IOŚ Inżynieria i Ochrona Środowiska 2018, 21(2), 163-170
Engineering and Protection of Environment
p-ISSN 1505-3695
e-ISSN 2391-7253
https://ios.is.pcz.pl/
DOI: 10.17512/ios.2018.2.4

Daniel POLAK, Maciej SZWAST
Warsaw University of Technology, Faculty of Chemical and Process Engineering
ul. L. Waryńskiego 1, 00-645 Warsaw
e-mail: 6012@pw.edu.pl

Preliminary Studies on Integrated Process of Microfiltration and Photocatalysis Used in Laundry Wastewater Treatment

Badania wstępne nad zintegrowanym procesem mikrofiltracji i fotokatalizy stosowanym do oczyszczania ścieków pralniczych

Industrial laundries generate wastewater in very large quantities. This wastewater is characterized by a high value of chemical oxygen demand (COD) and it contains substances suspended in the liquid that are responsible for wastewater turbidity. Furthermore, wastewater from industrial laundries contains several grams of detergents per litre of washing substances, mostly surfactants. Environmental and legal requirements force factories, including industrial laundries, to look for new and cost-effective methods of wastewater treatment. In the case of wastewater from industrial laundries, it is also important that a treatment method involves closing of the water loop in the plant and allows the plant to recover some of the detergents to be reused in another washing cycle. In order to address the problems related to wastewater from industrial laundries, the authors proposed an integrated process, which combined microfiltration and photocatalytic oxidation. This study presents preliminary results of the research carried out on actual wastewater generated in an industrial laundry. Results demonstrated the possibility of recovery of large amounts of purified water with detergents for the subsequent washing cycles. Thus, the integrated system of microfiltration and photocatalysis can be used in the technology of recovering water and detergents from industrial laundries. This technology enables to eliminate turbidity and remove some detergents associated with contamination caused by washing processes. Furthermore, purification degree is sufficient to reuse water in the pre-wash cycle.

Keywords: **integrated process, microfiltration, photocatalysis, laundry wastewater**

Introduction

Ineffective use of water resources, low degree of closing loops in industrial plants, inefficient and energy-intensive treatment processes and legal regulations lead to the development of new technologies of water recovery. Effectiveness of water treatment can be ensured by adjustment of the process to the type of the factory that produces specific and often toxic wastewater (dairy, tannery, laundry, galvanic and sugar refinery plants). Modern treatment processes should also involve closing the water loops in the plant.

A frequent problem is not only wastewater treatment but also recovery of specific valuable components which can be reused in the process. With respect to industrial laundry wastewater analysed in this study, such compounds include washing, complexing and bleaching agents, inhibitors, stabilizers and optical brighteners. The need for recovery of these substances is connected with both their negative impact on the environment (they lead to water frothing, make it difficult to transport oxygen in water, increase solubility of toxic substances) and reduction of their consumption in washing processes. It is worth emphasizing that production of surface active agents in Poland has increased in the last 20 years from 400,000 to 950,000 t [1].

No dedicated methods have been developed for the treatment of industrial laundry wastewater. Therefore, the need arises for developing methods which would allow for recovery of both water and part of surface active agents. An additional problem in such plants is a complex composition of the produced wastewater which, apart from detergents, also contains insoluble solids (fabric tissues, dirt from fabrics), salts such as nitrates (III) and (V), phosphates, fluorides, bromides and chlorides, bleaches such as sodium chlorate (I) and hydrogen peroxide, and softening agents [2]. This composition of the mixture is responsible for high chemical oxygen demand (COD), turbidity and alkaline reaction of wastewater. Due to this complex composition of the laundry wastewater and variability of this composition with time (depending on the type of fabrics washed, soil level, chosen washing program), conventional methods of wastewater treatment often fail to be effective or do not allow for recovery of detergents. Currently used techniques of wastewater treatment include biological methods, coagulation, foaming, oxidation, adsorption, electrochemical methods and ion exchange. A disadvantage of coagulation and adsorption is formation of waste streams which have to be removed at another stage of treatment or regeneration. Furthermore, biological methods often cannot be effectively used due to a substantial toxicity of wastewater [3]. High-efficiency technologies of laundry wastewater treatment include activated carbon adsorption and ozonation. However, their drawbacks include the lack of option of selective division of components. Furthermore components removed from water during these processes are collected at a surface of the activated carbon or oxidized, which prevents them from re-use [4, 5].

Integrated processes, composed of more than one unit process, are another option for laundry wastewater treatment. One of such solutions are membrane biological reactors (MBR) [6]. This technique allows for reduction in COD and BOD_5 (Biological Oxygen Demand) by over 90%. However this is also connected with removal of surface active agents at the level of 90%. Another integrated process proposed in this study is combination of membrane filtration with photocatalytic oxidation. The advantage of this method is absence of additional substances that represent a secondary load to the wastewater. Furthermore, the method allows for treatment of wastewater from substances coming from washed textiles while maintaining a high degree of washing agent retention.

This study presents preliminary research on an integrated process of microfiltration and photocatalysis used in the treatment of actual wastewater from an industrial laundry. The study is a part of the project aimed to partially close water loop in the laundry through returning the treated water from the main wash to the pre-wash cycle. An added value in the project is returning a part of washing agents with the treated water.

1. Integrated process

The study analysed an integrated process containing two unit processes: microfiltration and photocatalysis. The aim of the process is to recover water and surface-active agents from laundry wastewater contained in the permeate stream. Furthermore, in the case of e.g. materials from hospital or chemical plants, additional final treatment is needed in order to remove the organic compounds solved in water.

Microfiltration is the basic technology in membrane filtration. It allows for removing solids from liquids, with their dimensions over 0.1 μm. The driving force for the process is transmembrane pressure, which for this technique ranges from 1 to 5 bar. The mechanism of component separation is based on the sieving effect. Microfiltration allows for total removal of suspensions and reduction in COD and BOD depending on the type of inflowing compounds on the value of these indices.

Photocatalysis is numbered among advanced oxidation processes. Distribution of selected chemical compounds occurs on the surface of the photocatalyst irradiated at specific wavelength. Products of complete decomposition of organic compounds are CO_2 and H_2O. This reaction requires formation of electron-hole pairs in the structure of semiconductor that represents a photocatalyst. This state is generated by absorption of photons with specific energy [7, 8]. The method is particularly useful in decomposition of organic compounds such as colourants, pesticides, herbicides, pharmaceuticals, phenols, and humic and fulvic acids [9].

However, the use of each process separately for treatment of industrial laundry wastewater does not yield satisfactory results. The MF process allows for reduction in turbidity and COD. However, this level of purification is not sufficiently high, especially in terms of the content of organic compounds, which are connected with substances coming from washing textiles from hospitals and chemical or petrochemical factories. The decomposition of this type of pollutants can be performed using photocatalytic oxidation. High turbidity of wastewater without previous treatment (e.g. using microfiltration) reduces the efficiency of photocatalysis or it even prevents the process. Furthermore, contamination in the form of solids present in wastewater can lead to fouling of the photocatalyst. The boundary value of turbidity at which efficiency of the photocatalysis process declines rapidly is 30 NTU [10]. Efficiency of laundry wastewater treatment can be improved if microfiltration is followed by photocatalysis. This allows for obtaining a permeate with turbidity close to 0 with reduced COD, representing a feeding stream for the photocatalysis process. An additional benefit of this solution is the reduction in volume of the stream supplied at the second stage (the stream reduced by microfiltration retentate). The thickened retentate from the microfiltration process represents a waste in this technology that has to be handled. However, the volume of this waste stream is reduced with respect to the entire laundry wastewater stream.

2. Research apparatus and methodology

A system presented in Figure 1 was used for the experiments. At the first stage of the laundry wastewater treatment, the pump P1 pumps wastewater from a feed material container (Z1) through a membrane module (MF). The obtained retentate stream is returned to the feed material container and the filtrate is collected in the permeate container (Z2). This means a periodical process. The second stage of the process begins after obtaining the amount of permeate which allows for starting pump circulation (P2) of this permeate by the photocatalysis system (FC). Liquid circulates in the system for 8 hours, with time of liquid remaining in the reaction zone of 20 s on average. The temperature of all streams is maintained at the level of 25°C. Additional components of the apparatus are manometer of the feed material stream in the microfiltration process, terminals for receiving samples and control valves (not marked in the figure).

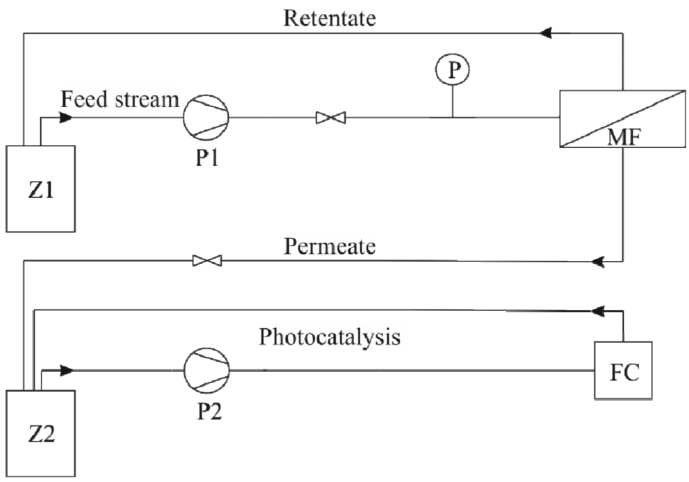

Fig. 1. Diagram of installation for the integrated process of microfiltration and photocatalysis

The feed material in the process of treatment was wastewater from the industrial laundry Hollywood S.A. in Sierpc, Poland. Value of physicochemical parameters that characterize raw wastewater are presented in Table 1.

It should be emphasized that composition of wastewater depends on the type of washed materials and washing program used. Nevertheless, the obtained sludge reach turbidity of over 50 NTU, conductivity of 1000 μS/cm, COD of at least 2000 mg O_2/dm^3, and are characterized by alkaline reaction.

Filtration examinations used a three-end capillary module designed by authors. A separation layer was represented by polypropylene membranes with external diameter of 2.6 mm and internal diameter of 1.8 mm and mean pore size of 0.25 µm [11]. Total surface area of membranes was 300 cm^2. Microfiltration process was performed at transmembrane pressure of 2 bars, with linear velocity of the wastewater stream of ca. 2 m/s. Mean volumetric flow rate for the obtained permeate was 0.06 dm^3/min.

Table 1. **Values of physicochemical parameters that characterize the wastewater examined in the study**

Parameter	Unit	Result
pH	–	9.9
BOD_5	mg O_2/dm^3	7
COD	mg O_2/dm^3	2191
Total nitrogen	mg/dm^3	31
Total suspended solids	mg/dm^3	98.5
Total phosphorus	mg/dm^3	4.2

Photocatalysis process was performed using the system designed by the authors. The semiconductor was titanium oxide(IV) (TiO_2) in the form of plates with total surface of 200 cm^2. The photocatalyst plates were manufactured using the method of compression and sintering of titanium oxide(IV). The plates with dimensions 5 cm x 5 cm x 1 cm and porosity of 45% were obtained. The plates were located on the reactor bottom. The wastewater stream flowing through the plates was irradiated from the top with UV-C diodes. Each of 200 diodes had luminous intensity of 400 mcd. Distance between diodes and catalyst surface was ca. 3 mm. The wastewater stream was recirculated through the reactor for 8 hours.

The following parameters were examined after catalysis in order to characterize the streams of feed material, permeate and product: conductivity, turbidity, COD, total nitrogen concentration and surface tension of the liquid. The measurement of surface tension of water represented the parameter that determined content of surfactants in the analysed streams [12]. Hanna Instruments measurement devices were used to measure conductivity and pH, Nanocolor cuvette tests and Thermo-Gensys10uv spectrophotometer - to measure COD and total nitrogen concentration, and Lovibond meter was employed to evaluate turbidity. Furthermore, surface tension was examined by means of an OCA 25 Dataphysics goniometer using the pendant drop method.

3. Results and discussion

Table 2 presents the results obtained for the feed material, permeate and product after photocatalysis.

Table 2. **Physical parameters of individual process streams**

Parameter	Unit	Stream		
		Feed material	Permeate	Product after photocatalysis
Conductivity	μS/cm	1050	1024	1030
pH	–	9.9	9.8	9.3
Turbidity	NTU	71.3	0	0
COD	mg/dm^3	2191	1764	1104
Total nitrogen	mg/dm^3	31	13	13
INF	mN/m	28.7	39.3	46.1

As expected, the microfiltration stage did not modify pH and wastewater conductivity. Furthermore, surface tension of the liquid examined was increased. The explanation for this observation is retention of a part of surface active agents by the membrane. Due to the dimensions of the particles of surface active agents and bigger size of pores in the membrane, only micelles of active surface agents could be retained, for example connected with solids. COD and total nitrogen concentration were reduced. This was caused by retention of solid contaminants on the membrane and part of surface active agents. Turbidity was substantially reduced. The transparent and colourless (subjective assessment) permeate was obtained after the microfiltration stage, whereas the feed material was noticeably yellow. The change in the colour could not be caused by removal of any colourants (due to the membrane pore size). This effect was most likely due to removal of the suspension and micelles of surface active agents which, if present in a solution, impact on its apparent colour.

A stream after this treatment, before the photocatalysis process, was tested under conditions of an industrial laundry. The treated stream (here permeate after microfiltration) was used for the pre-wash cycle. The quality of the product obtained during washing was especially analysed i.e. quality of the washed textiles. Assessment performed by the laundry indicates that returning the microfiltration permeate to the pre-wash cycle does not have a negative effect on the quality of the services provided by the shop. The recovery of a substantial part of the water stream to the process represents a technological accomplishment, which can be improved with the second stage i.e. photocatalysis.

The stage connected with photocatalysis allowed for further substantial reduction in COD. A decline in COD was attributable to the removal of organic compounds present in the liquid. These include in particular substances coming from washed textiles. However, these could also be surface active agents. This can be presumed based on the increase in water surface tension with no changes in pH, conductivity, and total nitrogen. Photocatalysis allows for final treatment of the permeate from organic compounds recovered from contaminated textiles. However, this also leads to the decomposition of part of recovered surface active agents, which, from the standpoint of the technology, represents an unfavourable phenomenon.

Conclusion

Initial results of the examinations indicate that the integrated system of microfiltration and photocatalysis can be successfully used in recovery of water and washing agents in industrial laundries. The integrated process allows for total removal of turbidity, reduction in COD and total nitrogen. Such water can be returned to the pre-wash cycle. This was confirmed by examinations of quality with respect to textile washed in industrial conditions. The method of laundry wastewater treatment proposed in the study also allows for recovery of part of surface active agents added to water during washing. At the current stage of research, the composition and accurate amount of the recovered washing agents were not analysed. However, the results lead to the conclusion that at the further stages of the development of this technology it will be possible to limit the amount of washing agents added to the washing bath during the pre-wash cycle.

Acknowledgements

The research was conducted within Polish-German collaboration and financed by the National Centre for Research and Development in the 2nd STAIR contest, the REWARD project.

References

[1] GUS, Rocznik statystyczny przemysłu, Zakład Wydawnictw Statystycznych, Warszawa 2017.

[2] Kowalska I., Zastosowanie polimerowych membran ultrafiltracyjnych do usuwania substancji powierzchniowo czynnych z roztworów wodnych, Rocznik Ochrona Środowiska 2008, 10, 593-604.

[3] Can O.T., Kobya M., Demirbas E., Bayramoglu M.,Treatment of the textile wastewater by combined electrocoagulation, Chemosphere 2006, 62, 2, 181-187.

[4] Ciabattia I., Cesaro F., Faralli L., Fatarella E., Tognotti F., Demonstration of a treatment system for purification and reuse of laundry wastewater, Desalination 2009, 245.1-3, 451-459.

[5] Šostar-Turk S., Petrinić I., Simonič M., Laundry wastewater treatment using coagulation and membrane filtration, Resources, Conservation and Recycling 2005, 44, 2, 185-196.

[6] Janus M., Mozia S., Bering S., Tarnowski K., Application of MBR technology for laundry wastewater treatment, Desalination and Water Treatment 2017, 64, 213-217.

[7] Bzdon S., Perkowski J., Szadkowska-Nicze M., Zastosowanie modyfikowanego TiO_2 w procesach fotokatalitycznego utleniania związków organicznych w roztworach wodnych, Prace Instytutu Elektrotechniki 2006, 228, 203-223.

[8] Bodzek M., Rajca M., Fotokataliza w oczyszczaniu i dezynfekcji wody. Część II, Usuwanie metali i naturalnych substancji organicznych, Technologia Wody 2013, 11(31), 18-30.

[9] Lazar M.A., Varghese S., Nair S.S., Photocatalytic water treatment by titanium dioxide: recent updates, Catalysts 2012, 2, 4, 572-601.

[10] Chong M.N., Jin B., Chow C.W.K., Saint C., Recent developments in photocatalytic water treatment technology: a review, Water Research 2010, 44, 10, 2997-3027.

[11] Szwast M., Fabianowski W., Gradoń L., Piątkiewicz W., Koncepcja wytwarzania membran kapilarnych oraz metody oceny ich jakości, Przemysł Chemiczny 2008, 87, 206-209.

[12] Rosen M.J., Kunjappu J.T., Surfactants and interfacial phenomena, John Wiley & Sons 2012.

Streszczenie

Ścieki w pralniach przemysłowych produkowane są w bardzo dużych ilościach. Ścieki te charakteryzują się dużą wartością parametru ChZT (Chemiczne Zapotrzebowanie Tlenu), zawierają substancje zawieszone w cieczy i odpowiedzialne za mętność tych ścieków. Ponadto w ściekach z pralni przemysłowych znajdują się znaczne ilości (do kilku gramów w litrze) środków piorących, w szczególności środków powierzchniowo czynnych. Wymagania środowiskowe i prawne zmuszają zakłady, w tym pralnie przemysłowe, do poszukiwania nowych, oszczędnych metod oczyszczania ścieków. W przypadku ścieków z pralni przemysłowych istotne jest również to, aby metoda oczyszczania uwzględniała zamknięcie obiegu wody w zakładzie i pozwalała na odzysk przynajmniej części detergentów i ich użycie w kolejnym cyklu prania. Do rozwiązania tak postawionego problemu wobec ścieków pochodzących z pralni przemysłowych autorzy zaproponowali zastosowanie zintegrowanego procesu, w skład którego wchodzi mikrofiltracja oraz utlenianie fotokatalityczne. Praca przedstawia wstępne wyniki badań prowadzonych na rzeczywistych ściekach powstałych w pralni przemysłowej. Wyniki wskazują na możliwość zawrócenia dużych ilości oczyszczonej wody wraz z detergentami do kolejnych cykli pralniczych. Zatem zintegrowany system złożony z procesu mikrofiltracji i fotokatalizy może zostać wykorzystywany w technologii odzyskiwania wody i detergentów z pralni przemysłowych. Technologia ta umożliwia całkowite usunięcie mętności oraz części detergentów związanych z zanieczyszczeniami z prania. Dodatkowo stopień oczyszczenia jest wystarczający, by ponownie wykorzystać wodę do prania wstępnego.

Słowa kluczowe: **proces zintegrowany, mikrofiltracja, fotokataliza, ścieki pralnicze**