Preparation and characterization of nano-filtration and its photocatalytic abilities via pre-coated and self-forming dynamic membranes developed by ZnO, PAC and chitosan
S. Mona Mirmousaei, Majid Peyravi, Mohammad Khajouei, Mohsen Jahanshahi and Soodabeh Khalili

ABSTRACT

In the current work, novel dynamic membranes (DM) were tested and introduced for cheese whey wastewater treatment based on resistant and inexpensive materials, polyesters, and chitosan. For the investigation of dynamic membrane (pre-coated and self-forming) characterizations, polyester as a low-cost and natural material with chitosan were chosen to provide the support of the target membrane. The inherent antifouling character of chitosan accompanied by its high hydrophilicity have made this polymer known as an attractive agent for membrane-based wastewater treatment operations. Zinc oxide (ZnO) and powdered activated carbon (PAC) were employed as the dynamic layer. Neat polyester had a chemical oxygen demand (COD) rejection ratio of about 57.61%, but the flux declined sharply. The higher removal efficiency was for the self-forming type: total phosphate (94%) and citrate (95.5%). Fouled dynamic membranes were backwashed by sodium dodecyl-sulphate (SDS), warm water, and distilled water. Results demonstrated that the pre-coated was reduced and fouling increased the flux recovery rate (FRR) (9.1%) while use of the self-forming DM exhibited an aggravation of fouling by decreasing of support FRR (11.1%). It was found that by substitution of deionized water and hot water with SDS, FRR was enhanced. In the following, the photocatalytic ability of the product was investigated. The UV light source increased the removal ratio and FRR. For example, self-forming COD rejection was enhanced (6.63%).

Key words | chitosan, cleaning, dynamic membrane, PAC-ZnO nanoparticle, polyester, UV irradiation

INTRODUCTION

The cheese production industry contains three waste types: (1) whey wastewater (one of the primary pollutants which is generated at a cheese production site); (2) whey (resultant of cottage cheese production); and (3) equipment washing water. Cheese whey wastewater characterizes an essential general problem regarding the environmental aspects, including high volumes and chemical oxygen demand (COD) content. Therefore, handling the issue is vital, and the wastes should not be directly discharged into the environment without an appropriate treatment (Palmieri et al. 2017; Khajouei et al. 2018).

The employment of membrane-based techniques has been increased due to the flexibility in operation and their complete solid retention, although the fouling phenomenon hinders the procedure. Fouling (including inorganic fouling, organic fouling, and biofouling) is the major problem of membrane-based separation processes (Saleem et al. 2017; Khajouei et al. 2018). This phenomenon occurs by the combination of certain chemical and physical interactions that can be controlled via membrane properties such as hydrophilicity, roughness and surface charge, feedstock water solution chemistry, etc. This obstacle can intensely limit the performance of the membrane in technical or economic aspects. Fouling results in a substantial decline in membrane permeability, increases the operation costs of the plant, obstructs the operational efficiency, and reduces the membrane lifetime (Balta et al. 2012; Geng et al. 2017; Khajouei et al. 2017a). Thereby, membrane fouling control in the...
processes has been the focused concept of research recently. Dynamic membranes (DM) are known as secondary membranes or also formed-in-place membranes, and have been mainly classified into two groups: (I) pre-coated and (II) self-forming membranes. Pre-coated membranes can be fabricated via passing DM solution over the surface of the support layer and self-forming membranes are generated by the DM particles which existed in the mixture of liquids to be filtered (Fan & Huang 2002; Chu & Li 2006). DM has potential preferences such as the capability of using inexpensive materials, ease of fouling elimination, and high flux. The most important feature is the forming and re-forming facility when the DM layer accomplishes wastewater treatment (Zhang et al. 2014). Dongwei Lu and his group (Lu et al. 2016) have studied the pre-coated and self-forming types of dynamic membranes via utilization of a ceramic membrane as the support layer and hydrophilic Fe₂O₃ as the dynamical layer. The pre-coated dynamic membrane increased the flux recovery rate of the ceramic membrane about 10% and the self-forming dynamic membrane decreased the flux recovery rate about 8.6% after four filtration cycles. Poostchi et al. (2015) also used a filter mesh to form the pre-coated dynamic membrane via the employment of PAC in a bioreactor. They showed the rejection capacity of the pre-coated membrane is comparable to that of the microfiltration membrane. DM may be formed on the different support materials such as filter cloth, nylon, membrane, mesh, etc. (Sreeda et al. 2018). Chitosan (CS) is a biomaterial which is synthesized from chitin. Chitin can also be extracted from a wide variety of sources like fungi, lobsters, shrimps, and crustacean shells (McKay et al. 1987). Chitosan is applied in the membrane fabrication process due to being environmental benign, and due to nontoxicity, solubility in weakly acidic aqueous solution, hydrophilicity and its functional groups (hydroxyl and amine). Additionally, it can be admirable as an anti-fouling agent (Kumar et al. 2015).

The ZnO nanoparticle (ZnO-NP) is a semiconductor, non-toxic, easy to prepare, and very economical with regard to its wide bandgap of 3.37 eV, long life-span and high UV absorption capability (Jing et al. 2004; Ba-Abbad et al. 2013). In recent years, the design processes of photocatalysts have embedded them onto porous materials and shown great significance with regard to their enhancement as the adsorbent of the support layer. The support material is considered an important factor to influence nano-adsorbent activities. One of the best support materials is activated carbon (AC) because of its well-developed porosity and high surface area. Powder activated carbon (PAC) is known as a potential agent to reduce membrane fouling and is also used as the supporting material due to its porous structure and high mechanical resistance (Khajouei et al. 2017b). ZnO and PAC as the catalytic supports have shown remarkable performance resulting in higher operation proficiency. Sobana et al. (2008) have investigated the influence of AC–ZnO photocatalytic efficiency on the degradation of 4-acetylated phenol by UV-irradiation.

Adsorption and photodegradation of 4-AP on AC–ZnO was higher than bare ZnO (removal increased about 20%). The higher efficiency of AC–ZnO is due to the synergistic effect between ZnO and activated carbon. Moreover, Saini et al. (2017) reported that ZnO loaded with activated carbon showed removal capacities for Orange G (OG) and Rhodamine B (Rh-B) dyes of 96% and 93% at room temperature, respectively.

The current study is focused on the preparation and characterization of PAC-ZnO and its usage as a dynamic layer for the development of self-forming and pre-coated dynamic membranes. In this work, the polyester that was modified by chitosan acted as the support membrane. After that, results of photocatalytic ability investigations under UV irradiation are reported. Synthesized composites are characterized by scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), and X-ray diffraction (XRD).

MATERIALS AND METHODS

Reagents

Powdered activated carbon (PAC, mesh = 200–350) and polyester were obtained from PICA (Australia). Chitosan with average molecular weight and zinc nitrate hexahydrate (Zn(NO₃)₂) (assay ≥99.0% KT, WGK Germany: 3) were purchased from Sigma Aldrich (Germany). Sodium dodecyl sulphate (SDS), n-hexane (purity ≥95), glacial acetic acid (100%), and sodium hydroxide were supplied from Merck (Germany). Nitric acid (65%) was obtained from Scharlau.

SDS was employed as the cleaning agent. Distilled water (DW) was used throughout the many steps of the experiment. Cheese whey wastewater was obtained from Kalleh Company, Amol, Iran (pH = 4.33 and COD = 47,400 mg L⁻¹), and was diluted with distilled water.

Preparation of chitosan (CS) solution

The chitosan gel solution contained the mixture of chitosan (1, 1.5, and 2 g/L) and 1% (v/v) dilute acetic acid as the
solvent. The obtained solution was stirred consecutively for 24 h at room temperature.

**Synthesis of the composite PAC-ZnO**

To prepare ZnO/PAC as the dynamic membrane material, 2 g PAC was dispersed and then added to 100 mL of NaOH aqueous solution (0.2 M). Then, 100 mL of Zn(NO₃)₂ aqueous solution (0.2 M) was added to the mixture and stirred for 2 h. After that, the precipitate was separated via a vacuum pump and was annealed in air at 400 °C for 2 h.

**Filtration experiment**

A laboratory-scale stainless steel flat sheet dead-end filtration setup and a backwash system were applied to investigate the wastewater treatment and flux recovery ratio of the dynamic membranes, respectively. The schematic diagram of the experimental structure and backwashing test are shown in Figure S1 (Supplement). The effective membrane area was 21 cm². To reduce the possible concentration occurring due to the polarization phenomenon, a magnetic stirrer was fitted in the feed side. Before the core tests, the membranes were pre-compressed for 15 min via pure water at 5 bar.

**Preparation of dynamic membrane**

For the generation of the dynamic membranes, polyester was modified by chitosan and acted as the support membrane layer. By applying a pressure of 1 bar, chitosan gel was fed; this method is known as the flow-through method (FTM) (Boributh et al. 2009). For the fabrication of the pre-coated membrane type, PAC-ZnO suspension (1 g/L) was dispersed in deionized water and then filtered via the wastewater. The PAC-ZnO composite acted as a protective layer and agent. The wastewater filtration process was conducted in three cycles. Each cycle contained a dynamic membrane preparation and a filtration process. The backwash operation via cleaning agents was engaged at 1 bar. The self-forming dynamic-type membrane was also generated through the filtration process. In this regard, 1 g/L PAC-ZnO particles were added to the wastewater and simultaneously filtered. The schematic diagram of dynamic membrane preparation is shown in Figure S2 (Supplement).

**The photocatalytic ability of dynamic membranes**

For the investigation and analysis of the generated membranes’ photocatalytic features, the particles were exposed to UV irradiation in an MDF box equipped with a Japanese Hitachi UV lamp 16 W for 30 min. To prepare a self-forming membrane type, mixtures of particles and wastewater were placed under UV irradiation, and for the pre-coated example, particles were placed under UV light power and were covered on the surface support membrane (neat membrane). Then, the wastewater was filtered and fed.

**DMs cleaning**

To clean the fouled membranes in the filtration process, sodium dodecyl sulfate (SDS), warm water (50 °C), and deionized water were utilized as the cleaning agents. It was anticipated that by using SDS as the cleaning agent, the efficiency of this step might be enhanced because of the interaction between oily particles of daily wastewater and the hydrophobic tail of SDS. The flux recovery rate (FRR) was also considered as an anti-fouling factor. The pure water flux of the membranes before and after the treatment processes was measured and the FRR was calculated to evaluate the antifouling performance.

**Membrane performance characterization**

For measuring the permeation flux, the permeate samples were collected and weighed at 10 min intervals. Permeation flux (PF) was calculated via Equation (1):

\[
PF = \frac{V}{A \times t}
\]

where \(V\) is the volume permeated, \(A\) shows the membrane area and \(t\) denotes the permeation time.

Equation (2) calculated the normalized flux:

\[
\text{Normalized flux} = J/J_0
\]

Equation (3) calculated the COD rejection:

\[
R_{\text{COD}} = \left(1 - \frac{C_{\text{Per}}}{C_{\text{Feed}}}\right) \times 100
\]

where \(C_{\text{Per}}\) is the concentration of permeate and \(C_{\text{Feed}}\) is the concentration of the feed.

For each experiment, the permeation concentrations were determined by measuring the absorbance using a UV–2100 spectrophotometer at two wavelengths. Absorbance at the wavelengths of 820 nm and 428 nm was carried out to determine the total phosphate and citrate.
concentrations (Nishanthi et al. 2017) and was used to confirm the membranes’ filtration capacity by concentration change before and after filtration. In this part, the total phosphate and citrate removal efficiency was calculated by Equation (4) where $\lambda_p$ and $\lambda_f$ are the concentrations in the permeate and feed, respectively:

$$R_{UV} = \left(1 - \frac{\lambda_p}{\lambda_f}\right) \times 100\%$$  \hspace{1cm} (4)

For the membrane fouling-resistance analysis, the flux recovery ratio (FRR) was calculated using Equation (5) where $J_{w1}$ defines the pure water flux before the wastewater treatment and $J_{w2}$ represents the pure water flux after backwashing:

$$FRR = \left(\frac{J_{w2}}{J_{w1}}\right) \times 100$$ \hspace{1cm} (5)

**Instrumentation and characterization**

SEM with a Cambridge scanning electron microscope (CamScan MV2300) was employed to study the cross-section and surface morphologies of the neat polyester and the chitosan-modified polyester membranes. Additionally, the composition of the membrane surface dynamic layer was also studied with this instrument. Membranes were cryogenically fractured in liquid nitrogen and then coated with gold to produce electric conductivity. An FTIR spectrometer was used to detect the membrane functional groups. FTIR spectroscopy was conducted on a TENSOR 27 (Germany) spectrometer. The samples were tested to evaluate the composites’ functional groups with the addition of the KBr. The FTIR spectrum was collected 16 times and improved for background noise. To characterize membrane surface hydrophilicity, a water contact angle test was utilized. The contact angle is commonly determined via dropping deionized (DI) water on the membrane sample surface. In our work, the contact angle between the water and the membrane surface was directly measured via a capturing instrument (Canon camera, Japan) at $25 \degree C$ and the DI water as a probe liquid was located on the membrane surface at seven random points; the average of the measured values was then reported as the membrane water contact angle. The XRD analysis of the samples was performed by the XRD technique using an X’Pert Pro (Panalytical) model; the data were recorded in the range of $2\theta = 0\degree - 80\degree$.

**RESULTS AND DISCUSSION**

**Structural properties of PAC-ZnO**

Fourier transform is a useful tool to demonstrate the presence of the functional groups and bonds in molecules. FTIR spectra were used to determine the nature of the PAC-ZnO composite surfaces. The results are depicted in Figure 1. With regard to these results: the peaks corresponding to the stretching vibrational modes of Zn–O bonds can be observed between 400 and 600 cm$^{-1}$ (Saleh et al. 2018). The peaks spotted at 1,210–1,320 cm$^{-1}$ can be due to C–OH stretching vibrations and those at 1,500 cm$^{-1}$ to 1,600 cm$^{-1}$ can be assigned to the C–O–C structure on the surface of the PAC–ZnO. The detection of the 2,900 cm$^{-1}$ peak indicates that the PAC surface was loaded with the ZnO nanoparticles. Meanwhile, the region in the range of 3,344–3,431 cm$^{-1}$ corresponds to hydroxyl group vibration bands (Sobana et al. 2012). These results endorse the formation of PAC-ZnO composite.

XRD was also employed to confirm the presence of ZnO nanoparticles in the PAC-ZnO. Figure 2 specifies the XRD patterns of PAC-ZnO. The detected peaks at ranges of $2\theta = 31.8\degree$, 34.5\degree, 36.4\degree, 47.5\degree, 56.7\degree, 63\degree, 66.38\degree, 67.9\degree, 69.1\degree and 77.1\degree which can be indexed as (100), (002), (101), (102), (110), (103), (200), (112), (201) and (202), were ascribed to ZnO (Park et al. 2008), while for PAC, there was a weak peak at $2\theta = 43.5\degree$ that confirmed a semi-crystalline graphitic structure of activated carbon and is associated with (101) (Yang & Lua 2006; Saleh et al. 2015).

![Figure 1 | FTIR spectra for PAC-ZnO composite.](image-url)
Characteristics of PAC-ZnO composite dynamic membranes

The results of contact angle analysis and the hydrophilicity of the neat polyester and the pre-coated dynamic membranes are indicated in Table 1. The contact angle of the neat polyester was reported as 60.25°. The deposition of chitosan led to contact angle reduction due to its intrinsically hydrophilic property. As a consequence the contact angle of PAC-ZnO pre-coated dynamic membrane was improved to 26.7°. This phenomenon can correspond to a hydrophilicity increase in the dynamic membrane compared with the neat and modified polyester. The hydrophilicity performance support (polyester/chitosan) was significantly improved because of the covering of the support surface by the PAC-ZnO layer, and the antifouling performance support (polyester/chitosan) was also modified. This phenomenon is due to the simultaneous deposition of oily particles of wastewater and dynamic layer materials on the surface of the membrane.

Surface and cross-sectional SEM images of neat polyester, modified polyester, and the surfaces of pre-coated and self-forming composite membranes are indicated in Figure 3(a)–3(f), respectively. It can be inferred from the images that the chitosan particles were involved in the polyester filaments and attached to the fibers. Moreover, the surfaces of the pre-coated and self-forming membranes were covered by a dynamical layer. It is evident that the self-forming composite membrane was prepared as a compact layer on the support surface.

Modified polyester

To comprehend the best effect of chitosan concentration on the polyester performance, different dosages of chitosan were tested (1, 1.5, and 2 g/L) by applying a pressure of 1 bar and room temperature. The results of the wastewater permeation test for the neat polyester and the modified polyester are shown in Figure 4. As can be inferred initially, the neat polyester has a high permeation flux with regard to the layer of chitosan that was created on the polyester surface and, consequently, produced extra resistance for the decline in permeation. Afterwards, the neat polyester showed a rapid decline because of wastewater particle penetration in the polyester and membrane blockage. Results demonstrated that the modified polyester gave a higher flux. It can be concluded from the SEM images that chitosan accumulated on the surface and also diffused in the pores of polyester. The flux increment can be explained with reference to the natural propensities of chitosan: (I) hydrophilicity that is due to the polar groups of the chitosan polymer, (II) permeability, and (III) antifouling properties. Results were determinate that the appropriate concentration was 1 g/L.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Contact angle</th>
</tr>
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<tbody>
<tr>
<td>Neat polyester</td>
<td>60.25°</td>
</tr>
<tr>
<td>Modified polyester (1 g/L)</td>
<td>44.61°</td>
</tr>
<tr>
<td>PAC-ZnO pre-coated DM</td>
<td>26.7°</td>
</tr>
<tr>
<td>PAC-ZnO self-forming DM</td>
<td>110.43°</td>
</tr>
</tbody>
</table>
chitosan. Increasing the concentration led to the permeation diminishing, from which can be concluded that increasing the dosage caused the reduction of pore size of the polyester, leading to a compact structure and finally lower flux.
Dynamic membranes to wastewater treatment

Figure 5 shows the normalized permeate flux of the self-forming and pre-coated dynamic membranes that have been formulated with PAC-ZnO as the membrane dynamic layer. All membranes showed meaningful declines in the flux, which resulted during the filtration process; this can be attributed to the membrane fouling phenomenon. Membrane fouling occurrence is ascribed to the adsorption of wastewater particles on the membrane surface or in membrane pores, causing cake layer formation. With regard to the results, it can be concluded that a higher permeation flux could be obtained by the pre-coated type and remained stable; and likewise, the self-forming type had a lower permeation flux. As is shown in Figure S2 (Supplement), in the pre-coated membrane type, dynamical particles played the barrier role between the support surface and the wastewater bulk and so could diminish the direct contact of the support with the wastewater particles; furthermore, the permeate flux remained stable.

According to the results, the self-forming DM showed lower flux compared with the pre-coated DM. This phenomenon can confirm the compact structure from self-forming. With reference to Figure S2 (Supplement), the compact structure was made in two ways: (1) simultaneous deposition of wastewater foulants and dynamic layer materials on the surface of the membrane; (2) absorption of some wastewater foulants and dynamic particles before deposition on the membrane in suspension of the self-forming DM. At the time of compact structure formation, some of the wastewater particles were stuck in the gaps of ZnO-PAC particles and deposition occurred together on the support. Thus these particles infiltrated into the pores of the support, and the flux declined. More particles were deposited over time, and the thickness of the barrier was increased, so the flux declined.

Figure 6 presents the total phosphate and citrate removal efficiency, and Table 2 shows the COD removal efficiency of all the membranes. All membranes showed high productivity and proficiency results for total phosphate and citrate removal. It is also noteworthy to say that the neat polyester indicated COD removal of more than 55%. The citrate removal efficiencies of the pre-coated and self-forming dynamic membranes after the third filtration cycle were 91.3% and 95.5%, respectively. These results indicate that the self-forming type can present superior results due to the formation of compact structure. COD rejection rates (R%) of all membranes (neat polyester, support (neat membrane), pre-coated, and self-forming) are listed in Table 2. The COD rejection rates of the support membrane (38.72%) and pre-coated (47.93%) were less than that of the self-forming (55.44%) after the third cycle. Results indicate that the self-forming type can provide higher removal efficiency in all factors, which can be ascribed to the formation of a layer with compact structure on the support membrane because of the simultaneous deposition of dynamic particles and wastewater particles during the self-forming type’s preparation. This dense layer can cause a smaller amount of wastewater particles to pass the support membrane, so removal efficiency improves. Furthermore, in the self-forming type, the adhesion of wastewater particles and dynamic particles can result in high removal efficiency.

Fouling mechanism

Flux recovery ratio is a factor in the calculation of antifouling performance. Results of the membrane flux recovery
analyses are reported in Figure 7. During the filtration process, all membranes showed a reduction in the flux recovery ratio due to the fouling phenomenon and cake layer formation. By increment of the filtration/backwashing sequences, the FRR of support, pre-coated and self-forming membranes diminished, so their permeability was gradually diminished. After the third filtration cycle, the FRR of support, pre-coated and self-forming membranes after backwashing by distilled water were reported as 82.3%, 88.6%, and 73.4%, respectively. It is evident that the pre-coated type could decrease the fouling by increasing the FRR because of the formation of an anti-fouling and hydrophilic layer on top of the support membrane. This layer acted as a protective layer that could decrease the disposal support surface from wastewater particles. Additionally, it caused foulant removal to increase from the surface during backwashing. In contrast, the self-forming type aggravated fouling by reducing the FRR. The self-forming has an inherent tendency to increase fouling. This phenomenon can be ascribed to the compact structure on the support due to adherence of wastewater particles on the PAC-ZnO in the suspension and deposition of wastewater particles and PAC-ZnO particles on the support, simultaneously.

Membrane backwashing

The dynamic membranes' anti-fouling performances were appraised by the FRR in each cycle of the filtration process. SDS, hot water (50 °C), and distilled water were used as cleaning agents. Figure 8 compares the flux recovery ratio (FRR amount) of pre-coated and self-forming DMs as an anti-fouling parameter. FRR of all membranes diminished as the number of the process (filtration/backwash) increased gradually. This phenomenon can be attributed to the fouling and cake layer in the filtration process. In addition, a higher cleaning efficiency was obtained by the pre-coated type. The pre-coated type is a desirable protective membrane to reduce fouling and enhanced FRR, where the self-forming type aggravated the fouling phenomenon and showed lower FRR. The results of filtration demonstrated that the pre-coated dynamic kind of membrane could be used as a protective membrane to diminish the fouling. In the pre-coated kind, the homogeneous formation of the PAC-ZnO layer on the membrane can act as a barrier and as a protective layer between wastewater particles and membrane

Table 2 | COD removal (%)

<table>
<thead>
<tr>
<th></th>
<th>Cycle1</th>
<th>Cycle2</th>
<th>Cycle3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat polyester</td>
<td>55.38</td>
<td>56.38</td>
<td>57.61</td>
</tr>
<tr>
<td>Support (neat membrane)</td>
<td>34.9</td>
<td>37.29</td>
<td>38.72</td>
</tr>
<tr>
<td>Pre-coated</td>
<td>44.2</td>
<td>46.01</td>
<td>47.93</td>
</tr>
<tr>
<td>Self-forming</td>
<td>52.7</td>
<td>54.39</td>
<td>55.44</td>
</tr>
</tbody>
</table>

Figure 6 | (a) Total phosphate and (b) citrate removal efficiency.

Figure 7 | Flux recovery ratio after backwashing by distilled water.

Figure 8 | Comparison of flux recovery ratio (FRR amount) of pre-coated and self-forming DMs.
surface and so can lead to the limitation of adhesion between wastewater particles and the membrane surface. In the pre-coated type during the membrane backwashing process, the access of cleaning agents and wastewater particles increased, so foulant was easily removed and consequently FRR was improved. In the comparison between cleaning agents, it was evident that SDS, hot water, and distilled water were the better agents for backwashing, respectively. This result can be attributed to the SDS structure. This agent has hydrophilic and hydrophobic terminations. After backwashing, micelles were formed. These micelles can solubilize, and so help to remove the foulants deposited on dynamic membranes. After SDS, the hot water (50 °C) was a good cleaning agent. For example, the FRR of the self-forming membrane after hot water (50 °C) backwash increased by 3.57% compared with after DI backwash. This suggests that hot water backwash can be implemented to remove the oil adhered weakly on the membrane which could more easily be washed off than with DI.

**Photolysis performance of dynamic membranes**

Figures S3 and S4 (Supplement) and Table 3 demonstrate the flux recovery rate, total phosphate–citrate removal efficiency, and COD rejection after UV irradiation, respectively. It is apparent that UV irradiation can enhance membrane cleaning, and improve the antifouling performance and also removal efficiency. According to the obtained results, the neat membrane showed a little improvement after UV, which can be attributed to the degradation of organic compounds by

![Flux recovery ratio after backwashing by SDS, hot water (50 °C) and distilled water.](image)

**Table 3**  COD removal (%) after UV

<table>
<thead>
<tr>
<th>Support (neat membrane)</th>
<th>Cycle_1</th>
<th>Cycle_2</th>
<th>Cycle_3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre-coated</td>
<td>45.5</td>
<td>46.98</td>
<td>48.81</td>
</tr>
<tr>
<td>Self-forming</td>
<td>55.64</td>
<td>57.04</td>
<td>59.38</td>
</tr>
</tbody>
</table>
UV light and, thus, the diminishing of pollution degree and degrading of wastewater particles after the application of UV.

It was observed that dynamic membranes which contained ZnO nanoparticles, under UV, had better results in comparison with the neat membrane, which may propose benefits for photocatalytic reactions. The obtained results can be ascribed to photocatalytic activation of ZnO under UV that led to the degradation of organic compounds in wastewater. The photocatalyst activation principle is the absorption of UV radiation with higher energy than the energy of the bandgap. UV irradiation creates a hole in the valence band and an electron in the conduction band. By irradiation, electron–hole pairs diffuse out from photocatalyst surfaces and can interact separately with other molecules. The positive hole in the valence band is able to oxidize a water molecule to a hydroxyl radical. The oxidation of organic contaminants seems to be mediated by a series of reactions initiated by hydroxyl radicals on the surface. The negative electron in the conduction band can reduce molecular oxygen to superoxide anions and create •O2− radicals. The organic pollutants in wastewater were decomposed by hydroxyl radicals and mineralized to CO2 and H2O.

\[ \text{ZnO} + h\nu \rightarrow e^- \text{ in CB} + h^+ \text{ in VB} \]  
(6)

\[ h^+ \text{ in VB} + H_2O \rightarrow H^+ + \cdot OH \]  
(7)

\[ h^+ \text{ in VB} + OH^- \rightarrow \cdot OH \]  
(8)

\[ e^- \text{ in CB} + O_2 \rightarrow O_2^\cdot \]  
(9)

\[ O_2^- + H_2O \rightarrow 2OH_2 \]  
(10)

\[ \text{OH} + \text{organic pollutants in wastewater} \rightarrow \text{CO}_2 + \text{H}_2\text{O} \]  
(11)

In the third filtration cycle, the pre-coated dynamic membrane without UV showed FRR (backwash by SDS), total phosphate and citrate removal efficiencies and COD rejection results of 91.8%, 91.2%, 91.7%, and 47.93%, respectively, while after use of UV these parameters were 92.2%, 92.3%, 92.9%, and 48.81%. The low enhancement in the pre-coated composite was confirmed by the UV irradiation procedure. These small changes occurred since during dynamic irradiation particles (PAC-ZnO) were not in contact with wastewater particles. Hence, the oxidizing ability of the organic components by ZnO was limited. Additionally, in the preparation procedure of the pre-coated type, first the PAC-ZnO suspension was irradiated separately, and then wastewater was fed. So, the pre-coated model did not show any considerable changes.

In particular, improvements were more evident in the self-forming case, which can be attributed to the degradation of organic compounds by UV and the ZnO exit electrons simultaneously.

In the third filtration cycle, the self-forming dynamic membrane without UV treatment showed FRR (backwash by SDS), total phosphate and citrate removal efficiencies and COD rejection results of 77.9%, 94.3%, 95.6%, and 55.44%, respectively, while after use of the UV these parameters were 82.4%, 96.5%, 98%, and 59.38%.

**CONCLUSIONS**

Neat polyester with regard to its higher resistance was studied for cheese wastewater treatment. According to the results, total phosphate–citrate removal efficiency and COD rejection were desirable processes as the pre-treatment step. However, neat polyester fouled sharply and had low flux. To address the issue, a dynamic membrane was prepared via a low-cost method and materials. To fabricate the support membrane, chitosan was used for polyester modification due to its anti-fouling character and high hydrophilicity. In what followed, two types of dynamic membranes were studied (pre-coated and self-forming). The data collected in the present work suggested that the pre-coated dynamic membrane had better performance in permeation flux and flux recovery ratio, which can mitigate the fouling of dynamic membranes. The self forming type promoted COD and total phosphate and citrate removal efficiency, which can be ascribed to the formation of a dynamic compact layer on the support.

By substitution of the cleaning agent from deionized water and warm water to SDS as a cleaning agent for fouled membrane backwashing, the cleaning efficiency (FRR) was enhanced, because this agent has hydrophilic and hydrophobic terminations. Additionally, use of the UV irradiation improved all parameters due to degradation of organic compounds by UV, and the ZnO exit electrons simultaneously.

**SUPPLEMENTARY MATERIAL**

The Supplementary Material for this paper is available online at https://dx.doi.org/10.2166/wst.2020.044.
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