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WHEY SEPARATION USING TIO_2-MODIFIED ULTRAFILTRATION MEMBRANE

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Nowadays, the membrane filtration technique is a commonly used method for the separation of whey. The most significant limitation of membrane applications is fouling, which causes flux decline. During this work, regenerated cellulose membranes covered by TiO_2-nanoparticles were investigated and applied to the separation of whey solution. Experiments were carried out in a dead-end ultrafiltration cell, and the changes in filtration parameters and the photocatalytic effects of the UV irradiated TiO_2 modified membrane surface on the membrane fouling were examined. Our results showed that the water flux decreased with increasing TiO_2 layer thickness, but the retention of turbidity and of COD increased. After separation, the membrane surface was cleaned by UV irradiation by means of photocatalytic oxidation. It was found that the original flux was recoverable, while the retention of the membrane decreased after cleaning.

Keywords: nanotubes, TiO_2, ultrafiltration, whey

Membrane technology is widely used in the food, chemical, and pharmaceutical industries. In food industry the whey separation is one of the most important applications, the recovered protein can be used by cheese industry as a raw material. Using UF membranes (with 6–8 kDa MWCO), more than 90% protein retention can be achieved at low transmembrane pressure (0.1–0.3 MPa) (Atra et al., 2005). The major drawback of the extensive use of membranes is membrane fouling. Fouling affects both the quality and the quantity of product water and ultimately shortens membrane lifetime, especially when it is irreversible (Chen et al., 2006; Luo et al., 2011). Therefore, membrane cleaning is an essential step in maintaining the membrane efficiencies used for the separation processes (Muthukumaran et al., 2004). A high number of different chemical and physical methods have been used for membrane cleaning, but these techniques interrupt the continuous filtration process (Chai et al., 1999; Muthukumaran et al., 2005). The heterogeneous photocatalysis using titanium dioxide (TiO_2) might be another method for reduction of membrane fouling, because of its photocatalytic effect that can decompose organic chemicals and kill bacteria (Li et al., 2009). Therefore, TiO_2 has been applied to surface modification of several membranes (Ebert et al., 2004). In earlier studies, polyvinylidene fluoride (PVDF) composite membranes were covered with nanosized TiO_2 particles. It was found that smaller nanoparticles could improve the anti-fouling property of PVDF membranes more remarkably (Cao et al., 2006).

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Therefore, the main objective of this study was to investigate the effects of the TiO_2 nanotubes attached to the surface of RC membranes on the ultrafiltration parameters. Furthermore, the effects of UV radiation on membrane structure were also investigated.

1. Materials and methods

Model solution was prepared from instant whey powder at 0.5% w/w (Table 1).

Table 1. Properties of model whey solution

pH (–)	Density (g cm^{-3})	Conductivity (mS cm^{-1})	Turbidity NTU	COD (mg l^{-1})	Viscosity (mPas)
6.02	0.9997	623	56.9	4330	1.37

A flat-sheet RC membrane (PL series, Millipore) with molecular weight cut-offs of 3 kDa and an effective membrane area of 0.001734 m^2 were used. The ultrafiltration (UF) experiments were carried out in a batch-stirred cell (Millipore), with a volume of 50 cm^3. Before UF experiments, the membrane was soaked at least overnight in distilled water to remove soluble processing chemicals and to wet the membrane pores perfectly. The membranes were covered in 1–2 or 3 layers with TiO_2 nanotubes at the University of Lausanne, using a special method (Tetreault et al., 2010; Horvath et al., 2012). The initial feed volume was 50 cm^3. The UF experiments were finished when 25 cm^3 of the total sample was filtered at 0.3 MPa transmembrane pressure. The measurements were carried out at 20 °C. Determination of the chemical oxygen demand (COD) was based on the standard method involving potassium dichromate oxidation; for the analysis, standard test tubes (Lovibond) were used. The digestions were carried out in a COD digester (Lovibond, ET 108) at 150 °C for 2 hours and then the values were measured with a COD photometer (Lovibond PC-CheckIt). The turbidity was measured with a turbidimeter (Hach 2100N, Germany). Scanning electron microscope (SEM) images were prepared with an SEM Hitachi S-4700 microscope.

1.1. Filtration laws

The various fouling mechanisms are described with different theories: cake filtration, intermediate filtration, standard pore blocking, and complete pore blocking (Hu & Scott, 2008; Banerjee & De, 2012; Kiss et al., 2013). The various correlations in each mechanism and reformulated in terms of flux per unit time are expressed as follows:

Table 2. Filtration laws (Hu & Scott, 2008; Banerjee & De, 2012; Kiss et al., 2013)

Fouling mechanism	Filtration law	Constant pressure filtration
Complete pore blocking	$J = J_0 e^{-k_b t}$ (1)	$\text{h}\,\frac{1}{J} = \text{h}\,\frac{1}{J_0} + k_b \times t$ (5)
Gradual pore blocking (standard pore blocking)	$J = J_0(1+k_s \times J_0^{0,5} \times t)^{-2}$ (2)	$\frac{1}{\sqrt{J}} = \frac{1}{\sqrt{J_0}} + k_s \times t$ (6)
Intermediate filtration	$J = J_0(1+k_i \times J_0 \times t)^{-1}$ (3)	$\frac{1}{J} = \frac{1}{J_0} + k_i \times t$ (7)
Cake filtration	$J = J_0(1+k_c \times J_0^2 \times t)^{-0.5}$ (4)	$\frac{1}{J^2} = \frac{1}{J_0^2} + k_c \times t$ (8)

In Eq. 1–8, J is the flux, J_0 is the initial flux, and k is the fouling coefficient.

The selectivity of a membrane for a given solute can be expressed by the average retention (R):

$$\text{R} = \left(1 - \frac{c}{c_0}\right) 100\% \tag{9}$$

where c is the average concentration of the solute in the permeate phase and c_0 is the concentration of the solute in the feed.

2. Results and discussion

In the first series of experiments, the effect of UV irradiation on the membrane surface was investigated. The water fluxes of the original and UV-irradiated RC UF membranes were compared. The changes in water fluxes show that the membranes were slightly damaged by UV irradiation (Fig. 1A), since the homogeneous structure of the top of the membrane was changed slightly (Fig. 1C) compared to the non-UV irradiated membrane surface (Fig. 1B).

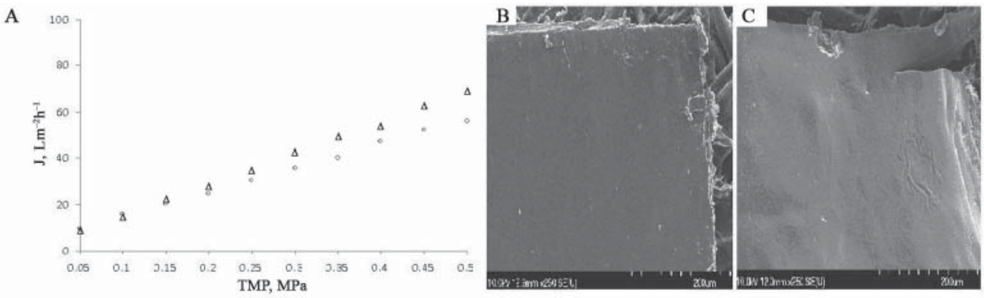

Fig. 1. Water fluxes of uncovered 3 kDa RC membrane in the function of TMP (A): Δ: before UV treatment, o: after UV treatment; SEM micrograph of the membrane surface without UV irradiation (B); SEM micrograph of the membrane surface after 30 min UV (C)

The second part of the experiments dealt with the effect of TiO_2-layers. The TiO_2 layers fouled the membrane pores, causing decreased fluxes (Fig. 2.)

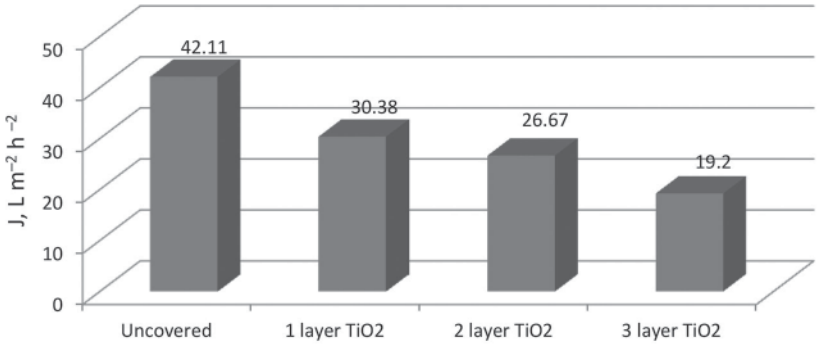

Fig. 2. Water fluxes of uncovered and TiO_2 nanotubes covered RC membranes at 0.3 MPa

The UV irradiation did not affect the water flux (Fig. 3A) of TiO_2 covered membranes. SEM photos showed that there is a wide variety of TiO_2 nanoparticles (Fig. 3B) on the surface of the membrane.

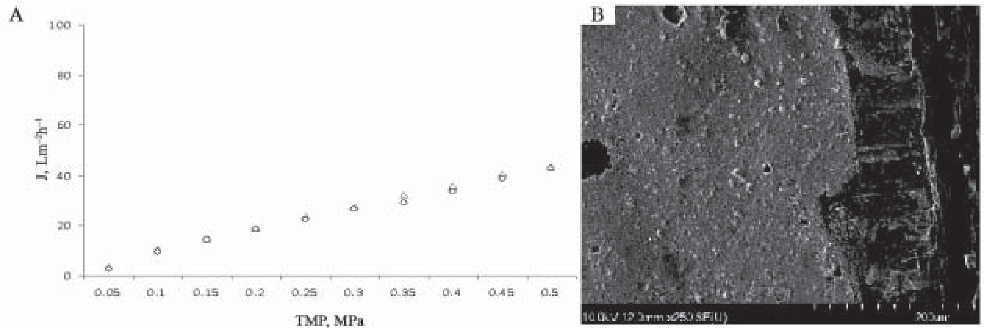

Fig. 3. Fluxes with increased TMP (A): Δ: before UV treatment; o: after UV treatment; SEM image of 1 layer TiO_2-covered RC membrane surface (B)

In the next series of experiments, model whey solution was filtered through membranes covered by either 2 or 3 TiO_2-layers.

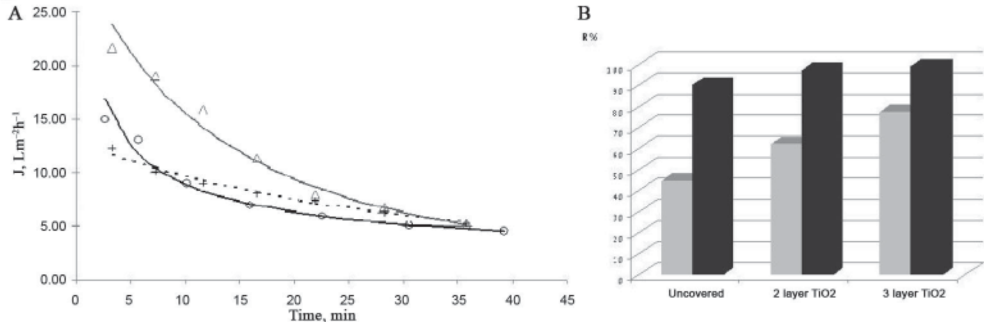

Fig. 4. Permeate fluxes of whey solution in the function of time (A): Δ: 3 kDa RC membrane, + 3 kDa RC+2layers TiO_2 membrane, o: 3 kDa RC+3layers TiO_2 membrane (dots: measured points, lines: fitted models).; (B): retention values ▨: R(COD)%; ■: R(turbidity)%

Analysis of the results was obtained by fitting the filtration models (cake filtration, intermediate filtration, standard pore blocking, and complete pore blocking) showed (Fig. 4A) that, in the case of uncovered and 2 layer-covered membranes, the standard pore blocking model (Eq. 2), and in the case of 3-layer covered membranes, the cake filtration model (Eq. 4) gave the best correlations (R^2=0.9871, 0.9919 and 0.9964, respectively). These results are in accordance with decreasing fluxes in the function of the number of TiO_2-layers: the protein molecules of whey may foul the pores of the ultrafiltration membrane, while the 3 layer covering compacts the TiO_2-layer, which "excludes" large molecules from the pores.

Retention of the turbidity and chemical oxygen demand were also measured. It was found that the retention values increased with the number of TiO_2 layers (Fig. 4B).

In order to clean the membrane, after filtration, the 2 layer-covered UF membrane was irradiated with UV light to perform photocatalytic degradation of fouling molecules. The reusability of the cleaned membrane was also examined.

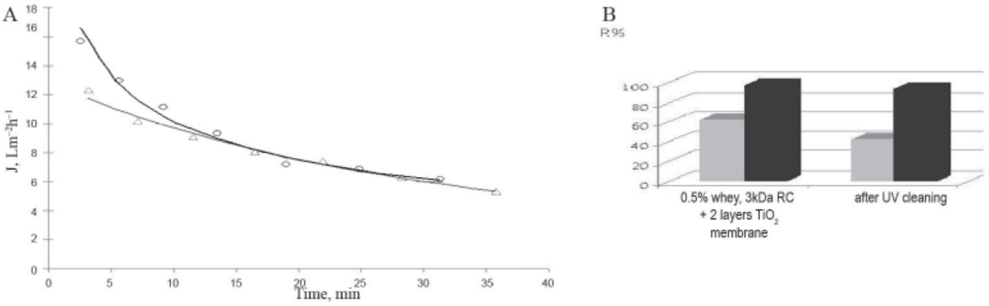

Fig. 5. Permeate fluxes (A) and retention values (B) of whey solution in the function of time (dots: measured points, lines: fitted models).
A: Δ: 3 kDa RC+ 2 layers TiO_2 membrane, o: 3 kDa RC+ 2 layers TiO_2 membrane, after UV cleaning.
B: ▨: R(COD)%; ■: R(turbidity)%

It was found that the water flux was recoverable by cleaning with UV irradiation, which can be explained by the photocatalytic effect of TiO_2: the reactive radicals produced degraded the organic molecules of whey (Fig. 6B, 6C). On the other hand, results obtained from the fitting of Eq. 1–8 to the experimental data showed that UF of whey through a UV cleaned membrane follows the cake filtration model instead of the standard pore blocking model. This can be explained by a change in the structure of the TiO_2 layers (Fig. 6A, 6C), which became more uniform. Although 30 min long UV treatment caused flux increases, the retention values were similar to the retention achieved with conventional RC membranes (Fig. 5A, 5B). This may be caused by the degradation residuals in the surface and pores of the membrane. This means that in further experiments, the cleaning method should be optimised.

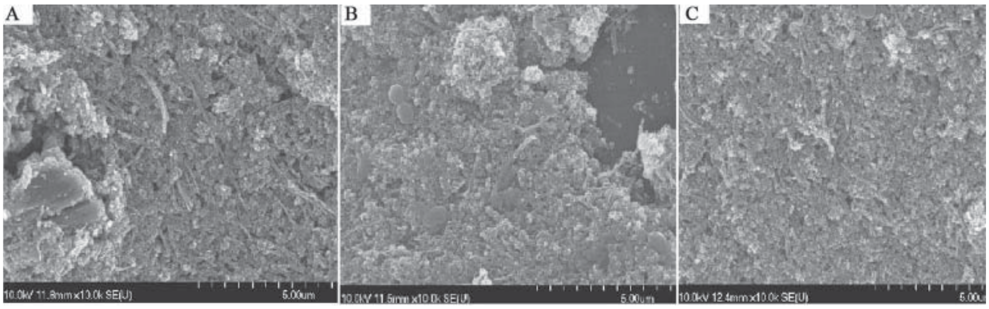

Fig. 6. SEM analysis results before whey separation (A); after whey separation (B); and after whey separation and 30 min UV (C)

3. Conclusions

Ultrafiltration of whey solution was performed in a batch-stirred membrane separation cell using regenerated cellulose (RC) membrane and RC membrane covered with TiO_2 nanotubes. Although the UV irradiation damaged the RC membrane, TiO_2-covered RC membranes were resistant to UV light. Analysis of the results shows that, in the case of uncovered and 2 layer-covered membranes, the standard pore blocking model describes the flux as a function of time, while in the case of 3-layer covered membranes, the cake filtration model gives the best correlation. The results show that the TiO_2 layers changed the original molecular weight cut-off of the membrane. The TiO_2-covered membranes were cleaned by UV light. The UV irradiation activated the TiO_2 nanotubes, degraded the polarisation-layer, and recovered the flux; therefore, UV irradiation can be used as a cleaning method.

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