 * \frac{\pi^2 * \langle D_{\text{cs}} \rangle^4}{4^2} * \langle D_{\text{cs}} \rangle} \tag{4.9}$$

which shows:

$$\text{TMP} = \frac{8 * f_D * \rho * L * J^2}{A_m * \alpha * \pi^2 * \langle D_{\text{cs}} \rangle^5} \tag{4.10}$$

After rearrangement of eq. 4.10 in order to get J, in case of a TMP-constant setup:

$$J = \sqrt{\frac{TMP * A_m * \alpha * \pi^2 * \langle D_{\text{cs}} \rangle^5}{8 * f_D * \rho * L}} \tag{4.11}$$

Substitution of eq. 4.3 into eq. 4.11:

$$J = \sqrt{\frac{\mathrm{TMP} * A_m * \alpha * \pi^2 * \left[\left(1 - \frac{m_{\mathrm{ad}}}{m_{\mathrm{cap}}}\right)^{1/2} * \langle D \rangle\right]^5}{8 * f_D * \rho * L}} \tag{4.12}$$

$$J = \left(\frac{TMP * A_m * \alpha * \pi^2 * \langle D \rangle^5}{8 * f_D * \rho * L}\right)^{1/2} * \left(1 - \frac{m_{ad}}{m_{cap}}\right)^{5/4} \tag{4.13}$$

The Darcy's law can be utilized to calculate the membrane resistance from the flow rate:

$$R = \frac{\mathrm{TMP}}{\mu * J} \tag{4.14}$$

Using eq. 4.13:

$$R = \frac{\mathrm{TMP}}{\mu * \left(\frac{\mathrm{TMP} * A_m * \alpha * \pi^2 * \langle D \rangle^5}{8 * f_D * \rho * L}\right)^{1/2}} * \left(1 - \frac{m_{\mathrm{ad}}}{m_{\mathrm{cap}}}\right)^{-5/4} \tag{4.15}$$

or, in its rearranged form:

$$R = \left(\frac{f_D * \rho * \mathrm{TMP}}{\mu^2} * C\right)^{1/2} * \frac{1}{(1 - a)^{5/4}} \tag{4.16}$$

where

$$C = \frac{8 * L}{A_m * \alpha * \pi^2 * \langle D \rangle^5} \tag{4.17}$$

is a membrane-dependent constant, and

$$a = \frac{m_{\mathrm{ad}}(t)}{m_{\mathrm{cap}}} = \frac{\int_0^t r_{\mathrm{ads}} \, \mathrm{dt}}{m_{\mathrm{cap}}} = \int_0^t \frac{r_{\mathrm{ads}}}{m_{\mathrm{cap}}} \, \mathrm{dt} = \int_0^t r_f \mathrm{dt} \tag{4.18}$$

is the ratio of the adsorbed material inside the membrane pores and the overall adsorbant capacity, both in terms of mass. It can also be interpreted as the integral of the fouling rate over time.

On a side note, at $t = 0$, according to eq. 4.18, $a_0 = 0$, and the second term of eq. 4.16 is removed; thus an approximation to the resistance of the virgin membrane is given in an MBR system with constant TMP.

4.1 Prediction of $\mathbf{t}_{\text{pr}}$

According to eq. 4.16, the resistance of an MBR system can be calculated if a handful of other variables are known. If R_0 denotes the resistance of the membrane at $t_0 = 0$, the following can be shown based on eq. 4.16

$$\frac{R_0}{R_1} = \left(\frac{f_{D,0} * \rho_0 * \text{TMP}_0 * \mu_1^2}{f_{D,1} * \rho_1 * \text{TMP}_1 * \mu_0^2}\right)^{1/2} * \frac{(1-a_1)^{5/4}}{(1-a_0)^{5/4}} \tag{4.19}$$

At $t_0 = 0$, the adsorption of contaminants have not been started, thus rendering $m_{\text{ad}}(t_0) = 0$. This way, $a_0 = 0$ according to eq. 4.18, and the following can be denoted:

$$\frac{R_0}{R_1} = \left(\frac{f_{D,0} * \rho_0 * \text{TMP}_0 * \mu_1^2}{f_{D,1} * \rho_1 * \text{TMP}_1 * \mu_0^2}\right)^{1/2} * (1-a_1)^{5/4} \tag{4.20}$$

In a real MBR setup, the resistances are monitored constantly, as this is the easiest measure of how the filtering process is progressing. Rearranging to calculate a_1:

$$a_1 = 1 - \sqrt[\frac{5}{4}]{\frac{R_0^2 * f_{D,1} * \rho_1 * \text{TMP}_1 * \mu_0^2}{R_1^2 * f_{D,0} * \rho_0 * \text{TMP}_0 * \mu_1^2}} \tag{4.21}$$

As seen in eq. 4.21, all variables can be monitored in the MBR system and a_1 can be calculated using this approach. This process can be reversed with an R_{lim} resistance, where R_{lim} is the limit of cost-efficient operation of a given MBR system. Using R_0, the corresponding a_{lim} can also be determined:

$$a_{\text{lim}} = 1 - \sqrt[\frac{5}{4}]{\frac{R_0^2 * f_{D,lim} * \rho_{\text{lim}} * \text{TMP}_{\text{lim}} * \mu_0^2}{R_{\text{lim}}^2 * f_{D,0} * \rho_0 * \text{TMP}_0 * \mu_{\text{lim}}^2}} \tag{4.22}$$

The environmental variables $f_{D,lim}$, ρ_{lim}, μ_{lim} may be assumed to stay constant after their last measured value. As for TMP_{lim}, in constant pressure setup, it should remain constant throughout the whole process.

At the same time, using eq. 4.18, a_x can also be expressed as:

$$a_{\text{lim}} = \int_0^{t_{\text{lim}}} r_f(t)dt = \int_{t_1}^{t_{\text{lim}}} r_f(t)dt + \int_0^{t_1} r_f(t)\text{dt} \tag{4.23}$$

By definition in eq. 4.18:

$$\int_0^{t_1} r_f(t)\text{dt} = a_1 \tag{4.24}$$

Expressing the unknown part of the integral:

$$\int_{t_1}^{t_{\text{lim}}} r_f(t)\, \mathrm{dt} = a_{\text{lim}} - a_1 \tag{4.25}$$

As the value of the integral can be calculated, the only question that remains is the value of t_{lim} at which the R_{lim} is reached by the MBR system. This can only be resolved by the precise estimation of r_f after the t_1 time. The efficiency of this prediction effects the difference between the t_{pr} foretold by this model and the actual t_{lim} at which R_{lim} is reached. However, an approximation of r_f is needed to further advance.

As defined by eq. 4.18, the r_f can be determined with r_{ads} and m_{cap}. By definition, m_{cap} is constant, while r_{ads} depends on the overall flux through the membrane pores and the concentration of contaminants entering the membrane with this water (eq. 4.2). But the calculation r_{ads} is problematic as it is dependent on the flow rate through the membrane pores and the concentration of contaminants entering the membrane with this water (eq. 4.2). As shown in eq. 4.13, the flux depends from a handful of other variables; and the concentration of contaminants entering the membrane is effected by the diameter of pores and foulants as a result of size exclusion (Zhang et al. 2016). While it is possible to incorporate these effects in an improved theoretical approach, the measurements needed for such theory requires costly instruments. At the same time, for some environmental variables such as the concentration of contaminants in different size ranges in the same sample, completing measurements could be impossible in the strict time limits dictated by a practical aspect. Therefore direct monitoring and calculation of r_f could also prove elusive in not controlled experiments. Furthermore, the inclusion of multiple different conditions make possible applications narrow for this model. Some effects, like complete and partial blocking of pores by particles is completely dismissed. While these may also be included in the theory, measurement of accurate concentration of particles in different size ranges, in the same solution, remains a problem, as mentioned above. That renders further theoretical improvements hardly useful in the current conditions.

Using purely theoretical models did not prove successful: they have proven to be either too simple to be able to model such a complicated system as the MBR, or became too complicated to be used in a not precisely controlled, industrial environment. In the following section, an effort is made to create an empirical method whose sole purpose is to predict when will such a system reach a certain predefined resistance value.

Empirical model

As the theoretical models did not prove to be successful or practically plausible solutions in the current situation, a simple empirical method was developed instead. The key was simplicity: as the only task is to predict how much time is needed to reach a predefined resistance, no environmental variables must be taken into account. The rate of resistance increase over a long time period can be defined as:

$$r_{\text{inc}} = \frac{R - R_0}{t - t_0} \tag{5.1}$$

The future rate of resistance increase is not known, but for the sake of simplicity, its value is regarded to be constant for the rest of the filtering process. This rate can be used to approximate how much time is needed to reach the R_{lim} from the current resistance:

$$t_{\text{pr}} = \frac{R_{\text{lim}} - R}{r_{\text{inc}}} + t \tag{5.2}$$

Despite its apparent overly simple fashion, the method seems to work really well even on the most varying data. First, every single data point has an assigned t_{pr}, unlike the exponential models. Moreover, these are not prone to change as abruptly as the exponential models after an initial time period has passed, as seen on Fig. 5.1.

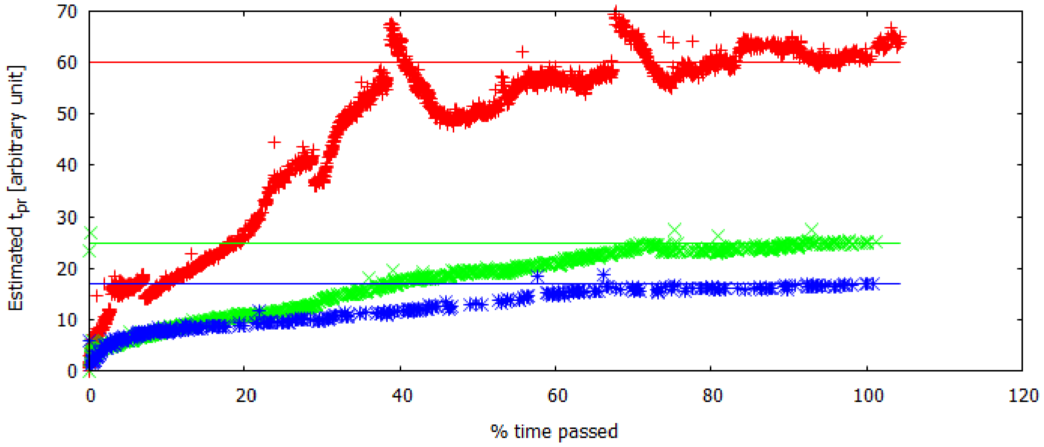

Figure 5.1: Estimated t_{pr} values returned by the empirical method. Differently colored dots denominate different data sets.

Based on the three data sets, the following was found: despite not predicting the endtime immediately well, the accuracy improves over time, its deviation from t_{lim} decreasing to 5-6% of it by the 75% of the time passed 5.1. In a practical sense, date of necessary intervention was estimated 10-12 days prior with ± 2 days accuracy in a 42 days long cycle. Also worth noting that this prediction usually underestimates the time still needed, which may also help to further clarify the exact date.

Although promising, further investigation of this method with many other data sets with different MBR setups is unavoidable to certify its usefulness and give a better overview on the accuracy of prediction in different situations. Even in such cases, the results can not be compared between different plants. At this point, there is neither a reliable and clear way to statistically tell when predictions are accurate enough to base off planning of later interventions in the MBR system, nor is there enough data sets for such an investigation.

The main advantages of this method are its speed and ease of use. As only a single mathematical operation is done, the result is returned in matters of milliseconds, while curve fitting may take 1-30 seconds, depending on data set size and complexity of the function. While this is not significant in live screening where the speed of data acquisition is slower than that of regression analysis, analysis of earlier data sets may take much more time even if automatized. Fitting of theoretical models may also need further data processing aside from data filtering, may need manual setting of initial values, and in case of exponential models, may not even return any plausible results. The current method is robust: it is not dependent on the actual MBR system setup, and with each data point, it will always return a new value for t_{pr}. It also works procedurally: when a new resistance value is accessible, it generates a new t_{pr} without taking into account the previous values. The latter negates the distorting effect of outliers. Finally, as no variables are used other than the resistance to flow, versatile application is possible without the need to install additional instruments othen than those measuring the flow rate and TMP in the system. The main drawback of the method is its empirical base: as an empirical method, it does not take other environmental changes into account, and any abrupt artifical interventions into the system's workings or natural occurrances in the MBR system like abrupt temperature, contaminant concentration, etc. changes may offset the prediction efficiency for a while significantly. As such, it takes time for this model to adapt to sudden interruptions which decreases this method's value.

Conclusion

The current thesis investigated multiple models to simulate the resistance changes in an MBR system. That was done in order to predict the time left until a limiting value of resistance is reached. Data was taken from a submerged membrane bioreactor, and data filtration to remove outliers and not relevant data was based on standard deviation from the moving average of data points. Variables who play a limiting role in filtering efficiency were set to leave about 0.02% of data points after filtering in order to return enough, but not too much data for fitting. Testing of possible models consisted of a simulation of a real MBR system setup, where data set size increased over time, and so did amount of available data for fitting. The goal of model fitting was to predict how much time must pass until the resistance from sorption in the MBR system reach a predetermined value. Model usefulness was measured by accuracy of prediction.

First, a first order exponential model was investigated which is a commonly used method to describe the resistance originating from sorption into and onto the membrane. Despite giving a good description of data, the model was unusable to predict future resistance values as its limiting value rarely reached the predetermined one, thus the model mostly did not return any value to examine.

A stretched exponential increase was also investigated with the same conditions. The model described data better according to goodness of fit indicators, and also returned data for analysis, but the predictions were not accurate, sometimes still did not have any result, and were prone to change rapidly.

That lead to development of a new detailed model, taking all environmental factors into account in the prediction process. The model efficiency was not evaluated because of unavailability of certain type data for the calculations in the used data sets. Those data types also require measurements that are currently not feasible with current the analytical equipment. It has been deduced that while simple models can easily describe data, their predictive value is low; and the attempted description with a more sophisticated theory require too complex measurements for its input data. Thus these model's application may be severely limited in not controlled situations.

Finally, an empirical method was applied where the time left until reaching given resistance value is calculated by using the long term average increase in resistance. This method was much more exact and robust than all previous ones in the examined data sets. All data points had an assigned predicted value. In all data sets, at 75% of time passed (where 100% is the time to be predicted) the returned values are within the $\pm5\%$ error bound of the endpoint. Applying this model proved to be easier and much less time consuming than fitting of either exponential models, allowing scrutiny of multiple data sets in a matter of a few seconds. While the small number and the variety of data sets did not allow more in-detail analysis of the predictive value of this model, it seems more useful in industrial environments to predict future dates of necessary interventions, compared to previously used models. A serious drawback of the procedure is its empirical base. As such, sudden changes iniate only belated answer using this method, and do not give a feedback about the nature of the problem occurred.

Further perspectives

The predictive capabilities of different theoretical models and an empirical method in terms of long term resistance increase in an MBR system was investigated in this thesis. While many short term effects also influence the resistance, these were out of the scope of this project. Improvement on existing models of long term fouling is necessary in order to increase efficiency of MBR systems to which this thesis can hopefully contribute.

A generic problem faced in fitting was the shift experienced with the value of the steady-state value of resistance from sorption. In order to give a better comparison of models used and increase these model's accuracy, determining this constant is necessary, but not part of the current thesis. Currently, the only procedure for estimation is to fit the function discussed in section 3.1, while not much hindsight is given about the factors influencing this value.

According to the limited amount of data sets provided, it was found that the resistance increase from sorption can be described better by a stretched exponential model than the currently used first order exponential model. Such a result suggests the existance of strange kinetics (Snopok 2014), where the speed of contaminant sorption into and onto the membrane changes over time. Further comparison of these two models may be important as the value of β (see 3.3) gives feedback about the rate-determinant step in the sorption process.

An attempt was made to create a new theoretical model based on adsorption of contaminants inside the pores of the membrane. While the model was not applied to practical data, and does not include partial and complete blocking of pores, it may serve as a base for further research. Under the appropriate conditions the theory may be put under test.

Finally, an empirical method was found to be able to predict the time needed to reach a predetermined resistance value. Unfortunately, its empirical base does not allow direct comparison between different MBR setups and does not give a hint about factors determining the rate of long term resistance increase. As such, that method remains sensible to sudden changes in MBR system, as its accuracy drops in such cases. Development may be undergone in this direction too; in such case a better estimation to resistance increase must be given in order to make an empirical method react faster to the altered environment and keep its accuracy high.

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