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MITIGATION OF FOULING OF SUBMERGED HOLLOW FIBER MEMBRANE IN MICROFILTRATION OF TiO_2 PHOTOCATALYST PARTICLES

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The subject of investigation is fouling of a polypropylene hollow fiber membrane by TiO_2 *catalyst particles, and mitigation of fouling during and after microfiltration. To remove or reduce fouling, two techniques were applied: back-flushing (BF) and ultrasound (US). The fouling caused by the* TiO_2 *particles is of the low extent, so the fouling resistances are more than twice lower than the resistance of the used membrane. From the flux stepping experiments, it was obtained that the critical flux is 60* $l\ m^{-2}\ h^{-1}$*. For the filtration below the critical flux, it is proved that application of back-flushing is more effective than the US, in removing a fouling cake layer which was already deposited on the membrane surface. Application of the US together with the filtration process was suitable for the prevention of fouling when it was applied from the beginning of the filtration process.*

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Introduction

Typical for textile and leather industries is large disposal of dye wastewaters (DWW), which causes severe environmental problems due to toxic and carcinogenic impact on aquatic life [1]. Conventional physical techniques for treatment of DWW, such are coagulation, flocculation and sedimentation, etc. modify a dye molecule to another product which also has an impact on the environment and has to be treated further. Among chemical methods of reduction, oxidation, neutralization, an advanced oxidation process (AOP) has recently proved to have potential as sustainable and cost-effective treatment of dye waters [2]. Some of the AOPs are based on heterogeneous photocatalysis using, as a catalyst, UV-exited, semi-conductive metal oxides such as TiO_2, ZnO or $SrTiO_3$. A frequently used catalyst is TiO_2, which can be suspended in the treated water or fixed on a carrier material. Compared to the fixed one, the suspended catalyst is more efficient because it has a larger surface, and consequently, a larger active area.

After exposure to UV light in the presence of a semi-conductive catalyst, a molecule of dye should be completely degraded to minerals, CO_2 and water. In this way, the treated wastewater should not have further impact on the environment. Nevertheless, the key challenge of the photocatalytic process is the recycling of the catalyst used. The catalyst should be separated from the treated water and reused in the AOP. For the purpose of recycling of suspended catalyst, membrane separation processes such are microfiltration (MF), ultrafiltration (UF), and nanofiltration (NF) can be successfully used. Moreover, the arranging of a photocatalytic reactor and membrane in one unit represents a hybrid system of the photocatalytic membrane reactor (PMR) having several advantages compared to the application of the photocatalytic reactor followed by coagulation-flocculation-sedimentation process [3]. In the PMRs, the photocatalyst remains in the reaction bulk, it is possible to control a residence time of the reaction mixture, and the system is operated in a continuous mode or the catalyst is continuously separated. A disadvantage of application of membrane process is that a membrane is subjected to the fouling by particles of catalyst.

In the PMR systems, the hollow fiber membranes are usually employed and operated in the dead end outside-in mode. Also, operation under the constant permeate flow is common. In that case, fouling causes an increase in the suction pressure. The rate of increase is low, but still there is a point when cleaning of the HF membrane should be performed. Several cleaning methods can be used such as: rinsing, back-flushing, partial cleaning by bubbling air, and ultrasonic cleaning.

Ultrasonic waves have been recently applied to alleviate reaction in the AOP systems using ZnO or TiO_2 as catalysts [4]. The synergistic effect of ultrasound and UV irradiation during this sonophotocatalytic treatment supports formation of free radicals in the aqueous medium, increases the formation of bubble cavities, and accelerates mass transfer of pollutant molecules onto the photocatalyst surface. Also, particle deaggregation induced by US may increase the active surface area of a photocatalyst. As a result the entire mass of catalyst participates in the oxidation reaction even if a concentration of catalyst is high, and only a small fraction of the reactor volume is irradiated with UV photons. Sonophotocatalysis, therefore, allows an increase in the catalyst concentration in the reactor above the limit permitted by the law of optics [4].

The ultrasound-assisted membrane processes have also been broadly investigated [5]. Ultrasonic waves are standardly used in several areas of the chemical industry such as extraction, emulsification, degassing, while the ultrasonic membrane filters have not found wider commercial application [6]. There are two modes of US application, during or after the filtration process. When applied during the filtration process, the US acts as mechanical force causing detachment and dispersion of deposited material from the membrane surface, and preventing deposition and formation of fouling layer. Mechanism of US wave's action consists of a series of compressions and decompressions through the solution. Consequently, cavitation bubbles form and collapse generating motion both in the fluid and in the neighbourhood of the membrane surface [9]. US-associated cleaning of various membranes and fouled by various systems has been investigated so far [6-10]. It is confirmed that US of low frequency effectively minimizes fouling and removes surface attached fouling materials, but not from the membrane pores. Removal of organic matter and chemical cleaning of membranes can also be effectively enhanced by the US, where it is possible to chemically clean the pores as well [11].

In the case of membrane cleaning by back-flushing, the permeate is pumped back into the feed channel periodically. In that way, deposited material is lifted off the membrane surface by reverse flow of permeate, so it is mainly effective in the case of surface fouling. When the deposits are attached strongly to the membrane, or if pore fouling occurs, it may be slightly effective. Back-flushing is carried out on a timed frequency, or in a dead-end system operating under a constant flow-rate it may be started when the transmembrane pressure achieves unacceptably high value. The back-flushing pressure should be the same or higher than the operating forward pressure. More prompt back-flushing known as back-pulsing or back-shocking is sometimes more efficient. Back-pulses are performed in duration of just 0.1 s or shorter and can be particularly useful when colloidal suspensions are filtered [12].

Application of the proper cleaning procedure is equally important as other elements of the membrane process design to obtain an efficient and sustainable process. We studied fouling of submerged hollow fiber membrane by TiO_2 particles and cleaning of membrane during and after filtration cycle. Two cleaning procedures were tested: ultrasonic and back-flushing. Efficiencies of both cleaning procedures were analyzed.

Material and Methods

The experimental setup consisted of a 10-l feed tank with a submerged membrane module connected to the suction part of a pump over a tube system with a valve at both ends of the module. A gear pump (Heidolph 5025, Germany) with driver capable of reversing direction was used, which provides relatively constant output regardless of changes in pressure and can easily be used for membrane back-flushing.

A hollow fiber polypropylene (PP) membrane module with the active filtering area of 0.94 m^2 (Zena, the Czech Republic) was tested. The module contains hollow fibers made of stretched polypropylene, which are potted in an epoxy resin at both ends of the membrane element. The fibers of 0.24 mm inside diameter have the mean volumetric porosity of 50 % and typical slot-like pores with the mean dimensions of 0.1×0.5 μm. The membrane was soaked at least overnight in propan-1-ol to maintain its hydrophilicity and to remove soluble processing chemicals.

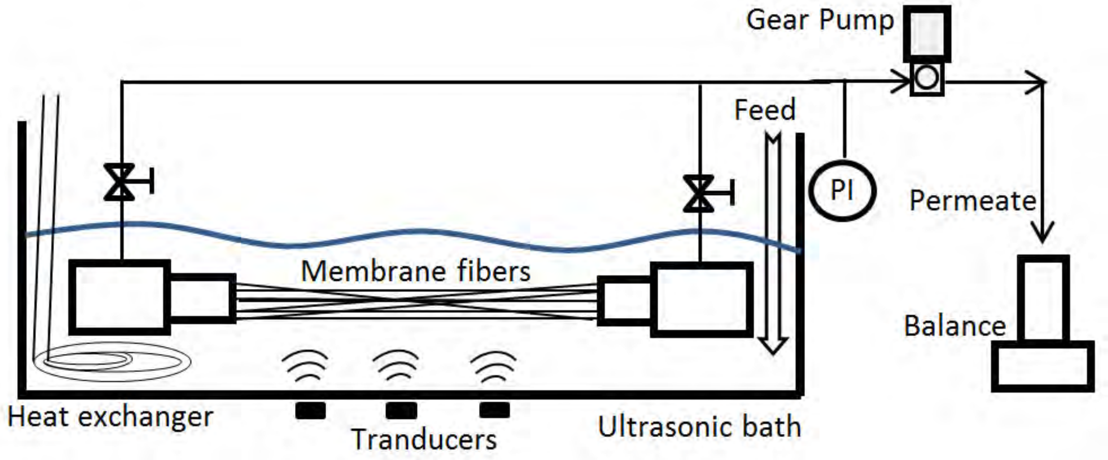

Fig. 1 Schematic illustration of a hollow fiber membrane system submerged in ultrasonic bath [13]

An aqueous dispersion of anatase TiO_2 photocatalyst (AV-01, Precheza, the Czech Republic) was used as a feed for filtration experiments. The tested concentration of TiO_2 particles was relatively high, 5.0 g l^{-1}. The particle size distribution was in the range from 0.08 to 3.3 μm determined by a particle size analyser (Malvern Mastersizer 2000, United Kingdom). Filtration was operated as outside-in dead-end mode under a constant flux of permeate. The fluxes were varied in the range from 20 to 100 l m^{-2} h^{-1}. The suction pressure was monitored during the filtration and cleaning of the membrane. During the filtration, a constant volume of bulk was maintained by recycling the permeate.

For the characterization of fouling, hydraulic resistances (***R***) were calculated based on the fundamental equation of Darcy's law and a resistance in series model (Eq. (1) and (2), respectively)

$$R_t = \frac{TMP}{\mu J} \tag{1}$$

$$R_t = R_m + R_f \tag{2}$$

where ***TMP*** is the transmembrane pressure [Pa], μ is the viscosity of permeate [Pa s], and ***J*** is the applied flux of permeate [m^3 m^{-2} s^{-1}]. The resistance of the membrane, $\boldsymbol{R_m}$, was calculated from measurements of the water flux through a new membrane. The fouling resistance, $\boldsymbol{R_f}$, was calculated by subtracting the membrane resistance from the total resistance, $\boldsymbol{R_t}$, which was obtained from the measurement of the pressure during filtration under a constant flux.

Two cleaning procedures were studied: by back-flushing and ultrasonic. The cleaning by back-flushing was performed after filtration by reverse flow of permeate under the flux of –100 and –40 l m^{-2} h^{-1} and in the duration of 5 and 10 s, respectively. During the US cleaning, the membrane was exposed to ultrasonic waves in the ultrasonic bath equipped with four transducers emitting a frequency of 35 kHz and overall effective power of 215 W (Bandelin Sonorex RK 156 BH, Germany). Two ultrasonic cleaning procedures were studied. In the first one, the filtration was performed for eight hours while at the beginning of the fifth hour the US was switched on, so the membrane was exposed to the US for the next four hours of filtration. In the second procedure, the membrane was exposed to the US from the very beginning of the filtration process.

The efficiency of cleaning procedures (***E***) in one cycle can be expressed over the hydraulic resistance of fouling remaining after the cleaning, and it is evaluated from the following equation

$$E(\%) = \left(1 - \frac{R_{n+1}^{initial}}{R_{fn}^{final}}\right) \times 100 \tag{3}$$

where ***n*** is the number of the filtration cycle.

Also, the reproducibility of cleaning procedure ($\boldsymbol{R_{cl}}$) was evaluated as a relative value by dividing the initial hydraulic resistance of the cycle by the initial hydraulic resistance of the following cycle

$$R_{cl}(\%) = \frac{R_n^{initial}}{R_{fn+1}^{final}} \times 100 \tag{4}$$

Results and Discussion

Fouling of Membrane

Beside the characteristics of filtered system and membrane, the operating conditions such as the applied pressure or flux, temperature, agitation, etc. have an influence on the extent of membrane fouling. It was suggested that in some membrane systems there exists a critical flux below which fouling does not occur or it is of low extent [14]. The concept of critical flux is dominantly used to define sustainable or limiting operating conditions in cross-flow membrane separation systems. Namely, in the ideal case without fouling, the transmembrane pressure remains constant in time for each flux. The critical flux was defined as the flux at which the transmembrane pressure starts to deviate from the line of pure water flux or, as the first flux for which irreversible fouling occurs.

In the case of dead-end filtration, it is more suitable to detect the critical flux by analysing irreversible fouling. Therefore, the suitable experimental procedure for the submerged dead-end MF is stepping of fluxes backwards and forwards with back-flushing of permeate between filtration cycles in order to prove irreversible fouling. In our case, between filtration cycles under the constant flux, back-flushing of permeate under the backward flux of $-100\ \mathrm{l\ m^{-2}\ h^{-1}}$ in the duration of 5 s was performed. The main assumption was: if the fouling is below critical point and reversible, the fouling layer can easily be removed by a mere back-flushing of permeate.

The hydraulic resistance of a new membrane and fouling resistances during filtration of TiO_2 suspension under the various stepping constant fluxes are presented in Fig. 2. Due to the nature of TiO_2 particles, membrane structure, and relatively moderate operating conditions, the fouling resistance is almost an order of magnitude lower than the resistance of the membrane itself. Noticeable increase in fouling rate can be observed during each filtration cycle under the forward and backward fluxes. In forward procedure, the highest resistance of $6\times10^{11}\ \mathrm{m^{-1}}$ was obtained for the flux of $100\ \mathrm{l\ m^{-2}\ h^{-1}}$. In this case of TiO_2 particles, the fouling is associated with the development of a cake layer at the membrane surface which is even appreciable because it acts as the secondary selective layer preventing penetration of smaller particles into the membrane structure. The back-flushing cleaning between filtration cycles was not so effective to provide removal of the cake layer completely. The remaining cake layer became more compact during filtration cycles due to an increase of suction of permeate, e.g., the forward flux. Hence, a gradual increase in resistance can be observed, and likewise during the backward procedure despite a decrease in the flux. In the backward procedure, the fouling resistance firstly increased and then slowly decreased after the backward flux of $60\ \mathrm{l\ m^{-2}\ h^{-1}}$. After several back-flushing cycles in the backward procedure compaction of cake decreased, still the resistances were higher than for the same

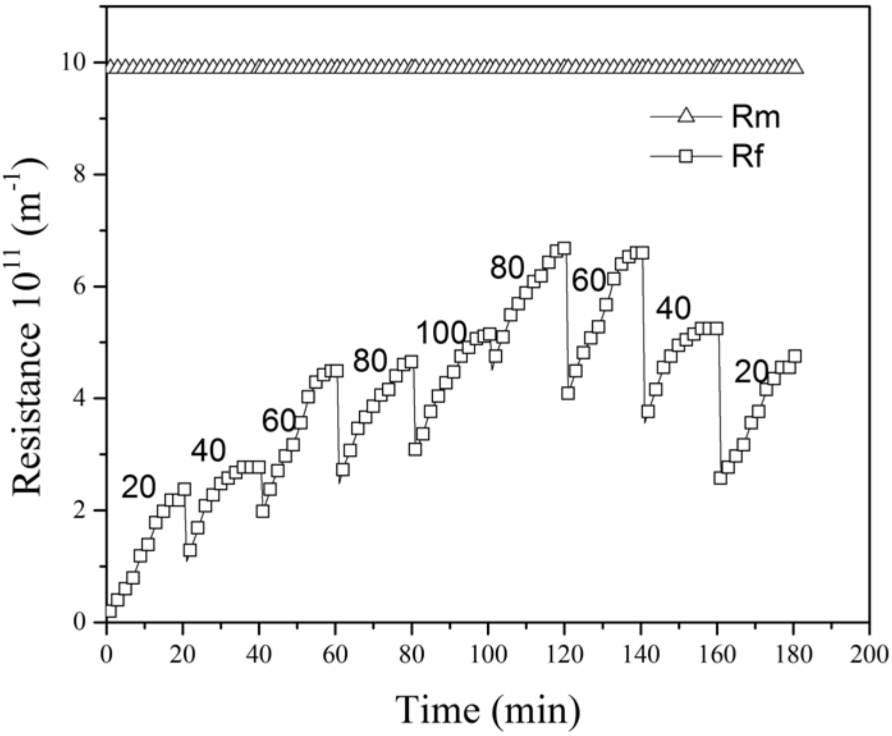

Fig. 2 Fouling resistances obtained from pressure measurements for stepping permeation fluxes from 20 to 100 l m^{-2} h^{-1} forwards and backwards. Initial catalyst concentration was 5 g l^{-1}, back-flushing frequency 20 min, back-flushing duration 5 s, and backward flux –100 l m^{-2} h^{-1}

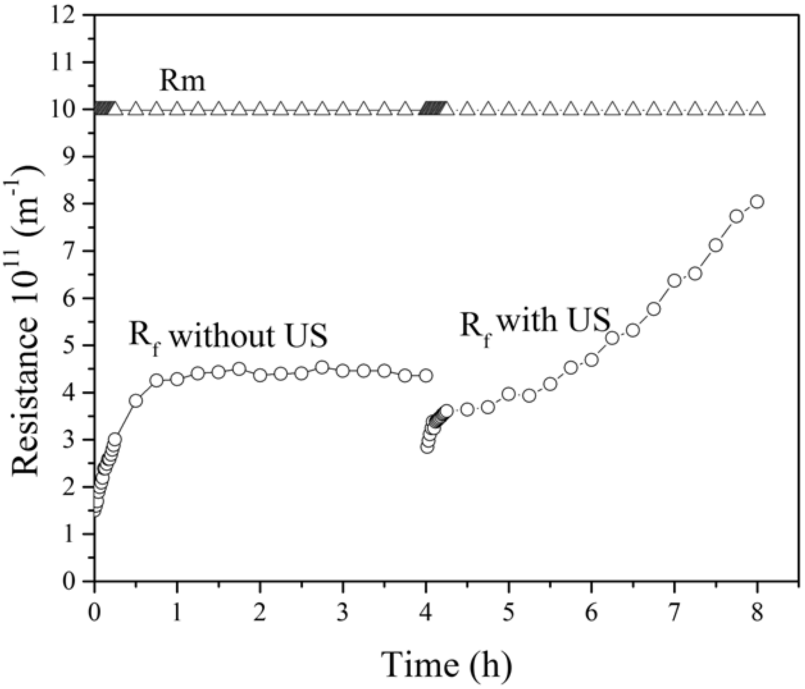

Fig. 3 Time dependency of fouling resistances during microfiltration of TiO_2 suspension without and with US irradiation under flux of 40 l m^{-2} h^{-1}. Initial catalyst concentration was 5 g l^{-1} and US frequency 35 kHz

conditions in the forward procedure.

Up to the flux of 60 l m^{-2} h^{-1}, operating conditions did not influence the compaction of the fouling layer at the membrane surface. Also an increase in suction pressure was relatively low and did not cause significant compaction of the cake layer. So, the cake layer could be easily removed by back-flushing and the initial resistance almost restored. After this flux, low removal of fouling layer was obtained by back-flushing. So, as the critical flux can be denoted the flux of 60 l m^{-2} h^{-1} below which fouling can be easily removed. The same results were obtained by similar analysis in previous publications [13].

Effect of Ultrasound

With an aim to study the influence of ultrasonic irradiation on fouling reduction by TiO_2 particles, two tests were performed. In the first one, the HF membrane was fouled with particles during four hours of filtration under the subcritical flux of 40 l m^{-2} h^{-1} and then US cleaning was introduced simultaneously with filtration also in the duration of four hours (Fig. 3). During the filtration without US, the fouling resistance was increasing in the first hour of filtration until all the TiO_2 particles settled on the membrane surface. After that, we did not observe further increase in fouling, and filtration was performed through the cake formed on the membrane surface.

When the ultrasound was switched on at the beginning the of 5-th hour of filtration, the fouling decreased, but the initial resistance was not restored because the fouling layer was only partially removed. During ongoing filtration with US irradiation, the fouling resistance increased, and after the 6-th hour of filtration the resistance exceeded the value of resistance during the filtration without US. At the end of filtration associated with US, the fouling resistance was almost twice higher than at the end of filtration without US. So the long term exposure of the fouled membrane to the US along with the filtration did not prove to be an effective procedure, not even for the operation under the critical flux.

When the fouled membrane was exposed to the US, the cake layer formed at the membrane surface was partially removed due to lift of particles from the membrane surface. Large particles can be easily lifted from the membrane surface, but they cannot be entirely moved back to the bulk. So, during the time of filtration, larger particles redeposit on the membrane surface while the smaller particles can penetrate within the cake structure making it more compact, so hindering the influence of US on fouling removal.

In the second test with US, the performance of conventional filtration in the duration of an hour was compared to the filtration with US irradiation from the very beginning of filtration and under the flux of 100 l m^{-2} h^{-1} (Fig. 4). During the conventional filtration, fouling resistance increased in the first 20 min of filtration until it achieved a steady-state value. During the US associated filtration, the fouling resistance was increasing in the first 10 min, but after that it started to decrease till the end of filtration cycle when the initial value of resistance was restored. Despite the high flux of 100 l m^{-2} h^{-1}, the US associated filtration, from the beginning of microfiltration process, enabled lifting of TiO_2 particles from the membrane surface and prevented the formation of the steady cake layer. Similar results were obtained in the other studies on the low frequency of US-associated membrane filtration treating wastewaters or organic systems [7,15].

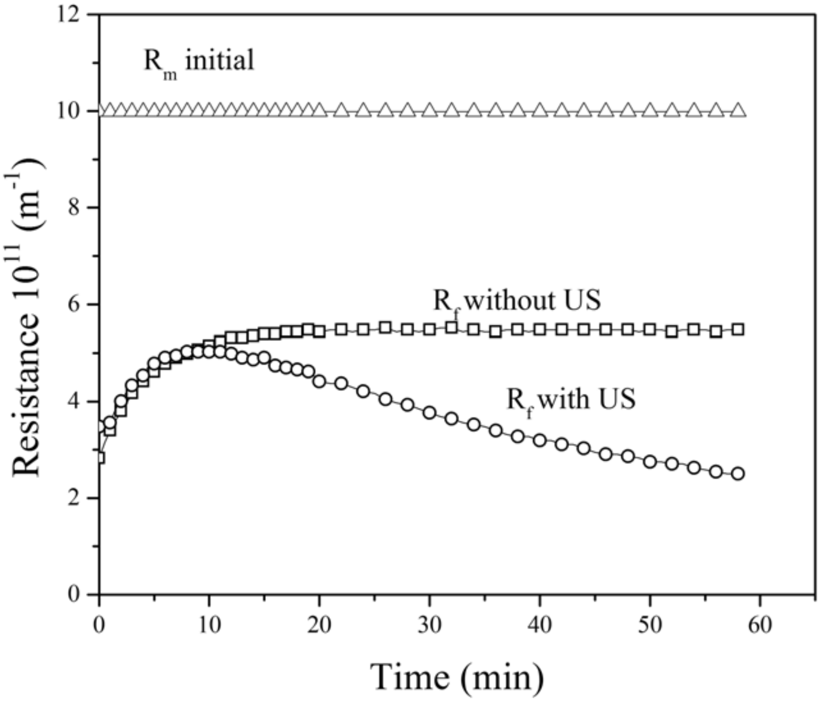

Fig. 4 Comparison of fouling resistances obtained by filtration without and with US irradiation from beginning of filtration under flux of 100 l m^{-2} h^{-1}. Initial catalyst concentration was 5 g l^{-1} and US frequency 35 kHz

Comparison of Cleanings by Ultrasound and by Back-flushing

In Fig. 5, resistances obtained during filtration after cleaning by the US, by the back-flushing (BF) and by the simultaneous application of those two modes of cleaning (BF+US) were compared. All cleaning procedures were performed for 10 s after fouling of the membrane under the subcritical flux of 40 l m^{-2} h^{-1}. The stabilized membrane was used for the experiments; in comparison to the new membrane it had additional but permanent initial fouling resistance of 2.5×10^{11} m^{-1}. It can be noticed that the initial resistance was restored after each cleaning cycle of both, BF and BF+US cleaning procedures. Nevertheless, in the filtration cycles it can be observed that the fouling rate was higher after the BF+US cleaning

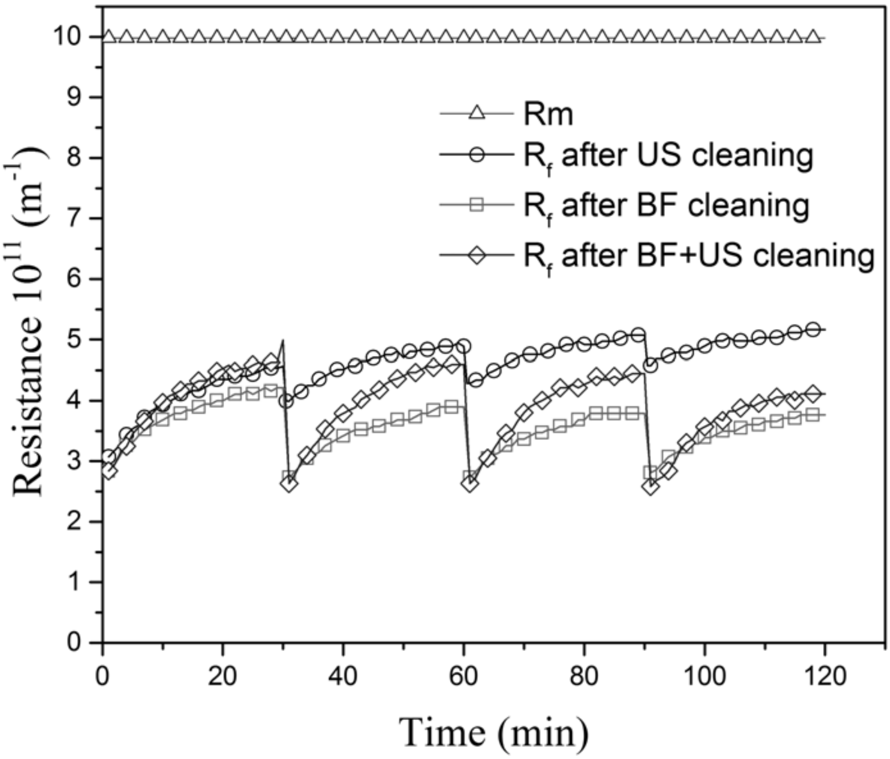

Fig. 5 Time dependency of resistances obtained for three different 10 s cleaning procedures between filtration cycles: US, back-flushing and combination of US and back-flushing. Initial catalyst concentration was 5 g l^{-1}, cleaning frequency 30 min, cleaning duration 10 s, backward flux –40 l m^{-2} h^{-1}, and US frequency 35 kHz

than after the BF cleaning. In the case of the US, the initial resistance was not restored after the first cleaning cycle and the resistance was gradually increased during the filtration cycles. This confirms the previous observation that long term exposure to the ultrasound makes the cake layer more compact, and consequently, more difficult to remove even in the combination with other cleaning procedures.

The efficiencies of all cleaning procedures are presented in Table I. It can be noticed that the efficiency of all three cleaning procedures slightly decreased over filtration cycles. The efficiencies of each cleaning cycle of BF+US and BF were about 40 and 30 %, respectively. Only initial permanent resistance led to a lack in efficiency of the studied cleaning procedures. Also, reproducibility of cleaning ($\boldsymbol{R_{cl}}$) for these two procedures was about 100 % and constant over the cleaning cycles. The most efficient cleaning procedure from the point of view of percentage fouling removal was the combination of the US and back-flushing. But this is only due to evaluation of efficiency as relative value, because in this case the rate of fouling during filtration period was higher. In the case of US cleaning, the cleaning efficiency was low despite the good reproducibility of cleaning. After the first filtration cycle followed by US cleaning, residual fouling remained on the membrane surface. US managed to lift only large particles and the irradiation time of only 10 s was very short for US to act effectively. In the next filtration-US cleaning cycles, it was possible to remove only cycle related fouling, built-up after the first cycle.

Table I Efficiencies of different cleaning procedures

Cleaning mode/Cycle		1	2	3
US	***E***, %	12.7	12.3	9.7
	R_{cl}, %	76.9	93.0	93.9
Back-flushing	***E***, %	35.4	30.0	26.1
	R_{cl}, %	104.4	100	97.1
US + back-flushing	***E***, %	47.3	42.7	41.9
	R_{cl}, %	107.6	100	101.9

Conclusion

Under the critical flux, fouling of the hollow fiber membrane by TiO_2 particles can be characterized as the surface fouling of the relatively low extent. It is proved that the cleaning by of back-flushing is more effective than the US one in the case of the removal of the fouling cake layer which was

already formed on the membrane surface. Application of the US together with the filtration process was suitable for the prevention of fouling when it was introduced from the beginning of filtration and thus prevented the build-up of the cake layer.

Acknowledgment

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