

Membrane fouling control by means of TiO₂ coating during model dairy wastewater filtration

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ABSTRACT

In this study, different TiO₂ coated PES microfiltration membranes were prepared, to investigate the effects of physical deposition of the catalyst on the membrane surface on membrane fouling during model dairy wastewater filtration. The appropriate catalyst coverage, catalyst layer stability, wettability changes and surface free energies of the membrane surface were investigated. The membranes were coated using the physical deposition method: by filtering the TiO₂ suspension in a dead end cell through the membrane. To investigate the membrane fouling properties, skimmed milk powder solution was used. Furthermore, the photocatalytic activity of the TiO₂ coated membranes under UV irradiation ($\lambda_{\text{max}} = 254 \text{ nm}$) and its effect on the filterability of the model solution were investigated. Membrane flux and fouling were measured and calculated. It was found that the fouling propensity of the membrane is highly determined by not only the structure of the TiO₂ covering but also the hydrophilicity of the surface and the chemical nature of the contaminants: a less hydrophilic membrane is prone to be more resistant to fouling by more polar degradation by-products, and in addition the membrane fouling property can be determined by surface free energies.

Keywords: TiO₂ coated PES membrane; Contact angles; Surface free energy; Membrane fouling; Milk powder; Aeroxide P25

1. Introduction

The dairy industry generates a large amount of wastewater with fluctuating quality. In many countries, it is considered the largest source of food processing wastewater [1,2]. Water is a key processing medium in the dairy industry, and is used in every step for cleaning, sanitization, heating, and cooling. Thus, dairy wastewater contains a high level of organic and inorganic load, which means it has a high chemical oxygen demand (COD) and high biological oxygen demand (BOD). There are works dedicated to the

instigation of the reuse of dairy wastewaters; membrane processes are a promising method to treat such wastewaters due to significant improvements in the efficiency and cost-effectiveness of the method. Earlier works proved that with membrane filtration an appropriate retention can be achieved and the permeate can be reused [3,4]. However, membrane fouling is a limiting factor in these processes [3,5,6]. One of the approaches to mitigate membrane fouling is to improve the surface hydrophilicity [7] by entrapping TiO₂ into the membrane material by adding it to the casting solution or to use the membrane as a support for TiO₂ deposition [7–12].

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Beside the desirable hydrophilic properties of TiO_2 , it is a commonly used photocatalyst due to its good physical and chemical properties, availability and photocatalytic activity. It is used for membrane modification to improve permeability, fouling mitigation and to take advantage of the photocatalytic activity, which ensures bactericidal and self-cleaning properties [7–12]. The most commonly used techniques to modify membrane surfaces with TiO_2 are dip coating [11,13], photografting [14,15] and physical deposition of TiO_2 layer [16,17]. Some authors specifically investigated approaches to modify PES membrane with TiO_2 to increase its hydrophilicity and to reduce its tendency to fouling [8]. According to Rahimpour and coworkers, the TiO_2 -deposited membranes had superior characteristics in terms of fouling mitigation compared to TiO_2 -entrapped membranes [8].

The aim of this work was to increase surface hydrophilicity and thus, based on earlier results, to decrease the fouling propensity of membranes during dairy wastewater filtration. PES microfiltration membranes (0.2 μm pore size) were coated with TiO_2 to investigate the effect on fouling and its photocatalytic properties. Since the morphology of the catalyst may affect the surface properties, in this work, two anatase-based TiO_2 catalysts with different morphology (commercial Aeroxide P25 and synthesized TiO_2 nanorods) were used and compared. The surface coverage with different amounts of catalysts, the stability of the catalyst layers, the hydrophilicity, surface free energies, and retention of the coated membranes and the effect of UV irradiation were measured and compared. To investigate the membrane fouling properties in detail, skimmed milk powder solution was used, since membrane filtration is an increasingly utilized method in the dairy industry.

2. Materials and methods

2.1. Membrane and catalyst characteristics

Polyethersulfone membranes (PES-MF (New Logic Research Inc., USA)) with a 0.2 μm pore size were coated with commercial TiO_2 Aeroxide P25 (Evonic Industries) and synthesized TiO_2 nanorods (NR). The preparation of TiO_2 nanorods was as follows: in 1 L of a 10 M NaOH solution 250 g of TiO_2 (anatase) was suspended, then for 24 h the suspension was stirred in a rotating autoclave at 3 rpm and 155°C. Then the resulting product was washed and protonated with 0.1 M HCl, and after maintaining a pH value between 3 and 4 for 30 min the product was washed with 0.01 M HCl for 3 d then with distilled water to remove the remaining chloride ions. The resulting TiO_2 nanotubes were dried at 80°C for a day. The TiO_2 nanotubes (NT) were then calcinated at 600°C for 6 h. The resulting product was TiO_2 NR. The synthesised TiO_2 nanorods, based on TEM images (TEM; Philips CM10), can be characterized with ~50–70 nm length, ~20–30 nm width and a ~54 $\text{m}^2 \text{g}^{-1}$ specific surface area (determined by nitrogen adsorption at 77 K, using the BET method; QuantaChrome Nova 2000 surface area analyzer). TiO_2 NR consists of 100% anatase phase based on the XRD diffractogram (NRs were registered in the $2\theta = 10\text{--}60^\circ$ range on a RigakuMiniflex II instrument, using $\text{Cu K}\alpha$ ($\lambda = 1.5418 \text{ \AA}$) radiation). Commercial Aeroxide P25 titanium dioxide was also used for our experiments,

having a spherical shape with a primer particle size of ~25 nm [18]; however, it should be noted that in a suspension it forms aggregates nearly 1 μm in diameter [19]. This titania is a mixture of anatase (90%) and rutile (10%) phase, and it has a similar specific surface area (49 $\text{m}^2 \text{g}^{-1}$) to that of our self-prepared TiO_2 NR.

2.2. Membrane coating and filtration

The membranes were coated by filtering through the membrane 50, 100, 150 and 200 mL of 0.4 g L^{-1} catalyst suspension in a dead end cell, at 0.1 MPa without stirring, which resulted in 0.6, 1.2, 1.8 and 2.4 mg cm^{-2} TiO_2 coating respectively. The filtration was carried out with a Millipore batch filtration unit (XFUF04701, Solvent-resistant Stirred Ultrafiltration Cell, Millipore, USA).

The filtrations of the model solution were carried out at 0.1 M Patransmembrane pressure with 300 rpm stirring at 20°C. The flux of the neat membrane was $198.4 \pm 9.8 \text{ L m}^{-2} \text{ h}^{-1}$. All the following relative fluxes are in proportion to this value. In each filtration, 250 mL water or model solution was filtered to volume reduction ratio (VVR) 5. VRR [-] was defined as:

$$\text{VRR} = V_F / (V_F - V_P) \quad (1)$$

where V_F and V_P are the volume of the feed and permeate [m^3] respectively at any time.

For filtrations combined with UV irradiation, the filtration unit cap was modified so that the UV light source could be fitted in it. In this way, a photocatalytic membrane reactor was set up (Fig. 1). The UV light source was a mercury-vapour lamp, 40W, $\lambda = 254 \text{ nm}$ (Germipak Light Tech, Hungary).

2.3. Model solution

The 0.3 $\text{m/m}\%$ model solution was prepared from distilled water and skimmed milk powder (Instant pack Kft., Hungary), the pH of the solution was 6.6, the turbidity was 10 NTU, and the initial COD was 270 mg L^{-1} . The milk powder consists of 0.32 g g^{-1} protein, 0.05 g g^{-1} milkfat and 0.5 g g^{-1} lactose. It was filtered through the membranes at 0.1 MPa and stirred at 300 rpm.

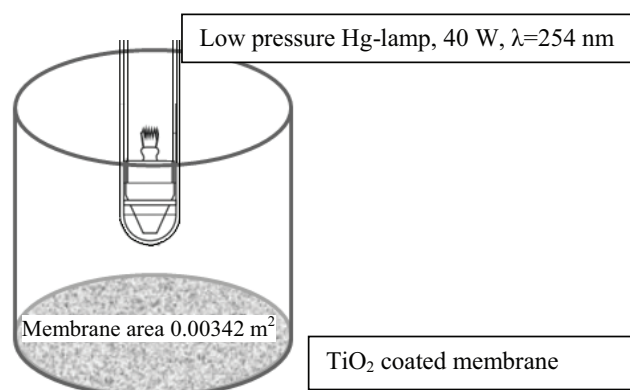


Fig. 1. Schematic of the photocatalytic membrane reactor.

Determination of the COD was based on the standard potassium-dichromate oxidation method; for the analysis, standard test tubes (Lovibond) were used. The digestions were carried out in a COD digester (Lovibond, ET 108) for 2 h at 150°C; the COD values were measured with a COD photometer (Lovibond PC-CheckIt).

2.4. Analytical methods and calculations

To determine the amount of foulants bonding to the membrane, the amounts of lactose, protein, milkfat and dry content of the samples were determined by a Bentley 150 Infrared Milk Analyser (Bentley Instruments, USA) and mass balances were calculated.

In order to inspect the top surfaces of the coated membranes a scanning electron microscope (SEM, Hitachi S4700) was employed.

Membrane hydrophilicity was quantified by measuring the contact angle that was formed between the (neat and coated) membrane surface and distilled water. 10 μ L of water was carefully dropped onto the membrane surface, and immediately measured. Contact angles were measured using the sessile drop method (Dataphysics Contact Angle System OCA15Pro, Germany). The same steps were taken to measure the glycerol contact angles. Every measurement was repeated five times, and the average values were calculated and are presented in this work. The surface free energies of membranes were calculated by the Owens, Wendt, Rabel, and Kaelble (OWRK) method, using the OCA15 software package (Dataphysics).

The retention (%) values were calculated by the following equation:

$$R = \left(1 - \frac{c}{c_0}\right) * 100\% \quad (2)$$

where c is the average COD of the permeate phase, and c_0 is the COD of the feed.

The adsorption of the pollutants on the membrane surface was determined by calculating the material balance based on the COD and protein, lactose, and fat content of the feed, permeate, and concentrate, and the deficit gives the percentage of the adsorbed pollutants.

The extent of the photodegradation was determined by measuring the COD of the feed before and after UV irradiation and was calculated by the following equation:

$$R_{UV} = \left(1 - \frac{c_{UV}}{c_0}\right) * 100\% \quad (3)$$

where c_{UV} is the average COD after 1 h of UV irradiation of the feed, and c_0 is the COD of the feed before the irradiation.

Fouling mechanisms were described with widely used filtration laws (complete pore blocking, gradual pore blocking, intermediate filtration and cake filtration) [20] to characterize membrane fouling.

3. Results and discussion

3.1. Examination of the stability and surface properties of the modified membranes

In the case of catalyst-coated membranes, the formation of a stable catalyst layer that does not wash off during operation is required. Furthermore, the membrane should be resistant to the reactive species generated by UV irradiation during heterogeneous photocatalysis. To fulfill these requirements, specific catalyst layers were formed on the membrane surface, by filtering through the membrane different amounts of TiO₂P25 and TiO₂NR suspensions in the dead-end stirring cell to achieve 0.6, 1.2, 1.8 and 2.4 mg cm⁻² coverages. To investigate the stability of the catalyst layers on the membrane, distilled water was stirred over them (300 rpm) and the turbidity change of the stirred water was measured after 24 h stirring, to verify the stability of the layer during operation. The results showed that the turbidity of the distilled water did not change; the catalyst did not re-suspend, thus the TiO₂ coating did not wash off.

In the next series of experiments the effects of the amount of the catalyst on the coverage of the membrane and on the flux were examined. First, to obtain information about the morphology of the deposited catalyst, SEM images of the top surfaces of 0.6, 1.2 mg cm⁻² TiO₂ P25 coated and of 0.6, 1.2 mg cm⁻² TiO₂ NR coated membranes were recorded and are shown in Fig. 2. There is a difference between the densities and evenness of their coverages. In both catalysts, the aggregates are larger than the membrane pores, thus depositing on the surface. TiO₂ P25 forms a thick layer of uniform aggregates on the membrane surface, while the NR coverage is more uneven due to the larger aggregates deposited on the surface.

Secondly, flux changes resulting from the coating were measured (Figs. 3 and 4). A slight flux decline observed in the membranes coated with 0.6, 1.2, and 1.8 mg cm⁻² TiO₂ P25 (Fig. 3) may be the result of a catalyst layer formation (Fig. 2a and 2c) [16], increasing the membrane resistance, while in the case of the 2.4 mg cm⁻² TiO₂ P25 and TiO₂NR catalysts, the layers were too thick and they split, resulting in a less compact catalyst layer with lower membrane resistance. The TiO₂NR formed less uniform aggregates on the membrane surface (Fig. 2b and 2d), which did not have the additional dense layer effects and had no significant influence on the flux (Fig. 4).

In order to utilize the photocatalytic properties of the catalyst layer, the membrane should withstand UV irradiation. To investigate the applicability of these coated membranes under the conditions arising during heterogeneous photocatalysis, flux changes after 1 h of UV irradiation were measured. Based on the water flux changes (Figs. 3 and 4), membranes with 1.2 and 1.8 mg cm⁻² coatings had no significant flux changes after irradiation, which suggests that no noticeable damage of the membrane occurs. In the following experiments, the membranes were prepared using 1.2 mg cm⁻² catalyst.

To characterize the surface properties of the neat and modified membranes, contact angles (with distilled water and glycerol) were measured, and the surface free energy values were calculated. Table 1 contains the contact angles of water and glycerol and the surface free energies. The con-

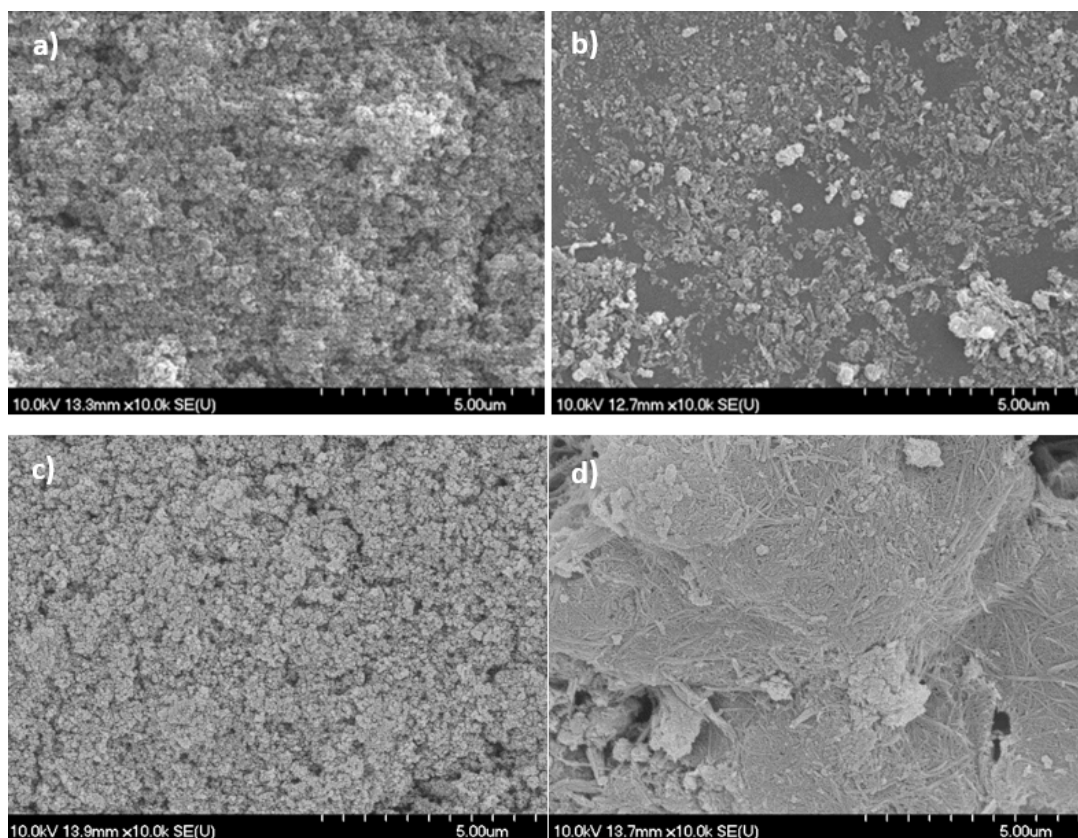


Fig. 2. SEM images of the TiO_2 coated membrane surfaces: a) PES $0.2 \mu\text{m} + 0.6 \text{ mg cm}^{-2} \text{TiO}_2$ P25; b) PES $0.2 \mu\text{m} + 0.6 \text{ mg cm}^{-2} \text{TiO}_2$ NR; c) PES $0.2 \mu\text{m} + 1.2 \text{ mg cm}^{-2} \text{TiO}_2$ P25; d) PES $0.2 \mu\text{m} + 1.2 \text{ mg cm}^{-2} \text{TiO}_2$ NR.

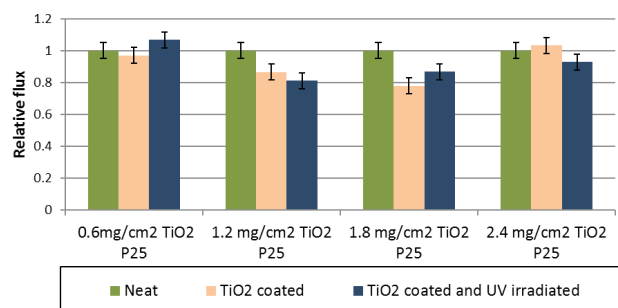


Fig. 3. Relative water fluxes before and after the membrane was coated with different amounts of TiO_2 P25 and after the coated membranes were irradiated with UV light for 1 h.

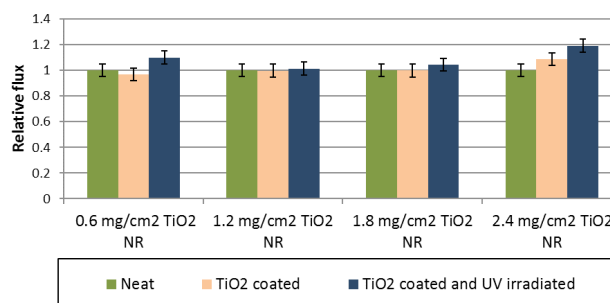


Fig. 4. Relative water fluxes before and after the membrane was coated with different amounts of TiO_2 NR and after the coated membranes were irradiated with UV light for 1 h.

tact angles of the TiO_2 P25 and TiO_2 NR coated membranes show that the catalyst forms a hydrophilic layer on the surface, due to the hydrophilic character of the catalyst [20]. In both cases, the hydrophilicity of the layer increases with the amount of the catalyst. In the case of lower amounts, the catalyst does not provide an even coverage and the character of the neat membrane determines the wettability. By increasing the amount of the catalyst, the wettability of the surface increases and is determined by the wettability of the catalyst, in accordance with the results obtained by SEM examinations.

According to earlier studies, lowering the surface free energy and increasing the hydrophilicity may improve the fouling resistance of a membrane [21,22]. In our cases, the coatings, beside the increased hydrophilicity, resulted in increased surface free energy, which may affect the fouling propensity of the membrane. In the case of the membranes coated with different amounts of TiO_2 P25, the more even coverage of the membrane (shown on SEM images and manifested by the evenly high hydrophilicity of the membranes coated with different amounts of the catalyst) resulted in similar surface free energies, which is deter-

Table 1
Average (water and glycerol) contact angle and surface free energy values of neat, different TiO₂P25 and TiO₂NR coated membranes

Membrane	Water contact angles (°)	Glycerol contact angles (°)	Surface free energy (m Nm ⁻¹)
neat PES	59.5 ± 2.2	55.3 ± 2.8	47.7 ± 0.4
PES + 0.6 mg cm ⁻² P25	12.4 ± 0.4	15.9 ± 0.9	151.1 ± 2.9
PES + 1.2 mg cm ⁻² P25	8.5 ± 0.6	12.6 ± 0.7	151.4 ± 1.1
PES + 1.8 mg cm ⁻² P25	7.9 ± 1.5	11.5 ± 1.3	148.7 ± 0.5
PES + 2.4 mg cm ⁻² P25	5.9 ± 1.2	11.2 ± 0.7	152.6 ± 0.4
PES+ 0.6 mg cm ⁻² NR	51.6 ± 6.7	43.1 ± 2.1	47.4 ± 5.5
PES+ 1.2 mg cm ⁻² NR	26.8 ± 3.9	21.5 ± 3.2	95.6 ± 7.7
PES+ 1.8 mg cm ⁻² NR	11.3 ± 6.8	12.1 ± 3.9	139.5 ± 11.4
PES+ 2.4 mg cm ⁻² NR	8.1 ± 1.2	11.5 ± 2.9	148.5 ± 7.6

mined by the catalyst. In the case of the TiO₂NR, the differences in the evenness of the coverage are also manifested in the differences of surface free energies.

According to earlier studies, the hydrophilicity of a membrane does not always give sufficient information about the fouling propensity of the membrane, and surface free energies should also be taken into account [23]. In the next series of experiments, the fouling and retention properties of the membrane were examined, to investigate which of the counterintuitive properties of the membranes were dominant.

3.2. Retention and photocatalytic activity of the coated membranes

To investigate the effect of the TiO₂ coating on the membrane retention, the model solution was filtered through the neat and coated membranes. The COD retention of the neat and coated membranes was measured and calculated using Eq. (2). The COD of the feed solution consists of 50% lactose, 38% protein and 10% milk fat; it can be expected that in a considerable amount only the protein and the milk fat will be retained by the membrane. The mass balance based on the analysis of the permeate and concentrate showed that, in the case of the pure membrane, bonding of the pollutants to the membrane could not be observed, while both the modified membranes (P25 and NR coated) bonded 14.1 ± 1.3% and 14.6 ± 1.2% of the protein content respectively. It was found that the pure membrane rejects 70.5 ± 3.5% of the protein content, while the modified membranes (P25 and NR coated) reject 58 ± 3.2% and 56 ± 3.1% of the proteins respectively. Despite the lower protein rejection of the modified membranes, the overall pollutant rejection was found to be higher due to the adsorbed protein layer (Fig. 5). The TiO₂NR coated membrane had a similar COD retention to the neat membrane (Fig. 5); the different behaviour of the NR catalyst can be explained by the uneven structure of the NR layer (compared to the P25 layer (Fig. 2c and 2d)). This allows the neat membrane surface material to partially determine the surface properties, as the wettability and surface free energy values show (Table 1), explaining the similar retention values to the neat membrane. These results show that, beside the higher wettability, the higher surface

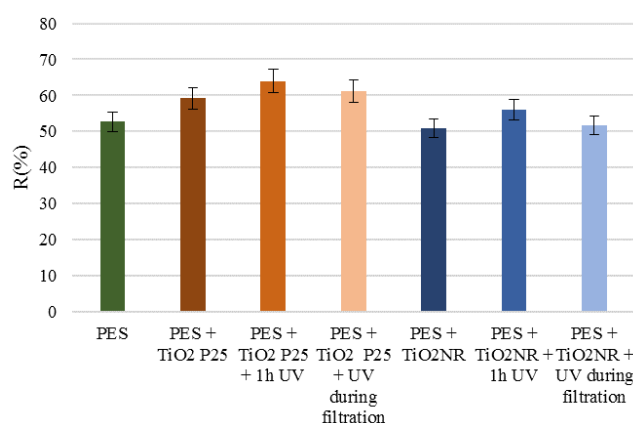


Fig. 5. COD retentions of neat, 1.2 mg/cm² TiO₂ P25 and TiO₂ NR coated membranes with and without UV irradiation as pretreatment and during filtration.

free energy also implies a higher fouling propensity caused by dairy wastewater components, as the increased retention of the TiO₂ P25 coated membrane (characterized by higher wettability and surface free energy) is caused by increased membrane fouling. The mechanism and extent of fouling were also determined and are discussed in Section 3.3.

In the next series of experiments, the effect of UV irradiation was investigated first as a pretreatment of the solution in the presence of coated membranes, and secondly during filtration with the coated membrane (Fig. 5). As a control, the effect of UV irradiation on the solution COD was also determined after 1 h of irradiation in the stirring cell without the presence of any catalyst, and it was found that the COD of the solution did not decrease. As a pretreatment, irradiating the solution in the presence of the coated membrane in both the TiO₂ P25 and NR cases resulted in a 9% of total COD decline of the feed solution, which proves that the coated membranes have photocatalytic activity. The photocatalytic reaction results in the formation of degradation by-products as small organic acids (e.g. oxalic acid), lowering the pH of the solution and changing the chemical nature of the larger protein molecules. In the case of milk powder solution containing salts, like Ca-salts, precipitation of Ca-oxalate or denaturation of protein molecules may present as a

result of oxidation reactions, causing the increased pollutant retention. This may explain why filtering of the pretreated solution through the TiO₂ P25 coated membrane resulted in an increased COD retention (Fig. 5) [24].

The behaviour of the TiO₂NR coated membrane during filtration of UV pretreated or continuously irradiated solution was similar to the P25 covered membrane. However, the membrane retention was significantly lower due to the uneven structure of the coating (Figs. 2d and 5).

3.3. Filtration model

The experimental fouling data was substituted in linearized equations of fouling models and k_c and J_0 values were obtained [25]. In the case of the model solution filtration, the correlation coefficients (R^2) were calculated. The cake filtration R^2 was the highest in all cases, which means that this model fitted the experimental data the best; in the case of the neat (0.874) and coated membranes (0.975 and 0.974 for the P25 and the NR coated membranes respectively), including experiments with UV irradiation (0.992 and 0.970 for the pretreated and continuously irradiated runs using P25 respectively, and 0.995 and 0.976 for the pretreated and continuously irradiated runs using NR respectively). The protein and other large molecules in the solution accumulate on the membrane surface forming a cake layer. The cake layer thickens during the filtration, which presents a growing resistance against the flow and manifests in decreasing permeate flux.

By fitting Eq. (4) to the experimental data, the initial flux values (J_0 [$L\ m^{-2}\ h^{-1}$]) and k_c fouling coefficients were calculated for each measurement [25].

$$\frac{1}{J^2} = \frac{1}{J_0^2} + k_c \cdot t \quad (4)$$

The results show that the neat membrane has the lowest k_c fouling coefficient (Fig. 6). By modifying the membrane with TiO₂ P25, the fouling index increased in accordance with the observed increased retention (Fig. 5). At the same time, the high hydrophilicity results in higher initial flux (Fig. 7) [26]. Compared to P25, the TiO₂NR layer showed a slighter increase of the k_c , while the initial flux was similar to the neat membrane (Figs. 6 and 7).

Using the one-hour long UV irradiation as a pretreatment on the wastewater resulted in a higher initial flux value in both coated membranes (Figs. 6 and 7). This could be a result of similar by-product generation during the photocatalytic processes, and is in accordance with the set of COD retention (Fig. 5).

By continuous irradiation during filtration, the TiO₂ P25 coated membrane showed higher k_c and a similar initial flux compared to the previous TiO₂ P25 cases (Figs. 6 and 7). This could be the result of the continuously changing content of the filtered solution – at the very beginning of the filtration the composition is almost the same as the initial feed solution, while, as the heterogeneous photocatalysis takes place in the feed side, the composition is changing, and photocatalysis degradation and particle precipitation occur. The continuous irradiation in the case of the TiO₂NR coated membrane resulted in a lower k_c and a higher initial flux compared to the previous TiO₂NR cases (Figs. 6 and 7).

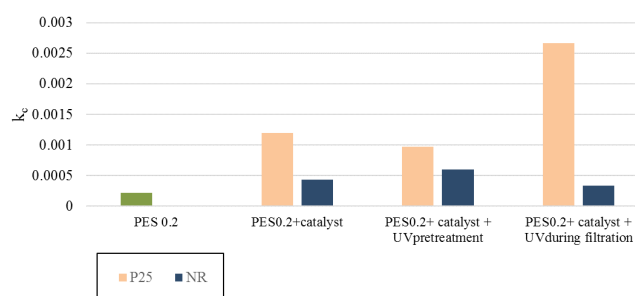


Fig. 6. k_c fouling coefficients.

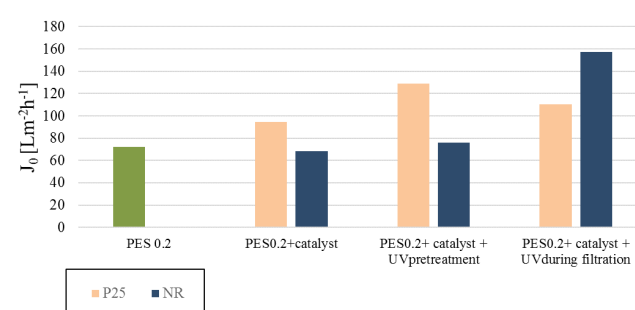


Fig. 7. Initial flux values (J_0).

4. Conclusions

Polyethersulfone microfiltration membranes were coated with commercial TiO₂ P25 and synthesised TiO₂NR. The appropriate catalyst coverage of the membrane surface was determined to be 1.2 mg cm⁻², in order to create a stable coating, which enables the membrane to withstand UV irradiation. The TiO₂ P25 and TiO₂ NR coated membrane surface become more hydrophilic compared to the neat membrane surface, while the surface free energy of the coated membranes increases. According to SEM images, the TiO₂ P25 coating forms a uniform dense layer on the membrane surface while the TiO₂NR coating is uneven. The TiO₂ P25 coated membrane had a significantly higher COD retention compared to the neat membrane, which can be explained by the density and hydrophilicity of the coating layer, which can reject the contaminants, degraded and precipitated oxidation by-products. The UV irradiation during filtration through the TiO₂ P25 coated membrane increases the retention, even compared to the non-irradiated coated membrane. The NR coated membrane alone and combined with UV irradiation during filtration has lower retention than the P25 covered membrane due to its less dense structure. Summarizing these results, it can be concluded that the fouling liability of the membrane is highly determined not only by the structure of the TiO₂ coating but by the hydrophilicity and the surface free energy values of the surface. The fouling of TiO₂ coated membranes is in a good correlation with the surface free energy values in the case of dairy wastewater filtration; higher surface free energies are related to higher fouling liability, which means that the wettability alone cannot provide enough information to the process industry about the fouling propensity. Taking into

consideration that the interactions between foulants and the membrane surface that determine the fouling are affected by several factors [27], further systematic measurements are needed to clarify the effect of the surface properties and the chemical nature of bonding components on membrane fouling.

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