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Combined Application of Membrane and Advanced Oxidation Processes for Removal of Pharmaceuticals from Water

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Abstract

The presence of pharmaceuticals in the aquatic environment is problematic in many aspects, mainly due to their specific mode of action, and physical and chemical properties that make them highly resistant to degradation. This new group of contaminants is frequently detected in conventional wastewater treatment plants.

Removal of pharmaceuticals from water by primary and secondary methods (filtration, sedimentation, biological treatment) is not satisfactory, therefore advanced methods involving membrane and advanced oxidation processes are increasingly being developed. The most significant advantage of membrane technologies is their wide industrial applicability while maintaining the highest water standards. Advanced oxidation processes can effectively decompose complex pollutants into simpler ones, and mineralize organic pollutants in wastewater without generating secondary waste. In order to improve their advantages, but also to eliminate disadvantages, these technologies are increasingly complemented and combined, resulting in higher efficiency in removing pharmaceuticals from water and reducing their toxicity.

Keywords

Pharmaceuticals, water pollution, membrane processes, advanced oxidation processes, hybrid systems for water treatment

1 Introduction

In recent decades, various human activities around the world have led to significant changes in the aquatic environment. In other words, water pollution has become a global challenge. Conventional wastewater treatment plants achieve a satisfactory level of water treatment, if the pollutants present are biodegradable. Thus, in addition to physical, physicochemical, and chemical processes (filtration, precipitation, coagulation/flocculation), the degradation of pollutants in such systems is mainly based on aerobic biological processes involving activated sludge in the aeration tank. On the other hand, with the development of sophisticated analytical instruments, with lower detection and quantification limits, it is possible to analyse substances at very low concentrations (in trace amounts).[1,2] This opens a new perspective on pollutants present in micro concentrations in water, *i.e.*, micropollutants. Pharmaceuticals, pesticides, and personal care products are just some of the micropollutants that have become the subject of intensive research. A major problem in wastewater is the presence of pharmaceuticals at very low concentrations ($< \mu g\, l^{-1}$), their high persistence, and resistance to degradation, which consequently leads to partial removal in conventional wastewater treatment plants. These findings have accelerated the development of new water treatment technologies such as membrane-based processes (MP) and advanced oxidation processes (AOPs). Pressure MPs of reverse osmosis (RO) and nanofiltration (NF) in the last two decades have confirmed their role in the retention (removal) of various organic, not just inorganic substances, for which they were originally intended. On the other hand, great expectations are placed on AOPs in terms of the removal or degradation of molecules with complex structures, such as pharmaceuticals. Currently, the main disadvantage of AOPs is their economic inequity compared to conventional biological processes. However, the high conversion rate and successful removal of highly toxic pharmaceuticals, and their metabolites and degradation products allow a different perspective on these processes.

2.1 Pharmaceuticals – fate and behaviour in the environment

Pharmaceuticals are one of the main groups of micropollutants in the environment. They are defined as compounds used to treat or prevent diseases in humans and animals, and as growth promoters in veterinary medicine.[3] Due to their specific physicochemical properties and their occurrence in both wastewater and natural waters, they pose a potential threat to the environment as well as to flora and fauna, and thus may affect the overall quality of life. Human and veterinary pharmaceuticals and their metabolites are constantly entering the environment, in the form of wastewater either from the pharmaceutical indus-

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try or through improper disposal of pharmaceuticals after use. In addition, pharmaceuticals can enter the environment through cellular secretions contained in municipal wastewater. The aforementioned reinforces their additional negative aspect for the environment. Moreover, the good water solubility and poor degradability of some pharmaceuticals cause them to pass through all-natural filters and water treatment plants, thus posing a risk to the quality assurance of drinking water supply systems.[2] Furthermore, the values of the octanol-water partition coefficient ($\log K_{OW}$) and solubility product constant (K_{sp}) define a certain tendency for sorption of pharmaceuticals to soil and sediment, which is a very important indicator for evaluating the possibility of penetration into groundwater and surface water, *i.e.*, retention in the sediment matrix.[3]

According to European legislation in the field of water protection, pharmaceuticals are classified as *contaminants of emerging concern*. The *Water Framework Directive*, as an overarching document at the level of the European Community, has established the basic principles for water protection against pollution. Water pollution control strategies include a list of 45 *priority substances* or groups of substances that pose a significant risk to the aquatic environment. Some substances on the list are additionally classified as priority hazardous substances based on properties such as environmental persistence, bioaccumulation, and toxicity. In addition to priority substances, the *Watch List* includes *emerging water pollutants*, encompassing pharmaceuticals and their precursors.[4]

Pharmaceuticals can enter the environment through a variety of pathways. These include diffuse sources (farms where pharmaceuticals, especially antibiotics, are added to animal feed to improve growth or treat or prevent disease; via manure on agricultural land from which they can leach into groundwater), and point sources (hospitals, improper disposal of unused pharmaceuticals, wastewater treatment plants).

After use and excretion, pharmaceuticals and their metabolites, which may differ in structure and properties from the initial substance, enter municipal wastewater. Conventional wastewater treatment plants have proven to be insufficiently effective in removing a large number of pharmaceuticals and their metabolites. In some cases, higher concentrations of pharmaceuticals have been found at the outlet of a conventional wastewater treatment plant than at the inlet.

The processes in conventional wastewater treatment plants can be divided into the following stages: mechanical or primary treatment, biological or secondary treatment, and physicochemical and chemical processes. Thus, inefficient removal in wastewater treatment plants results in pharmaceuticals entering the environment via watercourses, as does the disposal of activated sludge, in which such problematic compounds are retained because they can also adsorb to activated sludge flocs.[5]

Even when present at low concentrations, continuous uptake of pharmaceuticals into the environment may eventually lead to higher concentrations (bioaccumulation) and long-term adverse effects on aquatic and terrestrial organisms and humans. In addition, bacterial resistance to antibiotics present in the environment is likely to develop. In 2017, *Thai et al.*[6] found the presence of four groups of pharmaceutical compounds (beta-lactams, quinolone antibiotics, macrolides, and sulfonamides) at very high concentrations ($50–100\ \mu g\ l^{-1}$) during the analysis of wastewater from the pharmaceutical industry and sanitary wastewater (hospitals). In addition, the same samples were tested for antibiotic resistance, indicating that this wastewater is not only a very large source of antibiotic residues, but also of antibiotic-resistant bacterial strains.[6] This case shows how there should be high concern of antibiotic residue in the wastewater, which, if not properly treated, will be present in the effluent after the purification process. This might have long-term aftermath regarding the adaptation of different bacterial species on such compounds, therefore they will possibly have less effective medicative impact on target species.

Improving conventional water treatment methods very often requires the use of advanced processes such as membrane processes of RO/NF or AOPs, especially when the contaminants are very resistant, toxic, and problematic in many ways.

2.2 Advantages and disadvantages of membrane and advanced oxidation processes for wastewater treatment

Membrane processes are introduced as tertiary treatment of wastewater and represent the final stage of conventional treatment technology. Microfiltration and ultrafiltration (MF, UF) are most commonly used as filtration processes to remove micron-sized particles, followed by NF and RO in combination as the most effective separation processes. The result is high purity of the output streams (permeate), since the RO/NF separation is performed at the ionic and molecular level (removal of salts and organic components with low molecular weight).

The main disadvantage of MPs is fouling phenomena, which by its nature can be of inorganic, organic or biological origin. The consequences of membrane fouling are a deterioration of membrane performance (flux decline and lower solute retention), frequent cleaning and additional maintenance requirements, and overall shorter membrane life, which generally increases operating costs.

Another unavoidable and negative aspect of membrane processes is the concentration polarisation phenomenon, which leads to a higher osmotic pressure and therefore requires a higher operating pressure. It also reduces the retention of low molecular weight substances and salts.[6–9] Concentration polarisation is minimised under controlled hydrodynamic conditions.

Despite the negative side effects associated with membrane processes, membrane technology is becoming the predominant technology in the treatment of potable water and wastewater at the industrial level, mainly due to its high separation efficiency, non-destructive nature, environmental friendliness, and cost-effectiveness.[10]

Advanced oxidation processes have proven to be very effective for wastewater containing priority micropollutants. The oxidation mechanism is based on the *in situ* generation of hydroxyl radicals (•OH) through the application of chemical, electrical, mechanical or radiation energy under atmospheric conditions. Hydroxyl radicals are highly oxidative species ($E° = 2.8$ V) that are non-selective with respect to organic pollutants, have a short half-life, and are highly reactive at low concentrations ($<10^{-12}$ M) with kinetic constants in the range 10^6–10^{12} $M^{-1}\,s^{-1}$.[9]

The main advantages of such processes are the atmospheric operating conditions, the ability to degrade complex pollutants to simpler molecules, and the mineralisation of organic pollutants in wastewater with little or no secondary waste. AOPs are also very flexible in terms of their separate or combined use.

One of the main shortcomings of AOPs refers to their economic aspect, which in the case of persistent pollutants is justified by their high efficiency in decomposition or mineralisation.

AOPs in combination with membrane processes can significantly reduce membrane fouling by degrading all types of pollutants present.[8,9,11] AOPs are used as the most effective processes, especially with regard to organic components or *emerging contaminants* – pharmaceuticals.[12]

2.3 Combined application of membrane and advanced oxidation processes

The combination of membrane processes and AOPs results in a hybrid system that is highly efficient in the removal and degradation of persistent pollutants such as micropollutants.[8–12] As may be seen in Fig. 1, the number of published scientific papers on such hybrid systems has increased in the period from 2005 to 2021, indicating a growing number of studies. However, in the case of pharmaceuticals and hybrid processes, the trend of publishing is more or less the same and that is around ten papers *per* year.

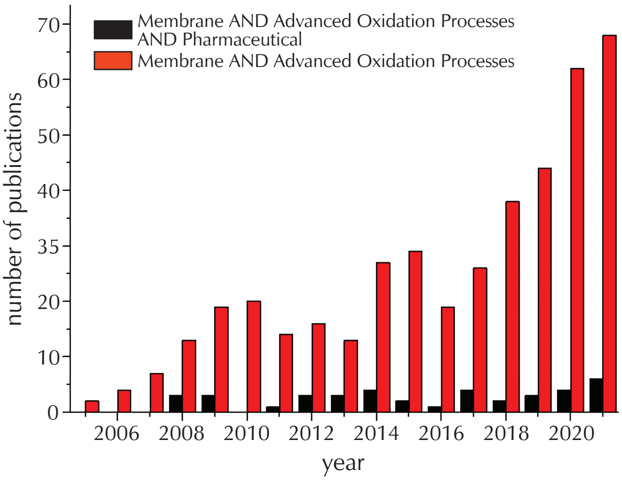

Fig. 1 – Overview of scientific publications on the combined application of membrane processes and AOPs in the period 2005–2021.

Slika 1 – Pregled znanstvenih publikacija iz područja istraživanja kombinirane primjene membranskih i naprednih oksidacijskih procesa u razdoblju 2005. – 2021.

AOPs can be used before or after membrane treatment, in both cases with high efficiency. Table 1 summarizes the scientific advances in the application of hybrid systems, as well as the types of pollutants and removal efficiencies. It may be seen that the combination of membrane processes and AOPs for the removal of pharmaceuticals have efficiencies ranging from 50 to 99 %. The methodology and mechanisms of the hybrid processes are explained below.

Table 1 – Literature review on combined/hybrid systems: membrane separation – AOPs

Tablica 1 – Literaturni pregled iz područja istraživanja kombiniranih/hibridnih sustava: membranski separacijski – napredni oksidacijski procesi

Membrane processes	Types of AOPs	Types of water contaminants	Concentration	Removal / %	Refs.
MBR	ozonation	naproxen, acetaminophen, ketoprofen, roxithromycin, trimethoprim	20–50 ng l^{-1}	55–95	13
MF (pre-treatment)	ozonation	erythromycin, lincomycin, roxithromycin, sulfamethoxazole, sulfamerazine, sulfapyridine	2–5 mg l^{-1}	50–65	14
PMR*		diclofenac	0.05–0.63 mg l^{-1}	>98	15
UF	photocatalysis (P25 TiO_2)	diclofenac, clozapine, simvastin, ibuprofen, paracetamol	0.5–1 mg l^{-1}	50–85	16
NF	ozonation	norfloxacin, ofloxacin, roxithromycin, azithromycin	0.3 mg l^{-1}	>98	17
NF/RO	photocatalysis (P25 TiO_2); photo-Fenton (Fe_2O_3/SBA-15)	diclofenac, acetamidoantipyrine, hydrochlorothiazide, sulfamethoxazole	10 mg l^{-1}	DCF: 99, other: 90	18

Table 1 – (continued)
Tablica 1 – (nastavak)

Membrane processes	Types of AOPs	Types of water contaminants	Concentration	Removal / %	Refs.
PMR (catalytic ozonation on a ceramic membrane doped with MnO_2-Co_3O_4)		benzophenone-3	0.5–3 mg l^{-1}	76	19
PMR		diclofenac, ibuprofen, naproxen	0.1 mg l^{-1}	45–70	20
UF	pre-ozonation	hydrophobic biopolymer molecules	15 mg l^{-1}	4–71	21
NF	UV/TiO_2	cimetidine, acetaminophen, sulfamethoxazole, propranolol	10 mg l^{-1}	47–86	22
UF, RO	electrochemical oxidation	ofloxacin, naproxen	10–149 µg l^{-1}	95	23
RO	activated carbon (adsorption)	trimethoprim, ciprofloxacin, naproxen, ibuprofen, diclofenac, carbamazepine, propranolol	3.8–1400 ng l^{-1}	81–98	24
MBR	UV/TiO_2	carbamazepine	10 mg l^{-1}	95	25
NF	Photooxidation (UV/H_2O_2)	salicylic acid	0.5 µM	80–95	8
MF	ozonation	erythromycin, carbamazepine, caffeine, trimethoprim, ofloxacin	0.5–2 nM	>90	26
MF, RO	photooxidation (UV/H_2O_2)	17-β- estradiol, atrazine, alpha-ethynyl estradiol	0.2–1 µg l^{-1}	88–98	27
MF (ceramic membrane)	UV photolysis / UV photocatalysis (TiO_2 P25)	ibuprofen, trimethoprim, sulfamethoxazole, naproxen, meprobamate	1 mg l^{-1}	25–100	28
NF (membrane photoreactor)	photocatalysis (TiO_2 P25)	lincomycin	25–75 µM	> 94	29
MF	Catalytic ozonation with TiO_2 – Al_2O_3 modified ceramic membrane	decolourisation of real water	TOC = 13.9 mg l^{-1}	80 of decolourization, 40 of TOC	31
MF	Photocatalysis (N-TiO_2)	carbamazepine	50 mg l^{-1}	90	37
UF	ozonation	dicloxacillin and ceftazides	1.5 mg l^{-1}	> 90	38
UF	Heterogeneous Fenton process (FeOCl-loaded ZrO_2/TiO_2 ceramic membrane)	sulfamethoxazole and 17α-ethinylestradiol	50 µM	92	39
NF	Photocatalysis (β-FeOOH/TiO_2)	doxycycline	30 µg ml^{-1}	90.1	40
UF	Photocatalysis (sulfonated graphene oxide and zinc oxide, SGO/ZnO (SGZ))	ciprofloxacin	10 mg l^{-1}	95.1	41

2.3.1 Membrane hybrid process with ozonation (HMOF) and catalytic ozonation

One of the most commonly used AOPs in hybrid systems is ozonation. Advanced ozonation is accomplished by direct injection of ozone, generated by electrical discharge in an oxygen stream, into a feedwater stream passing through the membrane separation system. The removal efficiency of the resulting filter cake depends largely on the type of membrane module, the type of membrane process, the type of membrane configuration, and additional sources of hydroxyl radical generation (addition of H_2O_2 and additional energy using the UV portion of the electromagnetic radiation spectrum). However, when ozone is added directly to the membrane module, the resistance of the membrane material should be considered. Polyamide membranes, for example, are better avoided for these purposes, not only because of oxidation but also because of the extremely alkaline pH conditions under which advanced ozonation takes place, which can destroy the polyamide structure of the membrane along with the performance of the membrane system. The use of ceramic membranes (based on titanium, zirconium, γ-alumina, and silica) has proven to be a possible solution due to their high thermal and chemical resistance. In this way, it is possible to perform catalytic ozonation, in which degradation is assisted by other radical species, such as the superoxide radical anion ($O_2•^-$), in addition to ozone ($O_3•^-$) and hydroxyl radicals (•OH). Dissolved ozone in contact with the ceramic membrane promotes the generation of radical species that break down existing contaminants into simpler molecules that can be further separated.[30] Certain studies have shown the high efficiency of membrane systems, in which a layer of photocatalytically active materials based on Fe, Mn, or Ti is deposited on the surface of the membrane by a special immobilisation technique. For example, *Zhu et al.*[31] showed that catalytic ozonation combined with a $TiO_2 – Al_2O_3$ modified ceramic membrane resulted in enhanced water flux due to a combined mechanism of indirect oxidation along with direct ozonation which targeted the breakdown of organic foulants. When both processes were applied separately, the efficiency of the process in terms of decolourisation of real water from the textile industry was 40 %, while the application of the hybrid process doubled the efficiency.

On the other hand, *Guo et al.*[19] investigated the degradation of 2-hydroxy-4-methoxybenzophenone (BP-3), benzotriazole (BZA) and 2-phenylbenzimidazole-5-sulfonic acid (PBSA) by a novel catalytic membrane prepared by coating a ceramic membrane with $CuMn_2O_4$. Bimetallic oxides were found to be more stable materials for long-term use in such systems. In this case, there were two main mechanisms of H_2O_2 formation during catalytic ozonation: (1) the interaction of ozone with the catalyst surface, and (2) the reaction of ozone with the pharmaceutical compound. Ozone molecule reacts with unsaturated organic molecules, resulting in the formation of a small amount of H_2O_2. On the other hand, the •OH radicals generated on the catalyst surface participate in the decomposition of O_3 and form $O_2•^-$ radicals, which indirectly oxidise the organic pollutants present. In addition, $O_2•^-$ radicals can react with O_3 molecules in solution to form •OH radicals. Furthermore, •OH can also react with each other to produce small amounts of H_2O_2. In addition, the degradation of effluent organic matter (EfOM) in wastewater, which often causes membrane fouling, was also investigated. Small, nontoxic hydrophilic molecules with unsaturated bonds were formed and separated so that flux across the membrane was not impeded.[19]

2.3.2 Membrane hybrid processes in combination with photocatalysis (HOMF)

Besides ozonation, photocatalytic processes in their combination with membrane processes are among the most studied processes. Such hybrid processes require a special design of photocatalytic membrane reactors (PMR), and the selection of the appropriate photocatalytically active material for the degradation of a single pollutant plays an important role. Photocatalysts are usually semiconductor-like materials that are active under the influence of UV radiation of the electromagnetic spectrum, and have a band gap of about 2 eV. Modifications in the form of doping and the production of composite materials enable their activity by radiation in the visible range (Vis) of the electromagnetic radiation spectrum. The choice of material for membrane fabrication is also important. The most commonly used materials are regenerated cellulose, polyvinylidene fluoride (PVDF), polyethersulfone (PES), ceramics, and steel.[32,33]

There are several important requirements in the selection of the membrane: its chemical stability, abrasion resistance, compatibility with the photocatalyst, and good hydrophilicity. Hydrophilicity is particularly important because the main prerequisite for successful photocatalysis is the adsorption of compounds on the surface of the photocatalyst. For the proper selection of the membrane type, as well as the type of photocatalyst and the process conditions, it is also important to know the physicochemical properties of the pharmaceuticals. The molecular structure of the pharmaceutical and its functional groups are responsible for numerous interactions with the membrane surface and/or the photocatalyst, and thus provide information about the mechanisms of adsorption or diffusion through the membrane pores.[33,34]

The configuration that is extremely effective in the removal/degradation of pharmaceuticals in wastewater refers to the application of a photoactive layer to the membrane skin. The degradation of pharmaceuticals takes place on the surface or in the pores of the membrane. This reduces the formation of the filter cake and membrane fouling. Under the influence of UV radiation, photogenerated electron-hole pairs (e^-/h^+) are formed on TiO_2 nanoparticles, which allow direct oxidation of the present pollutants or indirect oxidation by the formed •OH radicals. The incorporation of TiO_2 as a photocatalytically active material in the membrane structure leads to an increase in hydrophilicity and specific surface area, which supports the degradation of the organic pollutants present.[34]

On the other hand, *Yoon et al.*[35] studied the application of NF and UF membranes for the removal of 52 pharmaceuticals, with different values of the octanol-water partition coefficient ($\log K_{OW}$), and found that the tested hydrophobic components with a neutral or positive charge and high values of dissociation constant (pK_a) can be successfully retained by UF membranes. Hydrophobicity and polarity can often lead to adsorption onto colloidal particles of the filter cake, leaving them in the retentate. This indicates the fact that membrane systems are sometimes not effective enough to remove/retain pharmaceutical degradation products due to their: (i) hydrophobicity and high adsorption affinity for the membrane surface; (ii) concentration polarisation along the membrane surface as a result of electrostatic interactions; (iii) low molecular weight substances relative to the membrane pores.[36]

An example of effective degradation of pharmaceutical carbamazepine (CBZ) was given by *Horovitz et al.*[37] Using a photomembrane reactor with an immobilised N-TiO_2 layer and UV irradiation, the efficiency of CBZ removal was about 90 %. Vis-active photocatalytic material was deposited by sol-gel method onto Al_2O_3 microfiltration membranes, which also decreased permeability of membranes by 50 %. The degradation mechanism in this case can be summarised in several steps: (i) transfer of CBZ from the solution to the photocatalytic membrane surface, (ii) adsorption of CBZ on the photocatalytic membrane surface, (iii) reaction/decomposition in the adsorbed layer, (iv) desorption of degradation products, (v) transfer of degradation products into the solution. In this way, the degradation products are also subjected to photocatalytic degradation. Also, porous structure of the membrane provides significant increase in separation efficiency compared to smooth coated surfaces, because contact of molecules and active surface increases. To achieve high performance of such hybrid systems, it is necessary to optimise several different parameters, especially in the case of pharmaceutical contamination. *Alpatova et al.*[38] studied the application of the HOMF process for the removal of dicloxacillin and ceftazides, as well as their precursors and degradation products. They noticed that the application of advanced ozonation in a system with a ceramic membrane, as opposed to membrane filtration, significantly improved the removal of antibiotics and their precursors below the detection limit of the instrument. In this investigation, HOMF system was able to achieve goals of membrane fouling control despite the alkaline conditions of treated wastewater by optimisation of ozone dose and flow.

Zhang et al.[39] reported a preparation of a high-performance UF membrane loaded with heterogeneous Fenton catalyst iron oxychloride (FeOCl) for the effective removal of the pharmaceuticals in water at pH 6, which is much higher than conventional pH 3. The FeOCl-loaded ZrO_2/TiO_2 ceramic membrane (FeOCl-CM) was tested in the single-pass treatment of the pharmaceuticals sulfamethoxazole and 17α-ethinylestradiol. During the 4 h, 92 % of the degradation of the pharmaceuticals was achieved, with the addition of the H_2O_2 (2 mM), while the pH of the solution was 6.2, and water flux was $100\ l\,m^{-2}\,h^{-1}$. It can be concluded that the long-term efficiency of the membrane (during 120 h) can be attributed to both the surface chemistry of the catalyst itself as well as the layered structure with the size-exclusion properties (< 300 kDa), avoiding an invasion of the active sites.

In the study of *Zhao et al.*,[40] β-FeOOH/TiO_2 and core-shell functional nanofibrous membrane loaded with different functional nanoparticles were applied for the treatment of the doxycycline ($20\ \mu g\,ml^{-1}$) under simulated solar irradiation. Degradation of DC was 65–89 % in the case of different ratios of both materials, which form the membrane and the addition of H_2O_2 concentrations of $5\ mmol\,l^{-1}$. The β-FeOOH/TiO_2 composite nanoparticles prepared by doping at 1 : 1 form more heterostructures, and the utilisation of solar irradiation was higher compared with other composite particles, therefore such membrane achieved the highest efficiency. Matching the relative band potential of both materials, as well as the tunnel structure of β-FeOOH and the loose filling structure of TiO_2 resulted in good electronic and hole conductivity.

Boopathy et al.[41] (2020) evaluated the performance of the sulfonated graphene oxide (SGO), zinc oxide (ZnO), and SGO/ZnO (SGZ) nanomaterials incorporated into the polyethersulfone PES membrane, which exhibited better hydrophilic property with ciprofloxacin feed solution. Such SGZ nanomaterials incorporated into the PES membrane showed higher ciprofloxacin (95.1 %) degradation efficiency than SGO nanomaterial under UV light irradiation. In this case, the main mechanism of degradation can be related to the generation of the fast charge carriers of both materials as well as reduced recombination of electron-hole pairs and effective charge separation between both parts (ZnO and sulfonated graphene oxide). It can be concluded that this type of membrane this way also exhibited good self-cleaning properties.

4 Conclusion

Based on the literature review on hybrid systems, several conclusions can be drawn:

- Pharmaceuticals present in the aquatic environment are classified as micropollutants. Due to their physicochemical properties that make them persistent and resistant to degradation, the specific mode of action in the system, and the tendency to bioaccumulate, they are difficult to eliminate using conventional water treatment processes. Therefore, hybrid systems of membrane processes and AOPs are proposed for more efficient removal of pharmaceuticals.
- Membrane technologies are capable of retaining persistent contaminants such as pharmaceuticals, and concentrating them in the retentate stream while pure water permeates through the membranes. The application of AOP can improve retentate reduction.
- Retention of pharmaceuticals, their metabolites, and degradation products on the membrane surface modified with photocatalytically active components results in high degradation efficiency and mineralisation.
- The fouling phenomenon typical of membrane processes can be reduced significantly in combination with AOP processes, maintaining the stability of their flux and extending their lifetime.

List of abbreviations and symbols
Popis kratica i simbola

MPs – membrane processes
– membranski procesi

AOPs – advanced oxidation processes
– napredni oksidacijski procesi

MF – microfiltration
– mikrofiltracija

UF – ultrafiltration
– ultrafiltracija

NF – nanofiltration
– nanofiltracija

RO – reverse osmosis
– reverzna osmoza

PMR – photocatalytic membrane reactor
– fotokatalitički membranski reaktori

Vis – visible spectrum
– vidljivi spektar

PVDF – polyvinylidene fluoride
– poliviniliden fluorid

PES – polyethersulfone
– polietersulfon

BP-3 – 2-hydroxy-4-methoxybenzophenone
– 2-hidroksi-4-metoksi benzofenon

BZA – benzotriazole
– benzotriazol

PBSA – 2-phenylbenzimidazole-5-sulfonic acid
– 2-fenilbenzimidazol-5-sulfonska kiselina

EfOM – effluent organic matter
– organske tvari prisutne u efluentu

CBZ – carbamazepine
– karbamazepin

HOMF – membrane hybrid processes in combination with photocatalysis
– hibridni membranski procesi u kombinaciji s fotokatalizom

HMOF – membrane hybrid process with ozonation
– hibridni membranski postupak s ozonacijom

pK_a – negative base-10 logarithm of the acid dissociation constant
– negativan logaritam konstante disocijacije kiseline

E° – standard electrode potential, V
– standardni elektrodni potencijal, V

logK_{OW} – octanol-water partition coefficient
– koeficijent raspodjele oktanol-voda

K_{sp} – solubility product constant, –
– konstanta produkta topljivosti, –

FeOCl – iron oxychloride
– željezov oksiklorid

FeOCl-CM – iron oxychloride ceramic membrane
– keramička membrana od željezova oksiklorida

SGO – sulfonated graphene oxide
– sulfonirani grafen oksid

SGZ – sulfonated graphene oxide zinc oxide, SGO/ZnO
– sulfonirani grafen oksid cinkov oksid, SGO/ZnO

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SAŽETAK

Kombinirana primjena membranskih i naprednih oksidacijskih procesa za uklanjanje farmaceutika iz vode

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Prisutnost farmaceutika u vodama problematična je iz više aspekata, uglavnom zbog njihove specifične prirode djelovanja u sustavu u kojem se nalaze te pripadajućih fizikalno kemijskih karakteristika koje ih čine postojanim i otpornim na razgradnju. Osim toga, skloni su bioakumulaciji u vodenom okolišu te mogu imati toksičan učinak na žive organizme. Ta grupa onečišćivala redovito je detektirana u konvencionalnim sustavima za obradu otpadnih voda.

Uklanjanje farmaceutika iz voda konvencionalnim primarnim i sekundarnim metodama (filtracija, taloženje, biološka obrada) nije zadovoljavajuće, pa se sve više razvijaju i primjenjuju napredni postupci, u koje spadaju membranske i oksidacijske tehnologije. Najveća prednost membranskih tehnologija je njihova visoka razina industrijske primjene uz zadovoljavanje najviših standarda za vode. Napredni oksidacijski postupci karakteristični su po mogućnosti razgradnje složenih onečišćivala do jednostavnijih te mineralizaciji organskih onečišćivala u otpadnim vodama uz malo ili gotovo nikakvo nastajanje sekundarnog otpada. U svrhu daljnjeg poboljšanja njihovih prednosti, ali i otklanjanja nedostataka, te se tehnologije sve češće međusobno nadopunjuju i kombiniraju, što rezultira povećanjem učinkovitosti uklanjanja farmaceutika iz voda i smanjenjem njihove toksičnosti.

Ključne riječi
Farmaceutici, onečišćenje vode, membranski procesi, napredni oksidacijski procesi, hibridni sustavi za obradu otpadne vode

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