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ELIMINATION OF PHARMACEUTICAL COMPOUNDS FROM MUNICIPAL WASTEWATER BY PHOTOCATALYSIS, MICROFILTRATION AND NANOFILTRATION

Abstract
The aim of the study was to develop an innovative method for the removal of selected pharmaceuticals from biologically treated municipal wastewater. The photocatalytic oxidation in the presence of TiO_2 was carried out in a reactor irradiated with a UV lamp (power 150 W) and two-stage membrane filtration was also applied. In the first stage the catalyst particles were separated using a microfiltration membrane. In the second stage the wastewater was polished in a semi-industrial installation equipped with a flow-through tubular membrane module with a filter surface area of 240 cm^2. The system combining photocatalysis and membrane filtration allowed for complete elimination of the pharmaceuticals.

Key words
pharmaceuticals, sequential system, photocatalysis, microfiltration, nanofiltration

Introduction

Nowadays, more and more attention is paid to organic micropollutants classified as a group of xenoestrogens present in the aquatic environment. This group contains phenols, non-biodegradable halogenated organic compounds, pesticides, polycyclic aromatic hydrocarbons, surfactants, endocrine disrupting compounds but also pharmaceutical compounds. The main sources of pharmaceuticals in the aquatic environment are the waste waters from the pharmaceutical and cosmetic industry but also municipal waste water [1]. The growing problem of the presence of pharmaceutically active compounds in the environment is especially related to increasing production and consumption (even excessive) of drugs, especially those available over the counter. The pharmaceuticals that are the most commonly detected in the influent and effluents of waste water treatment plants include non-steroidal analgesic and anti-inflammatory drugs, namely diclofenac, naproxen and ibuprofen, psychotropic drugs represented by carbamazepine, as well as antibiotics, beta-blockers, hormones, and chemotherapeutic agents [2,3].

Directive of the European Parliament and of the Council 2013/39/EU of 12 August 2013 [4] amending Directive 2000/60/EC and 2008/105 /EC as regards priority substances in the field of water policy ordered the preparation of a substance watch list for monitoring purposes throughout the Union, which, according to the decision of the Executive Commission (EU) 2015/495 of 20 March 2015 [5], apart from nine other organic micropollutants includes diclofenac. The data obtained during the monitoring will determine whether this compound will be classified as one of the priority substances. The presence of these substances in the environment has a negative effect on the overall balance of the whole ecosystem including also human health and life. For example, the exposition of rainbow trout and salmon trout to diclofenac at 0.5 to 1.0 μg/dm^3 concentration can result in the formation of negative changes in kidneys, liver and gills [6,7]. Ibuprofen concentration range from 1 to 1000 μg/dm^3 can lead to a limitation of photosynthetic water organisms growth [8]. Thus, it is necessary to ensure complete elimination of this type of compounds from the aquatic environment, and especially from the water bodies that may be the source of drinking water.

The waste water treatment systems based mainly on biological treatment processes do not guarantee an effective removal of pharmaceutical micropollutants because of their polar structure and low susceptibility to

biochemical degradation. The observed removal efficiencies are in the range of 40 to 60% depending on the type of a pharmaceutical compound [9]. The concentrations of these substances detected in effluents from municipal waste water treatment plants can therefore be as high as 2.6 μg/L [10]. Even such small concentrations of chemically active substances can exert detectable biological effects on living organisms depending on the type of the compounds [11]. The advanced oxidation processes, which include ozonation, Fenton reaction, ultraviolet radiation, heterogeneous photocatalysis using semiconductors as catalysts, sonolysis, radiolysis and a number of electrical and electrochemical methods that are an alternative to the commonly used biological waste water treatment methods [12]. Rapid and non-selective oxidation of organic compounds is possible due to the reactions occurring in the presence of highly reactive free radicals such as hydroxyl radicals ($OH^{\bullet}$) and $O_2^{\bullet}$, $OH^{\bullet}$ and $ROO^{\bullet}$ radicals [13]. The effect of hydroxylation or dehydroxylation of organic compounds should be their complete mineralization to CO_2 and H_2O [14]. However, the degradation by-products generated in these processes are often more toxic than the parent compound.

High-pressure membrane techniques such as nanofiltration and reverse osmosis have been also widely used for the removal of pharmaceutically active organic micropollutants [15,16]. The removal efficiency of micropollutants in membrane processes depends on several factors, which include hydrophobicity, charge and pore size of the membrane, but also the operating conditions such as temperature, flow rate and transmembrane pressure. The retention of the compounds is also dependent on their physicochemical properties, concentration and chemical composition and pH of the solution in which they are present [17]. However, it should be mentioned that membrane separation generates not only the treated stream of permeate but also the retentate, which is a hazardous waste due to the high concentration of micropollutants removed in the process.

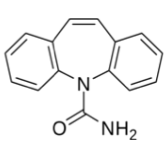
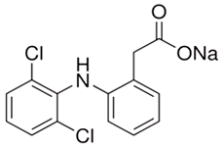
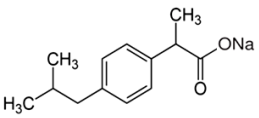
The integration of the advanced oxidation processes with the pressure membrane techniques offers satisfactory removal efficiency of organic micropollutants and their degradation by-products, which are formed not only in the treatment systems but also in the natural environment. Sequential systems based on the advanced oxidation processes can also be used to treat highly concentrated retentate stream, which is generated during the membrane filtration.

The aim of the study was to develop and evaluate a method allowing for the removal of pharmaceutical compounds from biologically treated municipal waste water. This treatment method was based on heterogeneous photocatalysis process and pressure membrane techniques. Specifically, the studied compounds included non-steroidal anti-inflammatory drugs (diclofenac and ibuprofen) and psychotropic drugs (carbamazepine).

Materials and methods

In this study, the secondary effluent from an activated sludge waste water treatment system was spiked with pharmaceutical compounds at a concentration of 1 mg/dm^3 and was subjected to the investigated treatment processes. Analytical standards of sodium salts of diclofenac (DCL) and ibuprofen (IBU), and carbamazepine (CBZ) (table 1) with a purity > 98% were purchased from Sigma-Aldrich (Poznan, Poland).

Table 1. The chemical characteristics of chosen pharmaceuticals

Compound			
Name	Carbamazepine	Diclofenac sodium salt	Ibuprofen sodium salt
Structural formula			
Characteristics			
Molecular formula	$C_{16}H_{12}N_2O$	$C_{14}H_{10}Cl_2NNaO_2$	$C_{13}H_{17}O_2Na$
Molecular weight, g/mol	236.3	318.13	228.26
Solubility in water, mg/L	17	50	100
pK_a	2.30	4.15	4.91
log K_{ow}	2.45	4.51	3.97

Source: own compilation on the basis of Bohdziewicz at al. 2015 [18]

The photocatalysis process was conducted in a 10-L batch laboratory reactor manufactured by Avantor Performance Materials Poland S.A. The reaction mixture was irradiated with a medium-pressure immersion lamp with a power of 150 W, which was introduced into the reactor. The lamp was placed in a cooling jacket, which provided a uniform temperature of the process 21±1°C. In order to provide sufficient amount of oxygen for the photocatalytic oxidation the reaction mixture was aerated with an aeration pump with a capacity of 4 dm^3 of air per minute. The reactor was placed on a magnetic stirrer, which prevented sedimentation of the catalyst particles. Commercial titanium dioxide purchased from Evonik Degussa GmbH was used as a catalyst. The dose of the catalyst was determined experimentally and fixed at 50 mgTiO_2/L. The contact time of the catalyst with the aqueous mixture prior to the irradiation process was 15 min. The irradiation was carried out continuously for 60 min. The separation of the catalyst from the reaction mixture was carried out using a membrane filtration system equipped with a 0.45 µm cellulose acetate microfiltration membrane from Millipore, which was connected to a vacuum pump from AGA Labor.

The nanofiltration process was conducted using a semi-industrial installation TMI 14 from J.A.M INOX Produkt, which was equipped with a tubular flow-through membrane module with a polyamide membrane AFC80 from PCI Membrane System Inc. (USA) with a filter surface area of 240 cm^2. The process of membrane filtration was performed until 20% of the feed was collected at a transmembrane pressure of 2 MPa.

The analytical monitoring of the investigated processes was performed using qualitative-quantitative analysis of pharmaceuticals by the GC-MS (EI) technique. In order to determine the analytes by chromatography, the studied pharmaceuticals were extracted by solid phase extraction (SPE) from 20 ml water samples using the SupelcleanTM ENVI-8 cartridges (volume 6 ml, 1.0 g bed weight) from Supelco. The filling of the cartridges prior to the extraction was washed with methanol (5 ml) and with deionized water (5 ml) at pH = 7. Next, water sample was added to the extraction cartridge. After the extraction the packing was dried for 5 min under vacuum. The extract was eluted with 3 ml of methanol and subjected to drying in a stream of nitrogen. Next, the extract was dissolved in methanol and subjected to chromatographic analysis. The analyses were performed using the Saturn 2100 T Varian (Warsaw, Poland) analytical system, which comprises a capillary gas chromatograph (GC) coupled on-line with an ion trap type mass spectrometer (MS). The eluent was separated in the SLBTM-5 ms column from the Supelco Company (Poznan, Poland) with dimensions of 30 m x 0.25 mm x 0.25 µm at the following temperature settings of the column oven: 80°C (8 min), 10°C/min up to 300°C (5 min). The other temperature parameters were as follows: injector - 230°C, ion trap - 180°C, ion source - 290°C. Helium was the carrier phase and the flow rate was 1.1 ml/min. Injections of the sample with a volume of 1µl were performed manually using a 10 µl Hamilton microsyringe. The qualitative GC-MS analysis was carried out using the selected ion monitoring mode (SIM) in the range of 70 to 400 m/z.

Results and discussion

In the first stage of the study, a single step membrane filtration was assessed for its efficiency in removing the selected pharmaceuticals from the treated waste water. The microfiltration process did not allow for the reduction of concentrations of the pharmaceuticals. However, in the case of nanofiltration the concentration of micropollutants decreased in the course of the process (Fig. 1). The retention coefficient for CBZ and DCL after 15 minutes of filtration was over 90%. The concentration of IBU decreased by 50% and it increased with increasing filtration time and increasing fouling intensity. This phenomenon consisted in deposition of organic and inorganic substances on the surface of the membrane. After 2h of the process the retention coefficient for all the three pharmaceuticals exceeded 91%.

However, it should be mentioned that membrane processes generate not only the treated stream of permeate but also the retentate, which contains elevated concentration of the compounds that are removed from the feed. Thus, the retentate is a toxic waste that requires further treatment and disposal steps.

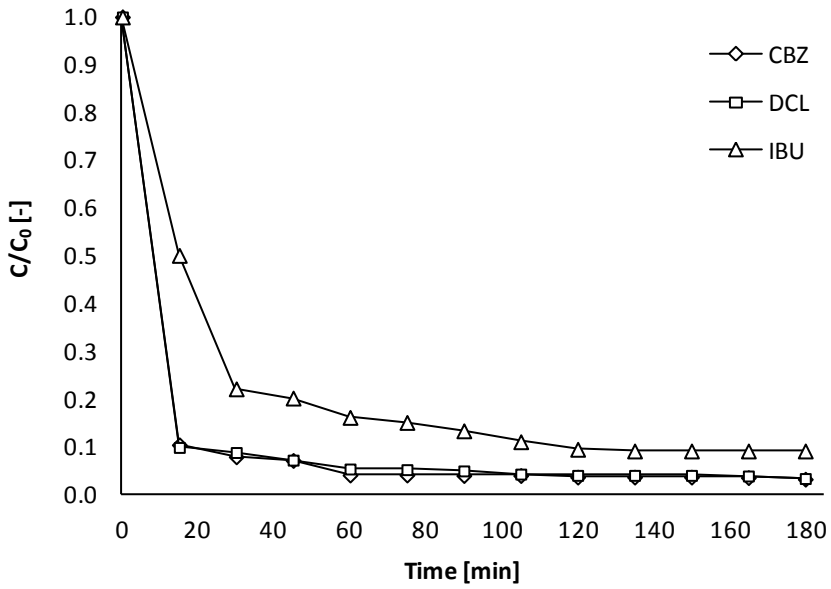


Fig. 1. Change of pharmaceuticals concentrations during the nanofiltration process
Source: own compilation

Figure 2 shows the removal efficiency of the pharmaceutical compounds during the process of heterogeneous photocatalysis. Time 0 corresponds to the reduction in the concentration of micropollutants achieved due to the sorption on the photocatalyst molecules. The degree of adsorption of the micropollutants on the surface of the catalyst particles has an impact on the efficiency of the photocatalysis process. Greater susceptibility for adsorption on the catalyst surface was observed for the compounds belonging to the group of non-steroidal analgesic and anti-inflammatory drugs - DCL and the IBU. This is due to increased hydrophobicity of these drugs (Table 1) compared to the psychotropic drug. Different degree of adsorption of the studied compounds can also predict the efficiency of their photocatalytic decomposition.

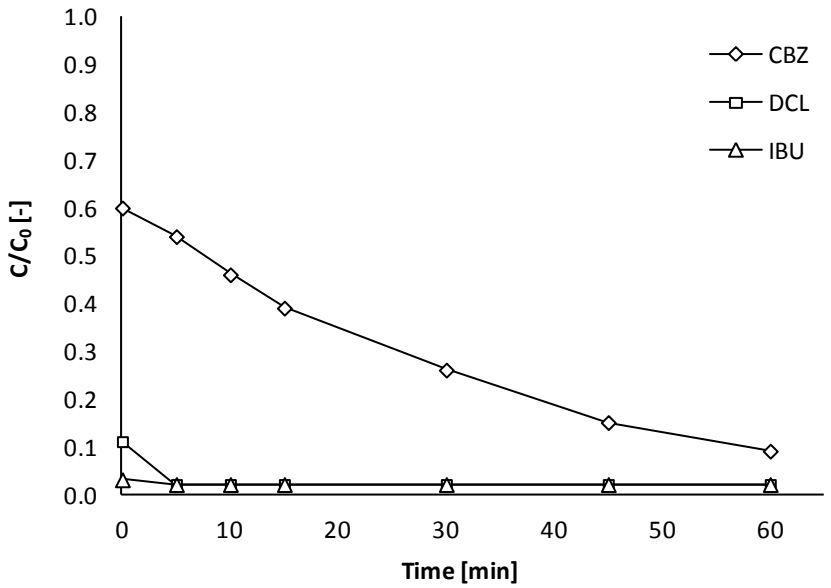


Fig. 2. Change of pharmaceuticals concentrations during the photocatalysis process
Source: own compilation

The efficiency of the removal of the compounds in the process of photochemical oxidation increased with increasing duration of irradiation. The removal efficiency of IBU and DCL after 5 min of the process was over 98%. The concentration of CBZ was reduced by 46% after the same irradiation time, and at the end of the irradiation process the removal efficiency of this pharmaceutical exceeded 91%.

It should be emphasized that the TiO_2 photocatalyst has a high chemical stability and it can be reuse after the separation in the microfiltration process. In some experiments the photocatalyst was reused up to five times without reducing the efficiency of treatment processes [19].

Chromatographic analysis showed that by-products of oxidation and reduction of the studied micropollutants were generated during the photocatalysis process. In the initial stage of the photocatalysis process (up to 10 min) three derivatives of diclofenac, among others, were identified: 4'-hydroxydiclofenac, 1-(2,6-dichlorophenyl)indolin-2-one and N-(2,6-dichlorophenyl)-2-aminotoluene, and 1-hydroxyibuprofen and 4-(1-carboxyethyl)benzoic acid, which are derivatives of ibuprofen. The following degradation by-products of CBZ: oxcarbazepine, 10,11-dihydro-10-hydroxycarbamazepine and carbamazepine-10,11-epoxide were identified at all stages of the photocatalytic oxidation process. The oxidation by-products can be much more toxic than the parent compound, which as a result can negatively affect the quality of the treated water.

The combination of the photocatalytic oxidation process with the process of two-stage membrane filtration appears to be a solution allowing to remove the oxidation and reduction by-products generated in photocatalysis processes and polish the retentate generated during the nanofiltration process. Therefore, in the further step of this study only the sequential combination of the process was considered. The schematic illustration in figure 3 shows a layout of the sequential system photocatalysis/microfiltration/nanofiltration for wastewater treatment. In the first treatment step the wastewater was subjected to the photocatalytic oxidation during 15 minutes, and then it was subjected to microfiltration to separate the catalyst particles from the mixture. The obtained permeate is directed to the second stage of membrane filtration in which nanofiltration membrane was used. The retentate generated during the process was recycled to the photocatalytic reactor.

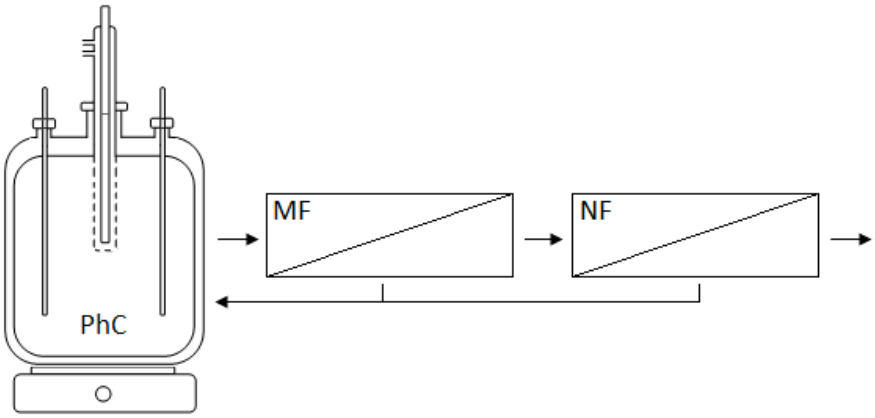


Fig. 3. Simplified scheme of the sequence system photocatalysis/microfiltration/nanofiltration (PhC – photocatalytic reactor; MF – microfiltration membrane; NF- nanofiltration membrane)
Source: own compilation

The wastewater treatment in the sequential system allowed to achieve complete elimination of pharmaceutical compounds (Fig. 4).

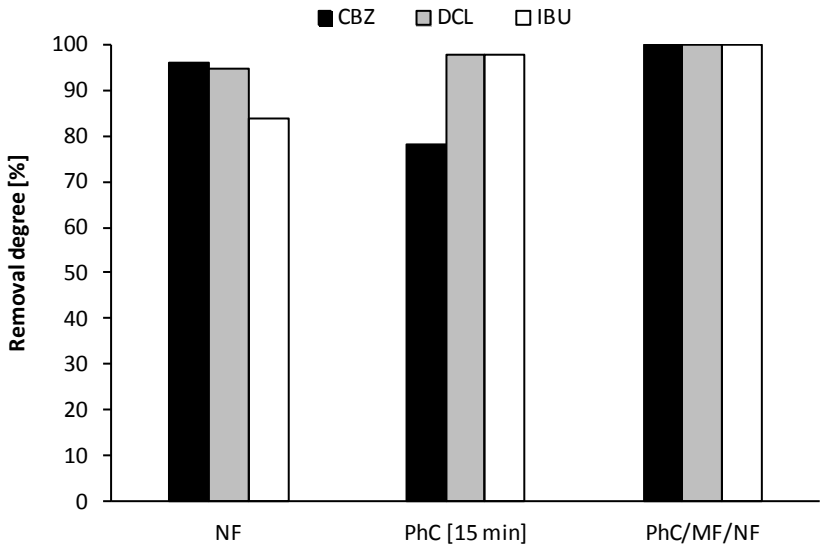


Fig. 4. Degree of pharmaceutical removal in single processes and in the sequence system
Source: own compilation

The pharmaceuticals and the by-products of oxidation and reduction of the drugs that were not mineralized in photocatalysis process were retained during nanofiltration already after 30 minutes of operation. Chromatographic analysis showed that the onset of the fouling phenomenon resulting in an increase of filtration resistance led to the elimination of both the parent forms of the pharmaceutical compounds, as well as their oxidation products that are characterized by significantly lower molecular weights and less complex structure of the molecule. This fact is attributed to formation of a so-called secondary membrane, which has lower porosity than the nanofiltration membrane on which it was formed. It can therefore be concluded that fouling caused by inorganic and high-molecular-weight subjected to chemical oxidation has positive effect on the retention of pharmaceuticals regardless of steric effects associated with the structure of micro-pollutants.

The efficiency of the sequential system after recycling the retentate from the mikro- and nanofiltration process was measured for three times. The obtain results do not indicate a reduction of the degree of removal of tested pharmaceutical micropollutants. Additionally, the filtration resistance noted in the third treatment process was about 1.5% higher than in the first process. In order to evaluate the economic feasibility of considered technology, further studies concerning inter alia the determination of the reduction of generated treated wastewater streams and the possibility of regeneration of membranes will be undertaken.

Summary and conclusions

The presence of pharmaceutical compounds in the aquatic environment may lead to an imbalance in the dynamic equilibrium within the entire ecosystem. Unit water treatment processes do not offer satisfactory removal efficiencies of organic micropollutants and their metabolites or generate toxic waste streams that require further purification. In contrast, the proposed wastewater polishing system that combines sequential processes of heterogeneous photocatalysis and micro- and nanofiltration allowed complete elimination of the investigated pharmaceutical compounds and their decomposition by products (both physiological metabolites and waste water treatment by-products). The obtained results can be used in the future as a basis of a technological design, which is a key element in designing or upgrading modern waste water treatment plants to meet increasingly stringent requirements for the elimination of organic micropollutants from the treated waste water.

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