European Water 58: 33-40, 2017.

Purification of Humic acids contained simulated wastewater using membrane ultrafiltration

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Abstract: Treatment of water from any industrial effluent can provide valuable profits towards the living environment. The resolution of the treatment of effluent is the minimization of water pollution and reuse of water. Several researches have already been performed to remove natural organic matters from wastewater. In our present work, simulated wastewater was treated using membrane batch ultrafiltration with polyethersulfone membrane. Commercial Humic acids was used as a common natural organic matter present in industrial wastewater. The effects of different transmembrane pressure drops (207, 276 and 345 kPa) on permeate flux and permeate quality were explored using 50 kDa molecular weight cut off membrane. The concentration of Humic acids in water was maintained at 50 mg L^{-1}. In order to overcome compaction effect of the membrane, the module was pressurized with deionized (DI) water for 2 hours at 345 kPa applied transmembrane pressure (TMP) drop. Maximum permeate flux was obtained at 345 kPa TPM drop. The percentage removal of pollutant was 93.8%. Flux decline was analysed using Hermia's pore blocking mechanism and artificial neural network. Apart from this, module performance was characterized by calculating total resistance during purification of synthetic wastewater.

Key words: Humic acids (HAs), natural organic matters, membrane ultrafiltration, wastewater

1. INTRODUCTION

Water pollution causing by natural organic matters has seemed to be a severe issue in recent times (Bhatnagar et al., 2017). The effective treatment and utilization of wastewater are the main objectives for the growing countries to control water pollution (Liu et al., 2017). The minimization of harmful organic components like, Humic substances present in the industrial effluent is a major concern in the recent years. The leaching of Humic substances and other organic matters from the untreated effluents into the fresh water is a critical problem towards the living environment (Jia et al., 2016). The natural substances are the mixture of a complicated matrix of heterogeneous organic components. Due to these substances, the test of drinking water becomes deteriorate (Bhatnagar et al., 2017). It causes severe problems including generation of toxic and disinfected by-products. The amount of dissolved oxygen in the water is also becoming decrease (Fu et al., 2017). Activated sludge process or any biological technology are not suitable to remove the natural organic materials from the industrial effluent totally (Andrews et al., 2014). However, researches have already been performed using chlorine disinfection process (Wang et al., 2017), the formation of toxic components like, dichloro and trichloroacetic acid, chloroform and other toxic chlorinated products trihalomethanes is the main demerit for this process (Lyon et al., 2014). Few studies were done to treat Humic substances or other materials using advanced oxidation, most of which was the changing of the structure of organic components (Choi et al., 2010; Wang et al., 2017). Apart from adsorption, liquid extraction, coagulation or previously said techniques; membrane ultrafiltration is an effective, time consuming, low cost alternative operation to treat wastewater contained natural organic maters (Galambos et al., 2004) because of its efficient operating system, very less chemical consumption, and non-polluting concept (Manttari et al., 2006).

In our current study, commercial Humic acids powder was used as a model natural organic matters present in many industrial effluents. A robust treatment technology, membrane ultrafiltration was carried out to remove the model organic matters from simulated wastewater varying different TMP drop from 207 to 345 kPa. The main aim of this project work was to analyze the flux decline behavior using artificial neural network (ANN) system. Cake filtration and intermediate pore blocking law were applied to identify the fouling mechanism with respect to ultrafiltration time.

2. MATERIALS AND METHODS

2.1 Materials

The ultrafiltration study was performed using lab grade Humic acids (HAs) powder obtained from Loba Chemie, India. Without further treatment commercial Humic acids (Has) powder was used during preparation of feed sample.

2.2 Membrane

A commercial flat sheet asymmetric polyethersulfone membrane (MWCO of 50 kDa), purchased from Permionics Membranes Pvt. Ltd., Vadodara, Gujarat, India was used to treat the HAs simulated wastewater. The active membrane surface area was 33.4×10^{-4} m^2. The water permeability (L_p, m Pa^{-1} s^{-1}) and fresh membrane resistance (R_{fresh}, m^{-1}) were found about 4×10^{-11} and 1.3×10^{13}, respectively.

2.3 Experimental design and procedure for batch ultrafiltration

An unstirred batch cell module was used to purify HAs contained simulated wastewater. The batch cell set up was made of stainless steel with the capacity of 0.35 L. A cylindrical vessel (77.5×10^{-3} m, inner diameter) was attached with flanges. To maintain the mechanical support on flat sheet membrane, a circular grid made of aluminum was used as a base. Two matching rubber gaskets were used to prevent the leakage during ultrafiltration. To maintain the transmembrane pressure drop (TMP) during separation, an air compressor was used. Figure 1 represents the schematic diagram of the batch cell module. At first, membrane was compacted with DI water for 2h in order to control the compaction effect on the membrane active surface area. The applied pressure was 345 kPa. To observe the permeate flux behavior at different TMP drops, the pressure was varying from 207 (30 psi) to 345 kPa (50 psi). The HAs concentration was 50 mg L^{-1}. The feed concentration was constant throughout the experiment.

2.4 Sample analysis

The concentration of HAs solution was measured at 254 nm λ_{max} using UV-vis spectroscopy (Thermofisher Scientific, India). An auto-ranging ion meter (VSI Electronics Pvt. Ltd., Punjab, India) was used to analyze the electrical conductivities (S m^{-1}) and total dissolved solids (TDS, mg L^{-1}) (Das et al., 2006). The pH meter (Jenway, Bibby Scientific UK) was used to check the pH of HAs solution.

2.5 Theoretical study for ultrafiltration and fouling characteristics

Theoretical analysis of batch cell ultrafiltration was performed using Darcy's law of permeation which is represented in the Eq. (1). Water flux (J_w) was calculated before starting the experiment.

$$J_w = L_p\Delta P = dV/A_m t \quad (1)$$

A_m was the active membrane surface area (m^2). Hydraulic permeability was L_p (m Pa^{-1} s^{-1}).

Variation of solute rejection (R_s, %) was studied using Eq. (2)

$$R_s\ (\%) = [1-(C_{pHumic}/C_{0Humic})]\times 100 \quad (2)$$

C_{pHumic} was the solute concentration in the permeate side (mg L^{-1})
C_{0Humic} was the solute concentration in the prepared feed solution (mg L^{-1})

In the present study, the formation of cake layer was analyzed using Hermia's cake filtration model. Eq. (3) signifies the Hermia's pore clogging model for any dead end filtration (Das et al., 2015).

$$d^2t/dV^2 = K\ (dt/dV)^n \quad (3)$$

The four different fouling models such as, complete pore blocking model (CPBM, $n=2$), standard pore blocking model (SPBM, $n=1.5$), intermediate pore blocking model (IPBM, $n=1$) and cake filtration model (CFM, $n=0$) have already been discussed in the previous work (Saha et al., 2015). Based on the regression coefficient (R^2) value, IPBM and CFM have been chosen for further discussion. In the present study, the stage wise analysis of IPBM followed by CFM has been discussed with respect to process contact time. In the Eq. (3), when $n=1$, it analyses irreversible pore blocking (IPBM) characteristics. The simplified form is as follows:

$$1/J_{ps} = (1/J_0) + k_{ii}t \quad (4)$$

where, k_{ii} ($k_{ii}=k_{Am}$) is model constant for IPBM (m^{-1}).

When $n=0$, it signifies the formation of cake layer (CFM) on the membrane surface

$$1/J_{ps}^2 = (1/J_0^2) + k_{clHumic}\ t \quad (5)$$

where, $k_{clHumic}$ ($k_{clHumic} = 2R_{cake}k_{DC}/J_0R_{fresh}$) is model constant for CFM ($m^{-2}s^{-2}$).

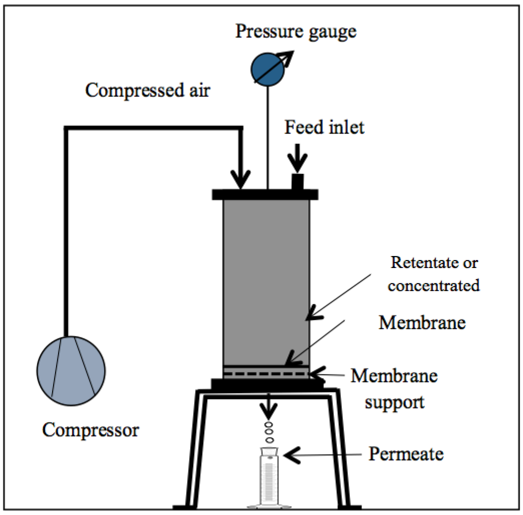

Figure 1. Schematic diagram of unstirred membrane batch ultrafiltration module

2.6 Artificial neural network (ANN)

An artificial neural network (ANN) is a theoretical model made by a computational approach based on the real function of human brain neurons. This computing process is prepared by a number of interconnected signalling elements. These process elements release the valuable information by the help of their own dynamic state response to the external objects. ANN are made of multiple nodes and they interact with each other to perform operations on the given data. The result is passed to the output node, called activation through the other internal nodes (Baguena et al., 2016). To predict the relationship between experimental and theoretical data, a two layered feed-forward Levenberg-Marquardt algorithm was applied during ANN analysis. The number of hidden neuron was 10. The total experimental points were circulated in the following stages: training: 19, validation: 9 and testing: 9 points. Root mean square error (RMSE) were performed to identify the highest regression coefficient (R^2) using MATLABR2015b neural network toolbox.

3. RESULTS AND DISCUSSIONS

3.1 Experimental and theoretical analysis of permeate flux decline with respect to time and transmembrane pressure drop (ΔP, kPa)

The deviation of permeate flux for the three different TMP drops has been represented in Figure 2. The theoretical study of the flux decline using ANN analysis with respect to time has also been shown here. The permeate flux deviates from its initial point with the process time for each case. The deviation of permeate flux is higher for low TMP drop of 207 kPa due to the pore blocking phenomena. At the high TMP drop of 345 kPa, the slower deviation has been noticed due to the gradual increasing of gel layer formed by retained solute particles. The detailed experimentation of the variation of transient flux decline with different parametric conditions has already been discussed in our previous research (Saha et al., 2015). The comparative study between theoretical and experimental flux deviation has been performed here. To identify the best fitting prediction using ANN model, a statistical analysis has been performed with the experimental data for all the TMP drops. Table 1 represents the statistical analysis of variance (ANOVA) for theoretical flux decline behavior during batch ultrafiltration of Humic acids contained simulated wastewater. The statistical analysis describes the error calculation and significant difference between the experimental and theoretical flux decline behavior. From the Table 1, it is clear that the comparative study is significant with 0.99 regression (R^2) for all the TMP drops. Figures 3(a-c) represent the prediction of theoretical and experimental flux decline analysis using ANN for different TMP drops condition. It is found that all the data points are very close to the diagonal line with perfect regression for all the TMP drops. The high F-value and low p-value remark the good model prediction during theoretical analysis of permeate flux decline. However, at low TMP drop of 207 kPa, a minimum mean square error of 0.71 is obtained than other TMP drops.

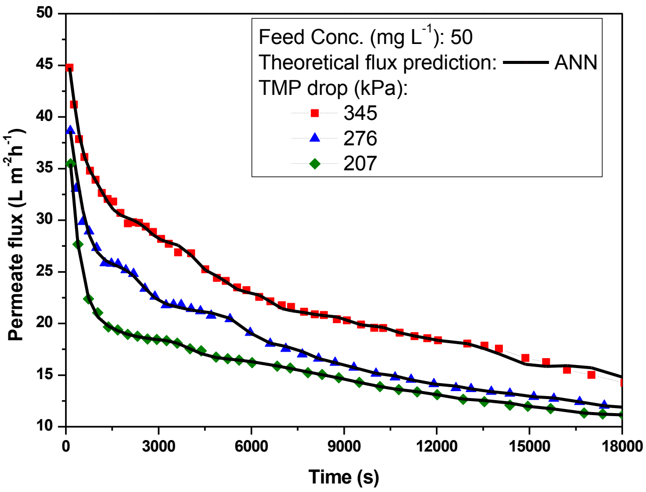

Figure 2. Experimental and ANN predicted transient flux decline behavior with respect to process time for different TMP drop (ΔP, kPa)

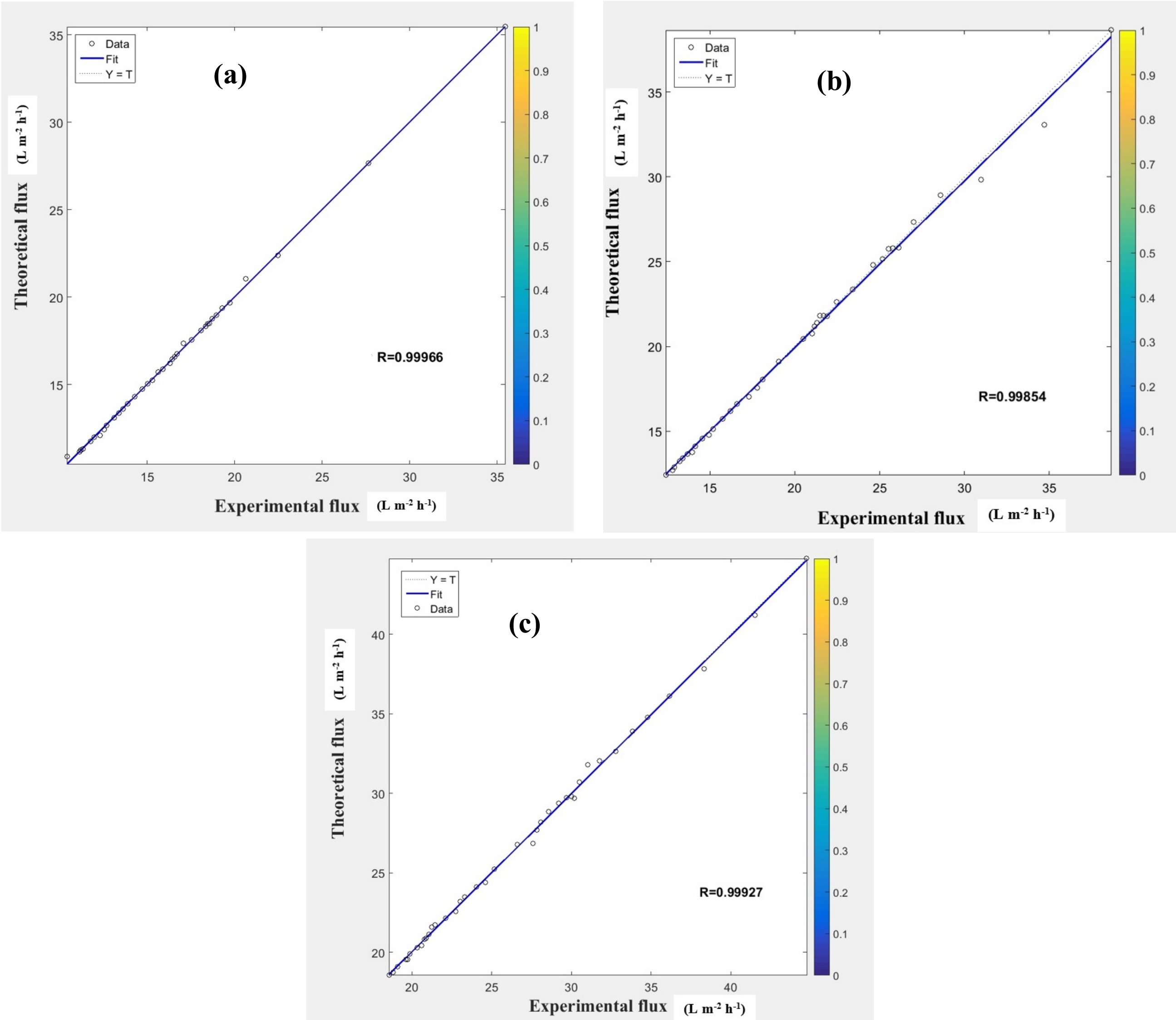

Figure 3. The prediction of theoretical and experimental flux values using ANN analysis at different TMP drops (a) 207, (b) 276 and (c) 345 kPa

Table 1. Analysis of variance (ANOVA) for theoretical permeate flux at different ΔP, (kPa)

Source *ΔP*, (kPa)	Sum of square	Degrees of freedom	Mean square error	F-value	p-value	Total error	Regression R^2
207	36.65	52	0.71	4.41	0.0001	8.47	0.99
276	506.63	52	9.74	375.38	0.0001	1.38	0.99
345	1091.34	52	20.98	216	0.0001	5.13	0.99

3.2 Analysis of permeate quality in terms of removal of TDS and conductivity

The analysis of permeate quality at different operating TMP drop (207 to 345 kPa) has been represented in Figure 4. The rate of decreasing of conductivity and TDS is linear with increasing TMP drop. The ionic conductivity has been decreased up to 0.0103 S m^{-1} from its initial state of 0.274 S m^{-1}. With the increasing of TMP drop from 207 to 345 kPa, the rejection rate of solute particles has been increased thus, the ionic conductivity is also decreased from the solution. The same trend has been found for the removal of TDS from the collected permeate. The initial TDS content was 45 mg L^{-1}. Whereas, with the increasing of operating pressure, dissolved solids has been removed from the permeate which has been shown in the following Figure. It is very clear that with the increment of TMP drop the permeate quality in terms of removal of TDS and ionic conductivity has been improved. On the other side, the maximum Humic acids (HAs) rejection (R_s, %) was found around 93.8% at high TMP drop of 345 kPa. With increasing TMP drop, the formation of gel layer on the active membrane surface has been increased. The gel layer provides an extra mass transfer resistance which increases the rejection rate at high TMP drop. Near about 90% reduction of Humic substance from water was reported using ferrate (IV) oxidization at pH 7.1 to 7.8 (Qu et al., 2003). This comparison reveals that membrane filtration has better rejection efficiency than other processes.

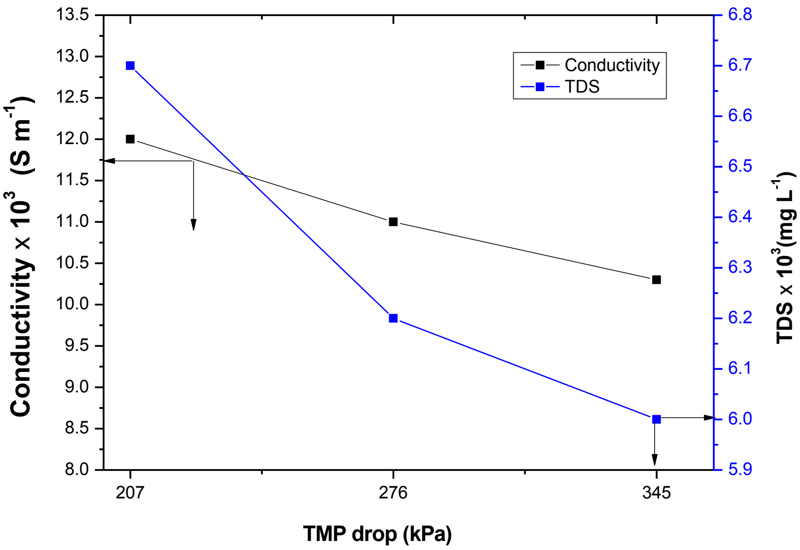

Figure 4. Variation of permeate quality in terms of TDS and conductivity at different operating pressure (TMP drop, kPa)

3.3 Prediction of cake layer formation with respect to time based on Hermia's pore blocking method

The formation of cake layer with respect to process contact time has been characterized using Hermia's power law model. The overall analysis of pore clogging characteristics of HAs ultrafiltration has already been discussed in our previous work (Saha et al., 2015). It was discussed that intermediate pore blocking mechanism (IPBM) revealed the good agreement with experimental data points. In the present study, the close observation of pore blocking mechanism with cake layer formation has been performed with the filtration time. The fitness of the two models is shown in Figure 5. A gradual change in slope decline has been observed in Figure 5(a). This criterion reveals that intermediate pore clogging occurs at the very beginning of the filtration. Whereas, a sharp slope decline is found in Figure 5(b). The change in slope decline reveals that the formation of cake layer happens after 50 min of process filtration. According to the predicted values, the cake layer model (n=0) fits the experimental data after 50 min of filtration, whereas IPBM (n=1) reveals the decline of permeate flux at the initial stage of filtration. The predicted regressions (R^2) and residuals for both the cases are enlisted in Table 2.

Table 2. Summary of the Hermia's model prediction of IPBM and CFM

	IPBM (n=1)				CFM (n=0)			
	Initial stage		Final stage		Initial stage		Final stage	
ΔP(kPa)	R^2	Residual sum of square	R^2	Residual sum of square	R^2	Residual sum of square	R^2	Residual sum of square
207	0.99	1.4×10^{-5}	0.99	1.7×10^{-6}	0.84	5.1×10^{-7}	0.99	4.7×10^{-7}
276	0.98	1.8×10^{-6}	0.98	7.1×10^{-7}	0.85	2.1×10^{-7}	0.99	1.1×10^{-7}
345	0.98	3.5×10^{-6}	0.98	8.9×10^{-6}	0.85	4.1×10^{-7}	0.99	5×10^{-7}

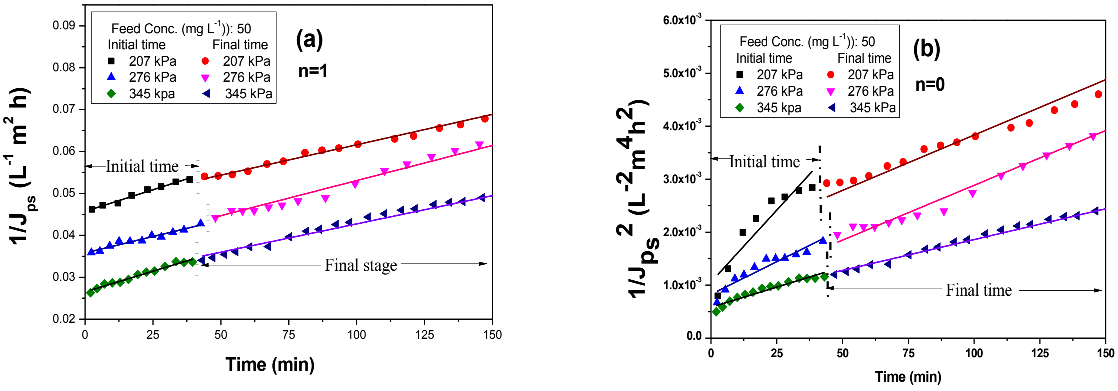

Figure 5. Fitness graph for (a) IPBM and (b) CFM during ultrafiltration

4. CONCLUSIONS

Treatment of HAs containing synthetic wastewater was performed using membrane batch ultrafiltration. The TMP drop was an important parameter to explore the permeate flux decline nature. Transient flux decline behavior was analyzed and compared with the theoretical approach using artificial neural network (ANN) system. According to ANOVA analysis, 0.71 mean square error at a low TMP drop of 207 kPa reveals the good theoretical prediction during membrane filtration. The permeate quality in terms of removal of ionic conductivity and TDS was also verified at different TMP drops. Moreover, 93.8% rejection of HAs was achieved at 345 kPa TMP drop. Pore blocking law reveals that the pores were clogged with solute particles internally at the very beginning of the filtration than cake layer formation on the membrane surface.

LIST OF SYMBOLS

A_m	Active membrane surface area (m^2)
C_{pHumic}	Solute concentration in the permeate side (mg L^{-1})
C_{0Humic}	Solute concentration in the prepared feed solution (mg L^{-1})
J_{ps}	Permeate flux (L m^{-2} h^{-1})
J_w	Pure water flux (L m^{-2} h^{-1})
J_0	Initial flux (L m^{-2} h^{-1})
k_{ii}	IPBM constant (m^{-1})
k_{Am}	Membrane surface blocked per unit of total volume permeated (m^{-1})
$k_{clHumic}$	CFM constant ($m^{-2}s^{-2}$)
k_{DC}	Cake layer area per unit of membrane filtration (m^{-1})
L_p	Water permeability (m Pa^{-1} s^{-1})
n	Hermia's pore blocking exponent
R_{cake}	Cake layer resistance (m^{-1})
R_{fresh}	Fresh membrane resistance (m^{-1})
R_s	Percentage of rejection coefficient (%)
R^2	Regression coefficient
ΔP	Transmembrane pressure drop (kPa)

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