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The Application of Integrated System in Dairy Wastewater Treatment

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1. Introduction

The dairy industry is generally considered to be the largest source of food processing wastewater in many countries. This sector has one of the highest water consumptions level and is one of the biggest producers of effluent per unit of production (Tikariha & Omprakash 2014). The dairy industry produces large quantities of wastewater often in the amount of thousand cubic meters per day. The wastewater from the dairy processing industry is characterized by: high concentrations of organic material (proteins, carbohydrates and lipids), high biological oxygen demand (BOD) and chemical oxygen demand (COD), high nitrogen concentrations and suspended solids (Wang et al. 2006). This all poses treat of envirnomanetal pollution (Banu et al. 2008). Several literature data suggest that appropriate treating of dairy wastewater are ecological treatment systems (aerobic and anaerobic reactors, clarifiers and wetlands) or physical-chemical treatment systems (membranes technology or an advanced oxidation proces-AOP) (Salazar et al. 2013). The AOPs are physical and chemical processes that involve the generation of transient species with a high oxidizing power, pointing out the hydroxyl radical (•OH) among others. This radical has a high oxidizing capacity and can be generated by photochemical substances, mineralizing organic pollutants in CO_2 and H_2O. (Salazar et al. 2013). Many semiconductors like TiO_2, ZnO, CdS, etc., have been used as photocatalysts. These processes have limitations which can potentially affect degradation efficiency through changing the pH, rapid organic-load variations, and also the ef-

fluent'sc physicochemical behawior. The efficiency of a photocatalytic system is also related to the form of TiO_2 and ZnO nanoparticle catalysts used as immobilized on surface or colloidal suspension (Mondal & Sharma IITK 2014, Chantes et al. 2015).

In the research, it was demonstrated which of the applied photocatalysts more effectively contributed to the oxidation of pollutants contained in dairy wastewater. The influence of both photocatalysts on the change in the efficiency and permeability of the assembly membrane was also evaluated.

2. Material and methods

The study examined industrial wastewater from one of the biggest dairy factories located in the Świętokrzyskie Voivodeship in Poland. The factory processes 400 000 litres of milk per day. The factory is equipped in its own wastewater treatment plant with capacity of up to 800 m^3/d. The dairy wastewater was characterized by the alkaline reaction (pH 8.2). The value of COD used for the examination of wastewater was on average 4020 mg/dm^3, with their mean value of BOD of 1750 mg/dm^3. High contents of TOC and total w nitrogen (1200 mg/dm^3 and 290 mg/dm^3, respectively) were also observed.

The process of photocatalysis was conducted in a 250 cm^3 photoreactor. The central part of the photoreactor contains a submersible medium-pressure UV-lamp with power output of 45 W, which emitted the waves with wavelength of 365 nm. The content of the reactor was mixed by supplying air from the bottom of the reactor and using the magnetic mixer (3000 rpm). The photocatalysts used in the study were titanium dioxide (TiO_2) and zinc oxide (ZnO). Both photocatalysts were in the form of nanopowders with particles smaller than 100 nm. Nanopowders were the materials of the puriss class of 99-100.5%, manufactured by Sigma-Aldrich (Germany).

Ultrafiltration posttreatment of the dairy wastewater was conducted using the research stand Millipore CDS-10. The system was operated in the dead-end one-directional arrangement at the pressure of 0.1 MPa. The membrane installation was composed of the ultrafiltration cell containing a flat membrane with active surface of 0.045 m^2. The cell was connected through a reducer with a gas cylinder (with oxygen). The

reducer allowed for adjustment of gas pressure in the range of 0.1 to 0.5 MPa. The study used hydrophilic ultrafiltration membrane made of polyethersulfone (PES) with cut-off of 50 kDa.

Dairy wastewater treatment was performed using two technological systems that combined photocatalysis with ultrafiltration (I – TiO_2+UF and II – ZnO+UF). Before the proper photocatalysis process, a photolysis process was conducted in order to determine the most beneficial time of irradiation and the reaction of the dairy wastewater subjected to the photooxidation. Raw wastewater (pH 8.2) and initially acidified (to the level of pH 3.5) wastewater was used in the process. After determination of the above mentioned most beneficial conditions of the process, photocatalysis was performed using the titanium dioxide and zinc oxide. The dose of titanium dioxide was changed from 1 to 40 g/dm^3, whereas the content of zinc oxide ranged from 1 to 6 g/dm^3. Evaluation of the efficiency of photocatalysis was made every 15 minutes and the treated wastewater was centrifuged in the medical centrifuge by 10 minutes (10,000 rpm) and next filtered using the soft filter. This filtration was connected with the necessity of initial removal of photocatalyst from the treated wastewater. Since the photocatalysts (TiO_2 and ZnO) were supplied to the photoreactor in the form of a suspension, the membrane in the next reactor represented an efficient barrier for their particles.

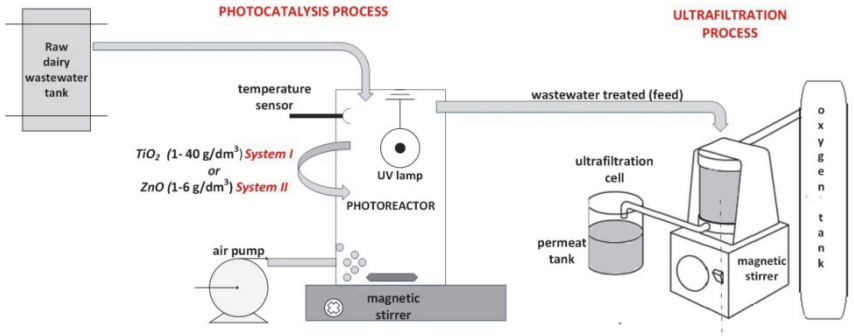
The efficiency of the unit processes used in the study was controlled based on the changes in the levels of COD, TOC and total nitrogen. The HACH DR/4000 spectrophotometer was used to perform the measurements of chemical oxygen demand (COD). BOD was determined using the respirometric method by means of the measurement set OXI Top WTW. Kiper TOC 10C Analyser PX-120 with AS40-Dione3.11 autosampler was used for the determination of total organic carbon (TOC) and total nitrogen (TN). CP-401/CP-40 ph-meter was used to measure pH during the AOP process.

The effectiveness of the membranes was assessed based on surfactant retention coefficient and permeate relative flux (Table 1).

Table. 1. Parameters for membrane process efficiency evaluation (Klimonda & Kowalska 2018)
Tabela 1. Parametry do oceny efektywności procesu membranowego (Klimonda i Kowalska 2018)

Parameter	Unit	Equation
Permeate flux	m^3/m^2s	$J = \frac{V}{t \cdot A}$
Retention coefficient	%	$R\frac{C_f - C_p}{C_f} \cdot 100$
Relative flux	%	$RF = \frac{J}{J_0} \cdot 100$

The study design and methodology of determination is presented in Fig. 1.



Rys.1. Schemat oczyszczania ścieków mleczarskich w procesie fotokatalizy
Fig.1. The scheme of dairy wastewater treatment in the photocatalysis proces

4. Results and discussion

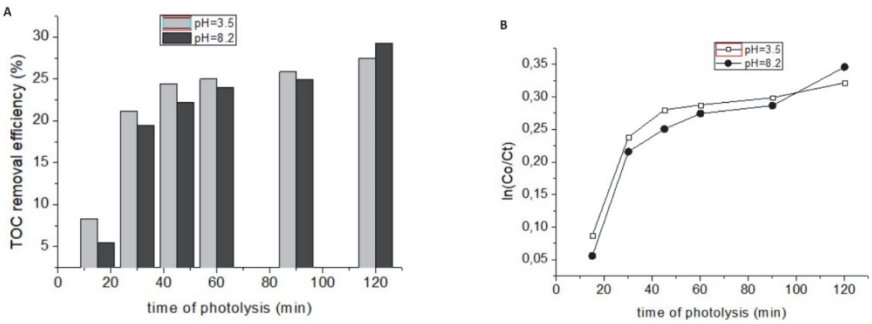
4.1. Dairy wastewater treatment using the photolysis process

The first step of the experiment examined the effect of initial value of pH of the wastewater subjected to photooxidation on the degree of degradation of TOC. Furthermore, the effect of the duration of the photolysis process on the value of TOC index in the treated wastewater

was determined. If the photolysis was performed for the initially acidified wastewater (pH 3.5), the degree of removal ranged from 8% (15 minutes of the process) to 25% (from 45 min to 120 min of the process) For the initially acidified wastewater TOC after 120 minutes of the process reduced from 1200 mg/dm^3 to 870 mg/dm^3.

It was found that the rate of TOC removal from the alkaline wastewater (pH 8.2) was, until 90 minutes, by 4% lower on average compared to the dairy wastewater whose reaction was initially corrected. However, after 120 minutes of photooxidation, TOC removal from alkaline wastewater reached a higher level (29%). These changes are illustrated in Fig. 2a.

It was observed that elongation of the process to over 60 minutes did not significantly improve the effectiveness of oxidation of contaminants from the wastewater. At this stage, changes in the TOC removal rate were also analysed. Also in this case, the TOC degradation rate was insignificantly higher for the initially acidified wastewater. For certain durations (from 5 min to 30 min), the TOC degradation process was in both cases the first order reaction which was next transformed into a quasi-static reaction (Fig. 2b).



Rys. 2. Wpływ pH w procesie fotolizy na stopień usunięcia OWO (a) i lnC /C_o (b)
Fig. 2. Effect of pH on the photolysis proces in of removal TOC (a) and lnC/C_o (b)

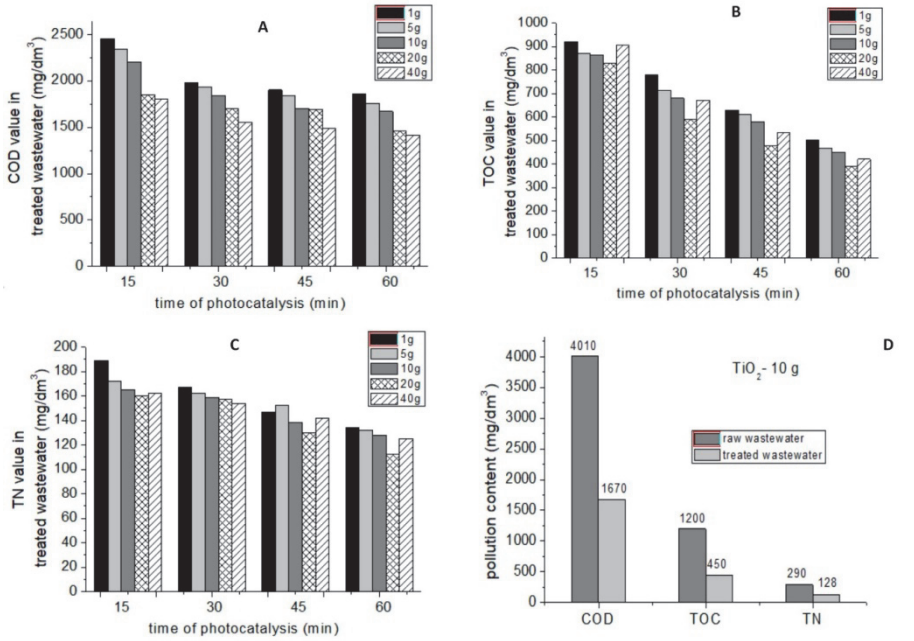
A constant reaction rate was determined based on the Langmuir–Hinshelwood formula (Kępa 2012). Analysis of the obtained results of constant TOC degradation rates revealed that oxidation of organic compounds contained in dairy wastewater occurs the fastest within the first 15 minutes. The value of k_{RTOC} for the wastewater with pH = 3.5 and

pH = 8.2 in the 15th minute of the process was 0.0079 min^{-1} and 0.0070 min^{-1}, respectively. In the 90th minute of the process, the values of these coefficients were substantially reduced, reaching 0.0026 min^{-1} (pH – 3.5) and 0.0028 min^{-1} (pH – 8.2), respectively. It was found that at the next stage of the examination, the dairy sewage would not be initially acidified and the photocatalysis process will be reduced to 60 minutes.

4.2. The use of titanium dioxide for dairy wastewater treatment

This stage of the examinations evaluated the effect of the amount of the titanium dioxide added to the reaction chamber on the degree of removal of contaminants from the dairy wastewater. Its dose was changed from 1 g/dm^3 to 40 g/dm^3. The weakest effects in oxidation of contaminants determined as COD were observed if smaller doses of the photocatalyst (1 g/dm^3 and 5 g/dm^3) were used. The 60 minute duration of the photocatalytic oxidation of dairy wastewater led to the reduction in contaminants determined as COD at the doses of 1 g/dm^3 and 5 g/dm^3 by 53% (1860 mg/dm^3) and 56% (1770 mg/dm^3), respectively. When the highest dose was used, i.e. 20 g/dm^3 and 40 g/dm^3, the COD removal rate after the same time of photocatalytic oxidation (60 min) was 63.5% (1460 mg/dm^3) and 64.8% (1410 mg/dm^3), respectively. In the case of TOC, it was found that its removal rate is more affected by the duration of the photocatalysis rather than the level of the photocatalyst dose. The TOC removal during photocatalysis increased on average from 23% (15 min) to 67% (60 min).

Oxidation of total nitrogen contained in the wastewater during photocatalysis occurred analogously to COD and TOC. After completion of the process (60 min), its level in the treated dairy wastewater with addition of 20 g/dm^3 and 40 g/dm^3 TiO_2 was 112 g/dm^3 (61%) and 125 g/dm^3 (57%), respectively. It was found that for all analysed doses of TiO_2, extension of the process time to over 30 minutes does not substantially impact on the increase in oxidation of the contaminants contained in the wastewater. The changes were presented in Figs. 3a, 3b and 3c. It was found that the best solution is photocatalysis supported by TiO_2 if its dose is 10 g/dm^3, with values of COD, TOC and total nitrogen in the treated wastewater after a 60 min process reaching 1,670 mg/dm^3, 450 mg/dm^3 and 128 mg/dm^3, respectively (Fig. 3d).



Rys. 3. Wpływ dawki TiO_2 na stopień usuwania ChZT (a), OWO (b), azotu ogólnego (c) oraz na jakość ścieków oczyszczonych przy optymalnej jego dawce (d)
Fig. 3. Effect of the TiO_2 dose on the removal efficiency COD (a), TOC (b), TN (c) and the quality of treated wastewater at the optimal dose (d)

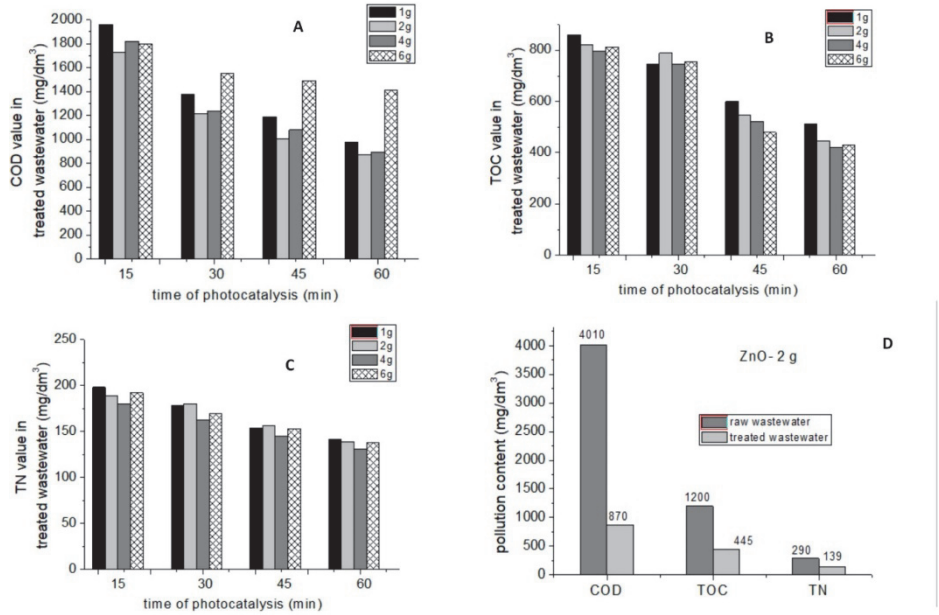
4.3. The use of zinc oxide for dairy wastewater treatment

The second photocatalyst used for oxidation of the contaminants contained in dairy wastewater was zinc oxide (ZnO). The doses were lower than in the case of TiO_2, and ranged from 1 g/dm^3 to 6 g/dm^3. It was found that the process of photocatalytic oxidation of the contaminants determined as COD occurred on average by 20% more effectively compared to the process conducted with titanium dioxide. In the case of the application of lower doses of ZnO i.e. 2 g/dm^3 and 4 g/dm^3, the degree of COD removal after 60 minutes of the process was 78.2% and 77.8%, respectively. It was also observed that the increase in the dose from 4 g/dm^3 to 6 g/dm^3 led to the reduction in the COD removal rate by 12% on average for all the analysed times (Fig. 4a). The 60 minute duration of the photocatalytic oxidation of dairy wastewater to the reduction

in contaminants determined as TOC at the smallest dose (1 g/dm^3) and the biggest dose (5 g/dm^3), by 57% (512 mg/dm^3) and 64% (430 mg/dm^3), respectively. These changes are illustrated in Fig. 4b.

In the case of TOC, it was found that its removal rate is more affected by the duration of the photocatalysis rather than the level of the photocatalyst dose. The TOC removal during photocatalysis increased on average from 28% (15 min) to 65% (60 min).

The efficiency of total nitrogen oxidation from the wastewater in the process of photocatalysis using the ZnO was closer to the effects obtained when the titanium dioxide was used (Fig. 4c). After completion of the process (60 min), its content in the treated wastewater with addition of 1g/dm^3 and 6 g/dm^3 ZnO was 141 g/dm^3 (51.3%) and 138 g/dm^3 (52.4%), respectively.



Rys.4. Wpływ dawki ZnO na stopień usuwania ChZT (a), OWO (b), azotu ogólnego (c) oraz na jakość ścieków oczyszczonych przy optymalnej jego dawce (d)

Fig.4. Effect of the ZnO dose on the removal efficiency COD (a), TOC (b), TN (c) and the quality of treated wastewater at optimal dose (d)

It was observed that for all analysed doses of ZnO, the extension of the process time to over 45 minutes does not substantially impact on the increase in oxidation of the contaminants contained in the wastewater. It was concluded that the most favourable option of the photocatalysis process is when the dose is 2 g/dm^3. The value of COD, TOC and total nitrogen in the treated dairy wastewater after 60 minutes of the process reached the value of 870 mg/dm^3, 445 mg/dm^3 and 139 mg/dm^3 (Fig. 4d).

There is not much research on the use of ZnO in the form of a nanomaterial for the treatment of wastewater from the food industry. It is often immobilized on the walls of photoreactors. An example of this may be research (Samanamud et al. in. 2012) where used ZnO was immobilized on a metal plate (coating thickness ZnO 100 μm). Removal efficiency for TOC was lower (31.7%) at pH 8.0.

Action ZnO may also be intensified by the addition of H_2O_2 to the photoreactor. As shown by the study, the use of 1 g/dm^3 ZnO and 30 mL H_2O_2 contributes to a significant removal of COD and total and thermotolerant coliforms from the wastewater (Abreu et al. 2013).

4.4. Ultrafiltration treatment of dairy wastewater

Combining the membrane process with photocatalysis along with improving the quality of treated wastewater is the ability to effectively separate the photocatalyst after the end of the degradation process. The separated photocatalyst can be used again (Zmudziński 2012, Moza et al. 2005, Mozia 2010).

Before the proper process of dairy wastewater treatment in the ultrafiltration process, the transport properties of the membrane used were determined (Bodzek et al. 1997). For the highest pressure used, i.e. 0.25 MPa, the ultrafiltration membrane was characterized by nearly 3 times higher ($24 \cdot 10^{-5}$ m^3/m^2·s) volumetric water stream compared with the smallest pressure (0.1 MPa- $8.8 \cdot 10^{-5}$ m^3/m^2·s).

After determination of the transport properties of the membrane, the filtration of the initially treated system I and system II was performed. Process of ultrafiltration (UF) was conducted at the pressure of 0.1 MPa. It was found that regardless of the type of wastewater treated (system I or system II), the efficiency of the membrane gradually decreased with the duration of the ultrafiltration (UF) process. The cause of this phenomenon was the deposition of contaminants in the membrane

pores and formation of the filtration cake, which resulted in blocking the pores and a decline in the flux of permeate (Bodzek et al. 1997).

During the treatment of the wastewater initially treated during the photocatalysis, higher volumetric flux of permeate was obtained when the wastewater with titanium dioxide were supplied to the titanium dioxide (system I). After 5 minutes of the UF process, the flux of permeate was by 16% lower compared to the flux of deionized water. If the dairy wastewater was initially treated using ZnO (system II), a 30% reduction was observed after the same time. After 30 minutes, the flux of permeates in both cases were stabilized and reached the values of $4.6 \cdot 10^{-5}$ $m^3/m^2 \cdot s$ (after TiO_2 10 g/dm^3) and $4.1 \cdot 10^{-5}$ $m^3/m^2 \cdot s$ (after ZnO; 2 g/dm^3).

Based on the determined initial values of the volumetric water flux and medium values of volumetric permeate flux, the relative permeability of membranes was determined for both types of feed material. It turned out that relative permeability of membranes after ultrafiltration treatment of initially treated wastewater using TiO_2 was nearly by 14% (0.65) higher compared to their efficiency when treatment concerned the wastewater with content of ZnO (0.56).

At this stage of examinations a change in the content of organic compounds was determined in filtrated samples (permeates) depending on the duration of the process, i.e. retention coefficient (Bodzek et al. 1997). As expected, the ultrafiltration process ensured a high degree of removal of the contaminants from the initially treated wastewater in both systems. It was found that the ultrafiltration process in the case of the feed material with TiO_2 led to the reduction in COD, TOC and total nitrogen by 78% (370 mg/dm^3), 72% (126 mg/dm^3) and 40% (80 mg/dm^3), respectively. Slightly lower degree of retention and wastewater with higher quality was obtained when the feed material contained ZnO. Removal rates for COD, TOC and total nitrogen were 68% (280 mg/dm^3), 66% (143 mg/dm^3) and 42% (76 mg/dm^3), respectively.

5. Conclusions

The results obtained in the study led to the following conclusions:

- Elongation of the duration of photocatalysis with TiO_2 and ZnO to over 30 min and 45 min, respectively, does not have a substantial effect on the increase in the degree of oxidation of the contaminants contained in the dairy wastewatr.

- In the case of treatment of dairy wastewater with TiO_2, the photocatalysis occurred most beneficially for its dose of 10 g/dm^3. Removal rates for COD, TOC and total nitrogen were 58% (1670 mg/dm^3), 62% (450 mg/dm^3) and 56% (128 mg/dm^3), respectively.
- Replacing titanium dioxide with zinc oxide (ZnO – 2 g/dm^3) in the photocatalysis allowed for obtaining higher degrees of removal of contaminants determined as COD, TOC and total nitrogen to the level of 77.8% (870 mg/dm^3), 62% (445 mg/dm^3) and 52% (139 mg/dm^3), respectively.
- It was found that relative permeability of membranes after ultrafiltration treatment of initially treated dairy wastewater using TiO_2 was nearly by 14% (0.65) higher compared to their efficiency when treatment concerned the wastewater e with content of ZnO (0.56).
- Furthermore, the permeate obtained during treatment of wastewater using the system II (with ZnO) was better. Degree of retention of the contaminants COD, TOC and total nitrogen were 68% (280 mg/dm^3), 66% (143 mg/dm^3) and 42% (76 mg/dm^3), respectively.

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Zastosowanie zintegrowanego systemu w oczyszczaniu ścieków mleczarskich

Streszczenie

W pracy zaprezentowano wyniki badań jakie otrzymano podczas oczyszczania ścieków mleczarskich w fotoreaktorze membranowy w którym sekwencyjnie skojarzono procesy fotokatalizę z niskociśnieniowym procesem

membranowymi. Celem badań było określenie skuteczności degradacji zanieczyszczeń znajdujących się w tego rodzaju wodach odpadowych w samodzielnie prowadzonym procesie fotokatalizy jak również w układzie kojarzącym go z procesem ultrafiltracji. Przeprowadzono szereg eksperymentów w celu ustalenia najkorzystniejszych warunków prowadzenia procesu fotokatalizy tj. dawka zastosowanych fotokatalizatorów (TiO_2 i ZnO), czas prowadzenia procesu oraz wartość pH ścieków poddawanych utlenianiu. Dawkę ditlenku tytanu zmieniano w zakresie od 1 do 40 g/dm^3 a tlenku cynku od 1 do 6 g/dm^3. Na podstawie uzyskanych wyników badań stwierdzono, że wydłużanie czasu naświetlania powyżej 30 minut (TiO_2) oraz powyżej 45 min (ZnO) w procesie fotokatalizy nie wpływa na zwiększanie usunięcia zanieczyszczeń z oczyszczanych ścieków mleczarskich. Wykazano również, że zwiększanie stosowanych dawek obu fotokatalizatorów nie skutkuje wzrostu efektywności ich oczyszczania. W przypadku oczyszczania ścieków mleczarskich z TiO_2 proces fotokatalizy przebiegał najkorzystniej jego dawce wynoszącej 10 g/dm^3. Stopień usunięcia ChZT, OWO i azotu ogólnego wynosił odpowiednio 58% (1670 mg/dm^3), 62% (450 mg/dm^3) i 56% (128 mg/dm^3). Zastąpienie ditlenku tytanu tlenkiem cynku (ZnO – 2g/dm^3) w procesie fotokatalizy pozwoliło na uzyskanie wyższych stopni usunięcia zanieczyszczeń oznaczanych jako ChZT, OWO i azotu ogólnego odpowiednio do poziomu 77.8% (870 mg/dm^3), 62% (445 mg/dm^3) i 52% (139 mg/dm^3). Z uwagi na fakt, że oba dawkowano do fotoreaktora w formie zawiesiny to znajdująca się w kolejnym reaktorze membrana była skuteczną barierę dla ich cząstek. Zaobserwowano, że wyższy objętościowy strumień permeatu uzyskano w trakcie prowadzenia procesu niskociśnieniowej filtracji membranowej ścieków wstępnie podczyszczonych w procesie fotokatalizy z ditlenkiem tytanu ($4{,}6\cdot10^{-5}$ m^3/m^2·s – TiO_2 i $4{,}1\cdot10^{-5}$ m^3/m^2·s – ZnO). Stwierdzono że wykorzystany proces ultrafiltracji w przypadku nadawy z TiO_2 przyczynił się do obniżenia wartości wskaźników ChZT, OWO i azotu ogólnego odpowiednio o 78% (370 mg/dm^3), 72 % (126 mg/dm^3) i 40% (80 mg/dm^3). Nieznacznie lepszej jakości permeat otrzymano, gdy nadawa zawierała proszek ZnO. Stopień retencji zanieczyszczeń ChZT, OWO i azotu ogólnego wynosił odpowiednio 68% (280 mg/dm^3), 66 % (143 mg/dm^3) i 42% (76 mg/dm^3).

Abstract

The study presented the results of the examinations obtained during treatment of dairy wastewater in a membrane photoreactor where photocatalysis was sequentially combined with low-pressure membrane process. The aim of the study was to determine the effectiveness of degradation of the contaminants contained in such wastewater during photocatalysis and in the arrangement that combined photocatalysis with ultrafiltration.

Several experiments were performed in order to determine the most beneficial conditions of the photocatalysis process, e.g. the dose of the photocatalysts used (TiO_2 and ZnO), duration of the process and pH of wastewater subjected to oxidation. The dose of titanium dioxide was changed from 1 to 40 g/dm^3, whereas the content of zinc oxide ranged from 1 to 6 g/dm^3. The results obtained in the study showed that the extension of the irradiation time to over 30 minutes (TiO_2) and over 45 minutes (ZnO) during photocatalysis does not lead to increased removal of contaminants from the dairy wastewater. It was also demonstrated that the increase in the doses of both photocatalysts does not lead to the increase in the efficiency of their treatment. In the case of treatment of dairy wastwater with TiO_2, the photocatalysis occurred most effectively for its dose of 10 g/dm^3. Removal rates for COD, TOC and total nitrogen were 58% (1670 mg/dm^3), 62% (450 mg/dm^3) and 56% (128 mg/dm^3), respectively. Replacing titanium dioxide with zinc oxide (ZnO – 2 g/dm^3) in the photocatalysis process allowed for obtaining higher degrees of removal of contaminants determined as COD, TOC and total nitrogen to the level of 77.8% (870 mg/dm^3), 62% (445 mg/dm^3) and 52% (139 mg/dm^3), respectively. Since both photocatalysts were supplied to the photoreactor in the form of a suspension, the membrane in the next reactor represented an efficient barrier for their particles. It was observed that higher volumetric stream of the permeate was obtained during the process of low-pressure membrane filtration of sewage initially treated in the process of photocatalysis with titanium dioxide ($4.6 \cdot 10^{-5}$ m^3/m^2·s – TiO_2 and $4.1 \cdot 10^{-5}$ m^3/m^2·s – ZnO). It was found that the ultrafiltration process in the case of the feed material with TiO_2 led to the reduction in COD, TOC and total nitrogen by 78% (370 mg/dm^3), 72% (126 mg/dm^3) and 40% (80 mg/dm^3). Slightly better quality of permeate was obtained when the feed material contained ZnO powder. Degree of retention of the contaminants COD, TOC and total nitrogen were 68% (280 mg/dm^3), 66% (143 mg/dm^3) and 42% (76 mg/dm^3), respectively.

Słowa kluczowe:
ścieki mleczarskie, fotokataliza, TiO_2, ZnO, zaawansowane metody utleniania, ultrafiltracja

Keywords:
dairy wastewater, photocatalysis, TiO_2, ZnO, advanced oxidation process, ultrafiltration