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1 ***Hybrid system coupling ozonation and nanofiltration with functionalized catalytic ceramic***
2 ***membrane for ibuprofen removal***

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13
14 **Abstract**

15 The investigations on the removal of ibuprofen (IBU) in a hybrid system coupling ozonation
16 and nanofiltration with functionalized catalytic ceramic membrane are presented. The gaseous
17 ozone into feed water in concentration of 11 g Nm⁻³ was supplied. Positive influence of catalytic
18 ozonation on ibuprofen decomposition was observed. The application of catalytic nanofiltration
19 membrane led to the ibuprofen removal of 91% after the first 15 minutes from the beginning of
20 the O₃/NF process, while at the same time for the pristine membrane it was equal to 76%. The
21 investigations revealed incomplete degradation of drug under pH 3 after 2 h, i.e. 89%. On the
22 other hand, the addition of inorganic salts did not affect the catalytic ibuprofen removal
23 efficiency. Under acidic pH the highest permeate flux decline (26%) was noted, whereas no
24 differences between permeate flux measured under natural and alkaline conditions were
25 observed. During the treatment process three IBU by-products were detected, which
26 significantly affected the permeate toxicity, however, after 2 h of catalytic nanofiltration the
27 product of treatment process was found as nontoxic.

28
29 **Keywords:** Ozonation; ceramic membrane; nanofiltration; ibuprofen; *Aliivibrio fischeri*;
30 toxicity

31
32 **List of symbols and abbreviations**

33 d_o/d_i - outer/inner diameter

34 ESI - Electro Spray ionization

35 IBU - ibuprofen
36 MBR - membrane bioreactor
37 MF - microfiltration
38 MWCO - molecular weight cut off
39 NF - nanofiltration
40 NSAIDs - non-steroidal anti-inflammatory drugs
41 PhACs - pharmaceuticals
42 UF - ultrafiltration
43 UV - ultraviolet
44 VIS - visible

45

46 **1. Introduction**

47 The pollution of the aquatic environment by pharmaceuticals has become a serious
48 problem. The discharge of brine wastewater containing pharmaceuticals degrades water quality
49 and thus water cannot be directly used as potable water, even after desalination, and for
50 industrial applications (Panagopoulos et al. 2022). Conventional technologies applied in water
51 or wastewater treatment plants are not efficient enough in drugs removal, therefore there is an
52 urgent need to develop new methods. Ozonation is an effective process for pharmaceutical
53 degradation (Schmitt et al. 2020; Brillas 2022), however, it can generate smaller and more toxic
54 by-products than the initial micropollutants. Hence, a promising solution could be the coupling
55 of ozonation with membrane filtration, which allows for rejection of by-products and other
56 molecules (e.g. colloids and ions) (Mansas et al. 2020a). Studies in literature survey related to
57 pharmaceuticals elimination with application of both ozonation and membrane filtration are
58 very limited. Most of the studies investigated ozonation or ozonation enhanced with H₂O₂ or
59 UV as either effective pretreatment stage for removal of organics in membrane filtration feed
60 stream or post-treatment stage to treat both effluent streams – permeate and retentate (Real et
61 al. 2012; Byun et al. 2015; Miralles-Cuevas et al. 2017). For instance, Real et al. (Real et al.
62 2012) studied the efficiency of combined some chemical oxidation processes such as ozonation,
63 chlorination, O₃/H₂O₂, UV or UV/H₂O₂ and membrane separation, i.e. ultrafiltration (UF) or
64 nanofiltration (NF) for removal of five PhACs (amoxicillin, hydrochlorothiazide, metoprolol,
65 naproxen and phenacetin) from various water matrices. They applied two approaches in their
66 investigations. In the first case, the membrane processes were used as a pretreatment step, and
67 effluents were subsequently treated by one of abovementioned chemical oxidation processes.

68 In turn, second approach involved application of chemical oxidation as a pretreatment stage
69 before NF. The best removal efficiency of PhACs for pretreatment via NF followed by
70 ozonation was found. In case of experiments conducted with natural water, the PhACs removal
71 in the permeate reaching values higher than 97% at initial ozone dose of 2.25 mg L⁻¹. When as
72 a feed matrix a secondary effluent was applied, significantly higher initial ozone dose, i.e. 3.75
73 mg L⁻¹, was needed to obtain the same effectiveness of pharmaceuticals removal. Treatment
74 with using chlorination as post-treatment stage or UF pretreatment, were characterized as less
75 effective. In turn, chemical oxidation pretreatment followed by NF, were much more effective
76 for PhACs removal. In other studies (Byun et al. 2015) the effect of feed water pre-ozonation
77 via reactions with molecular O₃ or with radical species as primary oxidants on the permeate
78 flux during NF of synthetic humic acid solution was investigated. Various combinations of pre-
79 ozonation pH, calcium concentration and O₃ dosage were evaluated. According authors on the
80 permeate flux strongly affected calcium concentration and ozone dosage rather than the
81 ozonation mechanism. The researchers emphasized that fouling was mainly due to cake
82 filtration and not pore blockage, and partial mineralization of feed organics compounds via
83 oxidation caused fouling mitigation. On the other hand, Miralles-Cuevas et al. (Miralles-Cuevas
84 et al. 2017) stressed the role of understanding the degradation pathways leading to the formation
85 of various degradation intermediates, since, based on the authors' research, more toxic products
86 were produced during the treatment process than the starting compounds in the feed. The
87 authors investigated the ozonation of NF retentates from real municipal wastewater treatment
88 plant in terms of microcontaminants removal and toxicity. Treatment of NF rejection needed
89 2.75–4.5 g O₃ m⁻³, while 4.5 g O₃ m⁻³, was less than 50% of the ozone required for direct
90 treatment of effluent.

91 The work of Ouali (Ouali et al. 2022) describes hybrid ozonation/NF process enhanced
92 with H₂O₂ for treatment of drinking and river water enriched with pharmaceuticals
93 (carbamazepine and sulfamethoxazole). Nevertheless, in this system flat sheet organic
94 polyethersulfone and polyamide, not ceramic NF membranes, were applied. Moreover, they
95 were not catalytic membranes. In the literature several processes which employed UF or
96 microfiltration (MF) catalytic ceramic membranes were investigated (Karnik et al. 2005; Park
97 et al. 2012; Zhu et al. 2012; Wang et al. 2013a; Mei et al. 2015). These studies mostly focused
98 on removal of humic substances (Park et al. 2012; Zhu et al. 2012; Wang et al. 2013a; Mei et
99 al. 2015) or trihalomethanes (Karnik et al. 2005; Wang et al. 2013a). Regardless of the
100 membrane type, the ozonation can be performed before membrane filtration or it can be
101 enhanced by membrane filtration, where the feed water and ozone are directly injected into the

102 membrane area. However, there are no literature reports regarding the hybrid systems utilizing
103 catalytic ozonation and membrane separation (nanofiltration), which proves the novelty of the
104 presented investigations. In addition, the cited works did not carry out toxicity analyses of the
105 purified solutions, which were presented in this article. In this context, the objective of the
106 research is to investigate the possibility of removal of a model pharmaceutical - ibuprofen
107 (IBU), being a representative of non-steroidal anti-inflammatory drugs (NSAIDs), with
108 application of the hybrid process coupling NF and catalytic ozonation. The NF is a promising
109 separation method, which could reject small organic contaminants (200 Da), whereas O₃ was
110 used to decompose the harmful pharmaceutical. In the experiments a tubular catalytic ceramic
111 membrane was applied, which is ozone-resistant, in combination with ozonation let for
112 achieving a high permeate flux without membrane damage in opposite to polymeric ones
113 (Karnik et al. 2005). The ozonation of the feed water and membrane filtration were
114 simultaneously performed. By the coupling of ozonation with the action of the catalyst
115 deposited onto NF membrane an enhanced production of hydroxyl radicals could be obtained
116 and, in result, the degradation of IBU was improved. During the research the effectiveness of
117 the treatment process was evaluated based on changes of ibuprofen concentration in time.
118 Moreover, the use of ozonation can be beneficial as it could reduce the NF membrane fouling
119 due to the strong oxidative properties of ozone, what has significant impact on the practical
120 application of this technology in a full scale. The membrane performance was analyzed during
121 the study based on changes of permeate flux in time as well. Since, the intermediates products
122 of ozonation could exhibit in some case higher toxicity than the initial contaminants (Gomes et
123 al. 2017), the monitoring of the toxicity not only of the treated feed water but the produced
124 permeate as well is of high importance. Hence, the standardized acute toxicity tests were
125 performed with application of bacteria *Aliivibrio fischeri* in order to evaluate possible
126 toxicological effect of feed and permeate, what further emphasizes the novelty of the presented
127 research.

128 Ibuprofen was selected for the investigations as a representative of non-steroidal anti-
129 inflammatory drugs. It is characterized by carcinogenic and non-steroidal endocrine disrupting
130 drug with harmful effects over fungal, bacterial, algae, microorganisms, crustaceans, fishes and
131 can be potentially hazard for human health (Brillas 2022). It is derived from propionic acid, and
132 a broad spectrum of action, making it one of the most consumed drugs worldwide (Almeida et
133 al. 2022). The pharmaceutical is widely found in the aquatic environment. Due to its complex
134 degradability, several intermediates formed during its decomposition are not completely
135 removed by conventional methods treatment (Almeida et al. 2022).

136 In the present investigation, the hybrid system coupling ozonation and NF with catalytic
137 ceramic membrane for ibuprofen removal was proposed. Especially, the effect of pH and
138 inorganic salts on the membrane performance and effectiveness of treatment process was
139 determined. Additionally, the ecotoxicity tests of treated solutions were conducted.

140

141 2. Experimental

142 2.1. Chemicals

143 Ibuprofen (IBU) ($C_{13}H_{18}O_2$, 206,28 g mol⁻¹) and inorganic salts (MgSO₄·7H₂O,
144 NaHCO₃, NaNO₃, NaH₂PO₄·2H₂O, CaCl₂) were obtained from Sigma Aldrich, USA. The
145 concentrations of the salts applied in the experiments were selected based on the literature
146 (Nawrocki and Kasprzyk-Hordern et al. 2010, Szymański et al. 2016a, Khuntia et al. 2016) in
147 order to evaluate the influence of typical inorganic compounds present in natural waters.

148

149 Table 1. Concentration of inorganic salts applied in the experiments. The values of
150 standard deviations are given in the brackets.

151

Compound	[mg L ⁻¹]
MgSO ₄ ·7H ₂ O	769(2)
NaHCO ₃	420(1)
NaNO ₃	3(0.2)
NaH ₂ PO ₄ ·2H ₂ O	8(0.2)
CaCl ₂	111(2)

152

153 2.2. Feed

154 During the experiments 10 mg L⁻¹ of ibuprofen was applied. In the experiments with
155 salts the proper amount of inorganic salts (Tab. 1) was added into distilled water and mixed
156 thoroughly.

157 2.3. Membrane

158 One channel asymmetric tubular ceramic membrane with outer/inner (d_o/d_i) diameter of
159 10/7 mm and length of 250 mm was applied (IKTS, Germany). The membrane had an effective
160 filtration area of $5.5 \cdot 10^{-3}$ m² and molecular weight cut off (MWCO) of 200 Da (according to

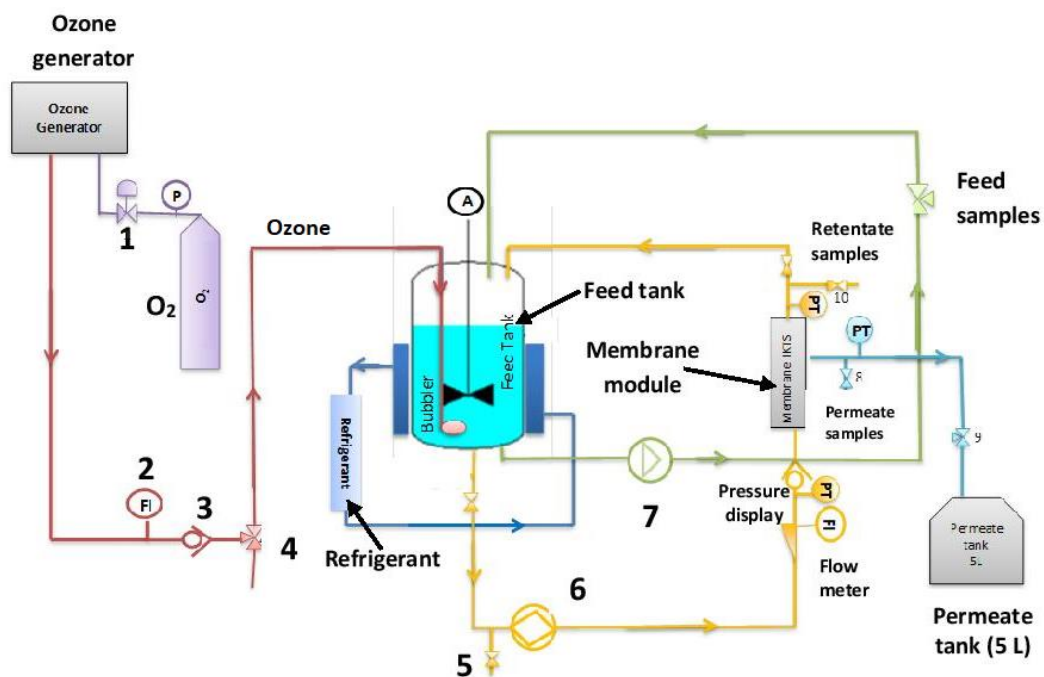
161 the manufacturer). The support of the membrane is made of α -Al₂O₃ and the microporous
162 separation layer is based on TiO₂.

163 This commercial ceramic nanofilter was functionalized by depositing an additional
164 mesoporous layer made of iron oxide (thickness of ~80 nm) on its microporous separative layer
165 (thickness of ~100 nm). Synthesis conditions as well as physicochemical characteristics and
166 catalytic efficiency of such functionalized membranes are detailed in a previous paper (Mansas
167 et al. 2020b).

168

169 2.4. The installation set-up and process conditions

170 The experiments were carried out in a laboratory scale installation, which scheme is
171 presented in the Fig. 1



172

173 Figure 1. Schematic diagram of the installation applied in the experiments. 1-Overflow, 2-
174 Brooks flow meter, 3-Check valve, 4-Three-way valve, 5,6,7-Valves.

175

176 The membrane was inserted in a stainless-steel module and was held in a vertical
177 position with clamps at its two ends. The total volume of the feed circulated in the system at
178 the beginning of the process was 4 L. The feed was pumped in the loop using a positive
179 displacement pump at a flow rate of 69 L h⁻¹ with a tangential speed of 0.5 m s⁻¹. The
180 transmembrane pressure was 10 bar and the temperature of the feed was kept at 20 °C. The gas
181 flow rate of O₃ injected in the tank reactor was 20 L h⁻¹ and the concentration of the injected

182 gaseous ozone was 11 g Nm⁻³. Before opening the permeate valve and starting ozonation the
 183 feed circulated in the system for 2 hours up to reaching the stable concentration of IBU
 184 (adsorption of ibuprofen onto membrane) was performed. During the experiments the
 185 weighting of the collected permeate during 2 hours were performed and permeate flux after
 186 determined time intervals was evaluated. After each experiment, the membrane was rinsed with
 187 pure water, cleaned by filtration of ozonized water during 40 min and again rinsed with distilled
 188 water. The permeability of the pristine and functionalized membranes with O₃ as well as
 189 without ozone was measured. The pH was corrected to a value of 3 with using HCl. While after
 190 adding inorganic salts to the water it was 8.5. In this case no correction of pH was needed.

191 The summary of experiments carried out during the research has been presented in the
 192 Tab. 2.

193 Table 2. The experiments carried out during the investigations on ibuprofen removal.

Experiment	Process description
Pristine, NF	pH 6.5, process time: 2 h, IBU concentration: 10 mg L ⁻¹
Pristine, O ₃ /NF	pH 6.5, process time: 2 h, IBU concentration: 10 mg L ⁻¹ , injected gaseous ozone: 11 g Nm ⁻³
Functionalized, NF	pH 6.5, process time: 2 h, IBU concentration: 10 mg L ⁻¹
Functionalized, O ₃ /NF	pH 6.5, process time: 2 h, IBU concentration: 10 mg L ⁻¹ , injected gaseous ozone: 11 g Nm ⁻³
Functionalized, O ₃ /NF_pH 3	pH 3, process time: 2 h, presence of salts: MgSO ₄ ·7H ₂ O, NaHCO ₃ , NaNO ₃ , NaH ₂ PO ₄ ·2H ₂ O, CaCl ₂ , IBU concentration: 10 mg L ⁻¹ , injected gaseous ozone: 11 g Nm ⁻³
Functionalized, O ₃ /NF_pH 8.5	pH 8.5, process time: 2 h, presence of salts: MgSO ₄ ·7H ₂ O, NaHCO ₃ , NaNO ₃ , NaH ₂ PO ₄ ·2H ₂ O, CaCl ₂ , IBU concentration: 10 mg L ⁻¹ , injected gaseous ozone: 11 g Nm ⁻³

194
 195 In the first stage of the research, the reference experiments with using pristine membrane
 196 and in the presence or in the absence of ozone were conducted (Tab. 2). No salts were added
 197 during these processes. In case of second stage of the studies, the experiments with application
 198 of functionalized catalytic membrane were performed (Tab. 2). Herein, the processes with or
 199 without ozonation were carried out as well. Moreover, the influence of salts and pH during
 200 hybrid ozonation-NF processes was evaluated (Tab. 2).

201 2.5. Analytical methods

202 The concentration of ibuprofen and presence of by-products were determined using the
 203 high-performance liquid chromatography coupled with two mass spectrometers (LC/MS/MS)

204 using an e2695 apparatus from Waters Alliance and mass spectrometers of Quattro Micro and
205 PDA 996 types. The involved equipment was as follow: a Waters 2695 pump, an autosampler
206 with a 20 μl loop, a Waters 2695 separation module (HPLC), and a Waters Micromass
207 (Wythenshawe, Manchester, UK) a Quattro Micro mass spectrometer (MS) equipped with a
208 Electro Spray ionization (ESI) probe in negative mode. A column (C18 Waters HSS-T3 : 100
209 mm * 2.1 mm, 3.5 μm particle size) was used with a buffer A (95% LC grade water + 5% LC
210 grade acetonitrile + 0.1% formic acid) and a buffer B (100% LC grade acetonitrile + 0.1%
211 formic acid). For ozone analyses, the indigo method was used (Bader 1982). It is based on the
212 decolorization of the indigo reagent by ozone. The absorbance at 600 nm was measured using
213 a UV-VIS spectrometer (Jenway 7315). The pH was monitored with using pH meter (Thermo
214 Fisher Scientific). Conductivity was determined using Ultrameter™ 6P (MYRON L
215 COMPANY, USA).

216

217 2.6. Toxicity measurements

218 The toxicity of feed and permeate samples was evaluated using the Microtox® LX
219 system (Modern Water, USA). In the Microtox® toxicity test, marine bacteria *Aliivibrio*
220 *fischeri* for evaluating the toxicity of substances are applied. The test is based on the decreasing
221 of bioluminescence of bacteria after exposure to the toxic factors (Ngwoke et al. 2021). In brief,
222 the idea of the test is as follows: 1) freeze dried cultures of *A. fischeri* were reconstituted and
223 their luminescence was measured, 2) then the bacterial culture was gently mixed with a sample
224 and incubated for 15 min, 3) the luminescence was read after 5 min and again after 15 min, 4)
225 the changes of luminescence intensity were given as a nominal % change value compared to
226 the luminescence measured in the control sample.

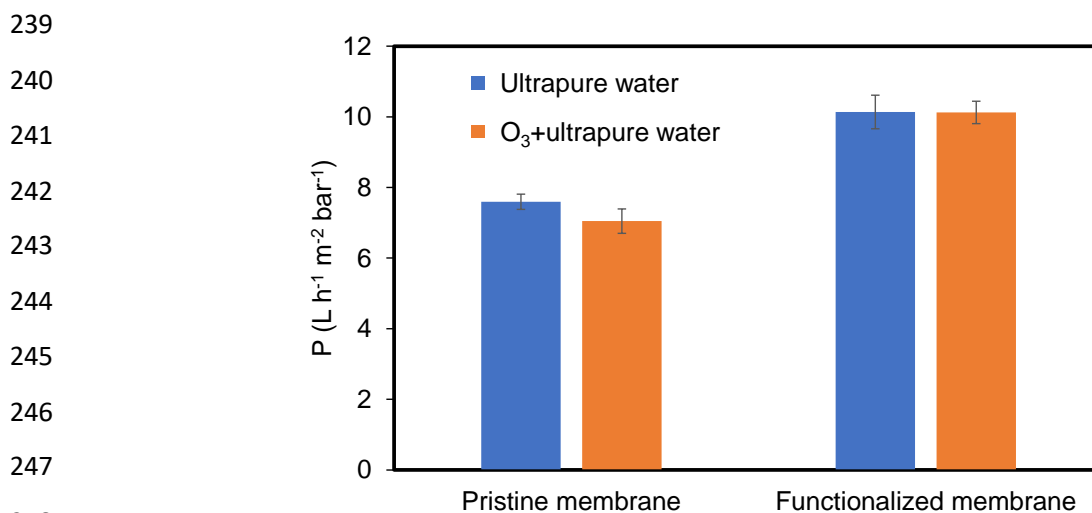
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228 3. Results and discussion

229 3.1. Permeability of the membranes

230 The water permeability of the both ceramic pristine and functionalized NF membranes
231 were determined to be 7.6 and 10.1 $\text{L m}^{-2} \text{h}^{-1} \text{bar}^{-1}$, respectively for pure water. During
232 application O_3 the permeability of pristine membrane slightly decreased to value 7.1 L m^{-2}
233 $\text{h}^{-1} \text{bar}^{-1}$, and in case of catalytic membrane there was no influence of ozone (Fig. 2). The
234 observed results could be related to the ozone consumption during the crossing through the
235 catalytic layer of the functionalized membrane (Mansas et al. 2020b). On the other hand,
236 the presence of ozone nanobubbles positioned indirectly next to the micropores of the TiO_2

237 layer of pristine membrane could cause pores blockage and, in results the decreasing of
238 permeance (Fig. 2).



249 Figure 2. Permeability of the pristine and functionalized membranes for pure water and with
250 ozone application.

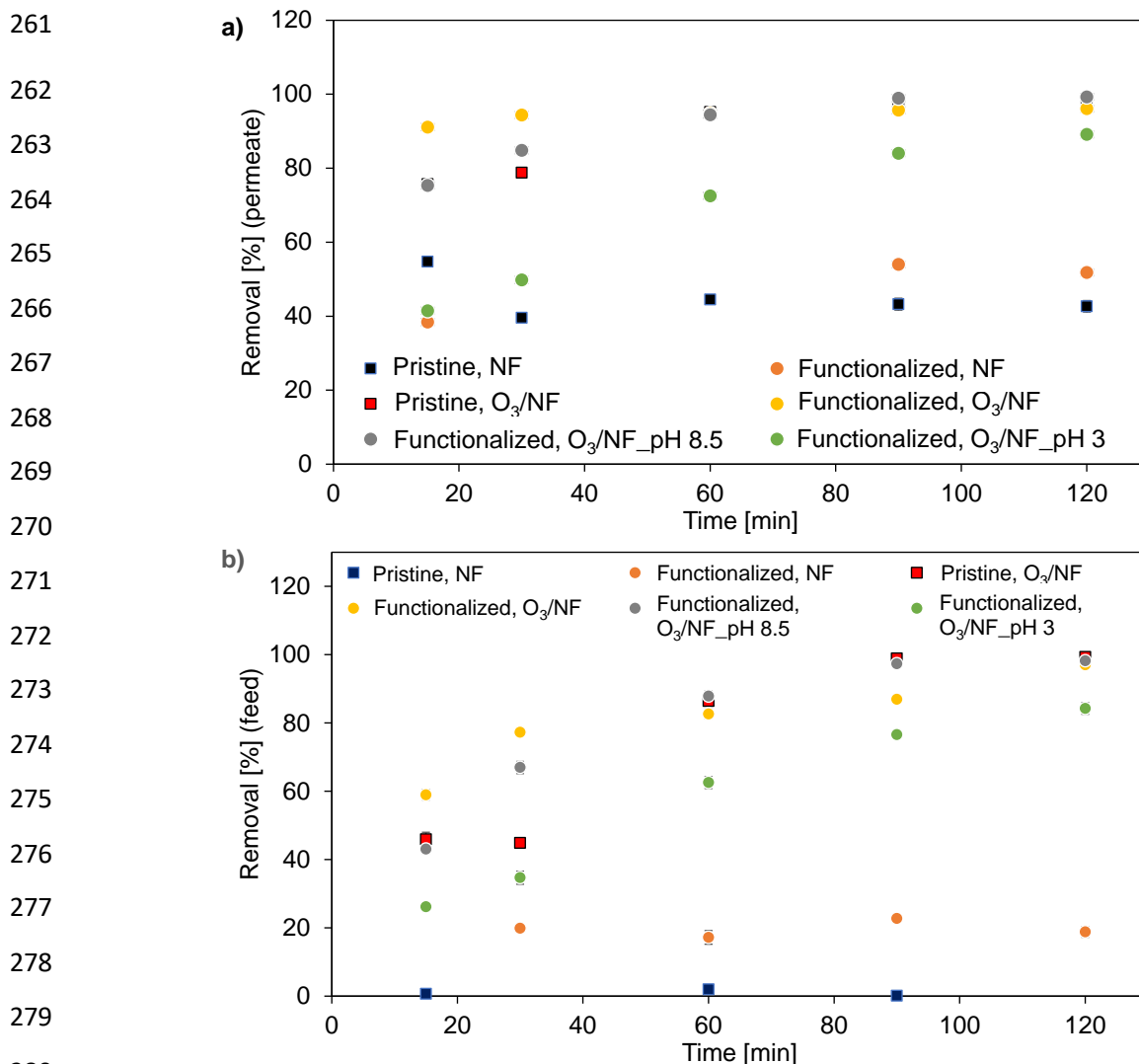
251

252 3.2. Ibuprofen removal

253 Before each NF process, the ibuprofen adsorption step (NF carried out with closed
254 permeate valve) was carried out for 2 hours. After this time, the permeate valve was opened
255 and, additionally, in the case of processes with ozone, the ozone generator was switched on.
256 Then, for the next 2 hours of the process, the removal of the model pharmaceutical in the
257 feed and permeate was assessed. The functionalized membrane was used in the experiments
258 at different pH. The results are presented in the Fig. 3 for various feed characteristics.

259

260



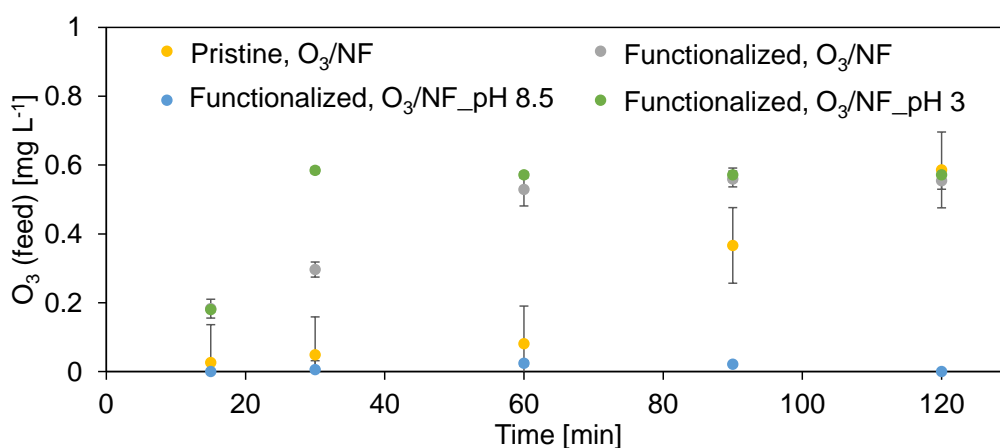
281 Figure 3. Effect of feed composition on the ibuprofen removal in the a) permeate and b) feed.
 282 Initial concentration of ibuprofen in the feed: 10 mg L⁻¹, transmembrane pressure: 10 bar.

283
 284 As a comparison, the **NF** processes were performed using both a pristine and a catalytic
 285 membrane. In this case, the pristine membrane separated the ibuprofen for about 40%, and the
 286 functionalized one, for more than 50% (Fig. 3a). The application of ozone led to remove the
 287 pharmaceutical after 90 minutes of the O₃/NF process in more than 90%, while after two hours
 288 of the process, almost complete removal of ibuprofen was noted, both for the pristine and
 289 catalytic membranes (Fig. 3a). It should be also emphasized that in the case of the catalytic
 290 membrane, the ibuprofen removal reached the result of 91% after the first 15 minutes from the
 291 start of the O₃/NF process, while at the same time for the pristine membrane it was equal to
 292 76% (Fig. 3a).

293 In the next stage of the research, the influence of the presence of inorganic salts in the
 294 feed and pH was analyzed. In the presence of salt and pH 3, the removal of the model
 295 pharmaceutical was significantly slower from the beginning of the process. After 15 min it was
 296 41% solely, and after 2 h of the process it was 89% using functionalized membrane. In turn, at
 297 pH 8.5, after the first 15 min of the experiment, the removal of IBU was almost two times higher
 298 (75%), and after 90 min it reached the value of 99% (Fig. 3a).

299 Considering the ibuprofen removal results in the feed (Fig. 3b), a similar removal trend
 300 for this pharmaceutical can be seen. Nevertheless, it should be emphasized that in the previous
 301 case the removal of IBU in the permeate was influenced by ozone and the membrane, while in
 302 the feed only by ozonation. Based on the results shown in the Figs. 3a and b it can be concluded
 303 that the main role in the ibuprofen removal was due to the ozonation process, however,
 304 membrane separation contributed to the quite high overall treatment efficiency.

305 Since the decomposition of ozone in solution to form OH radicals is highly pH
 306 dependent, the present results could find the explanation in the O₃ evolution during the process
 307 (Fig. 4). It is established that there is strong correlation between ozone decomposition in water
 308 and pH – it occurs faster with an increase of pH (Nawrocki and Kasprzyk-Hordern 2010). No
 309 changes of pH after adjusting the pH to 3 or 8.5 during the process were noted. In case of
 310 catalytic ozonation-NF experiment (O₃/NF) the pH was 6.5 and maintained constant during 2
 311 h.



321 Figure 4. Changes of dissolved ozone concentration in the feed during the process. Operation
 322 conditions: continuous ozonation, ozone gas concentration 11 g Nm⁻³.

323
 324 Generally, alkaline conditions during ozone oxidation of organic compounds are in
 325 favor of the indirect hydroxyl radicals forming (oxidation potential 2.80 V), and could be
 326 beneficial to the degradation of targets than acidic conditions (O₃ oxidation potential 2.07 V)

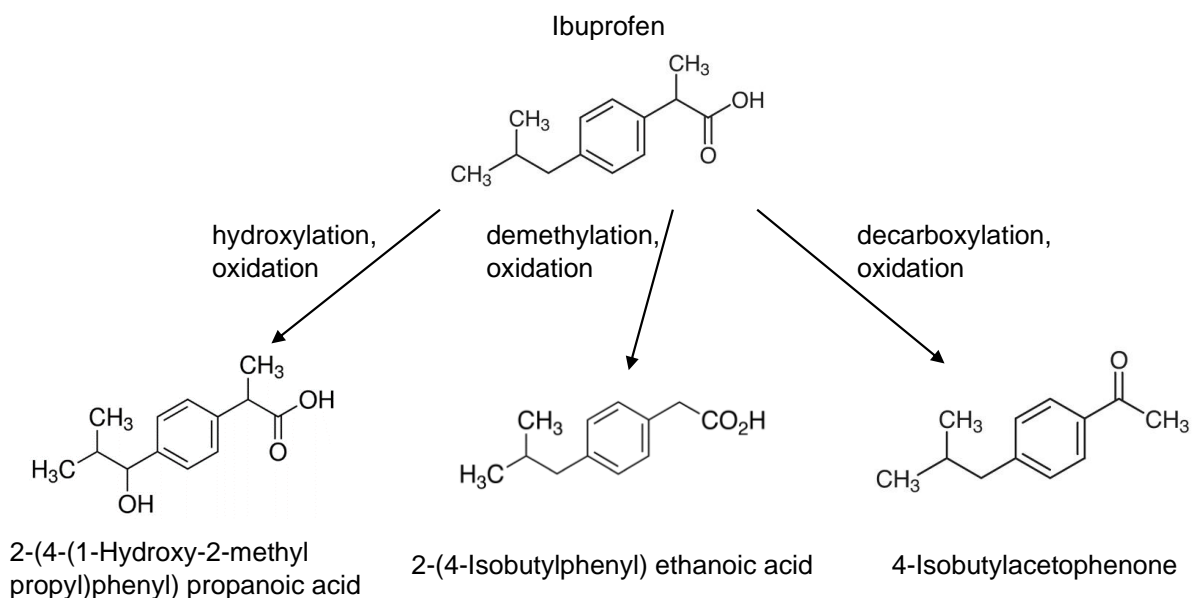
327 (Miao et al. 2015), what is reflected in the present investigations. When the pH increases, the
328 IBU decomposition enhancement is observed, since the larger amount of OH radicals is
329 generating, due to more OH anions forming on the catalytic membrane surface (Ejhih et al.
330 2010). Taking into account the results in the Fig. 4, it can be seen that the lowest O₃
331 concentration during the whole process carried out in the presence of salts under alkaline
332 conditions was noted. Considering the abovementioned ibuprofen removal results, it can be
333 concluded that from the first minutes of the experiment ozone was consumed for IBU
334 degradation (Fig. 3b) under these conditions. On the other hand, in the case of acidic pH, ozone
335 consumption was significantly slower (Fig. 4). It means, some small amount of O₃ was used for
336 hydroxyl radicals production. In turn, for catalytic membrane, a fast increasing of the ozone in
337 time was observed, due to high transfer of ozone to OH radicals and IBU decomposition. A
338 significantly slower ozone concentration increasing in case of pristine membrane was caused
339 by lower amount of hydroxyl radicals forming and not so fast using them for oxidation of
340 pharmaceutical. Catalytic ozonation, contrary to application of ozonation solely, enables the
341 formation of hydroxyl radicals also at a low pH (Nawrocki and Kasprzyk-Hordern 2010).

342

343 3.3. *By-products detected during the IBU degradation*

344 Reactions of ozone with ibuprofen led to formation of by-products and among them the
345 most probable are ketones, aldehydes and carboxylic acids (Ikhtlaq et al. 2015). A high number
346 of papers have reported the generation of some by-products of IBU upon the action of the OH
347 radicals generated during ozonation (Michael et al. 2014; Saeid et al. 2020; Huang et al. 2021;
348 Brillas 2022; Krakstrom et al. 2022). Three parallel oxidation pathways after initial degradation
349 of ibuprofen by •OH are possible: hydroxylation, demethylation and decarboxylation (Fig. 5)
350 (Brillas 2022). Additionally, they can interact with each other and create various by-products
351 (Brillas 2022). The obtained results revealed three intermediates, i.e. 2-(4-(1-Hydroxy-2-methyl
352 propyl)phenyl) propanoic acid formed during hydroxylation and further oxidation (Saeid et al.
353 2020), 2-(4-Isobutylphenyl) ethanoic acid (demethylation and further oxidation) (Michael et al.
354 2014), and 4-Isobutylacetophenone in result of decarboxylation and further oxidation (Fig. 5)
355 (Huang et al. 2021). The molecular masses of the identified by-products are as follows: 221.12
356 Da, 193.12 Da and 177.13 Da, respectively.

357



358 Fig. 5. Ozonation pathways and by-products of ibuprofen during hybrid O₃/NF process.

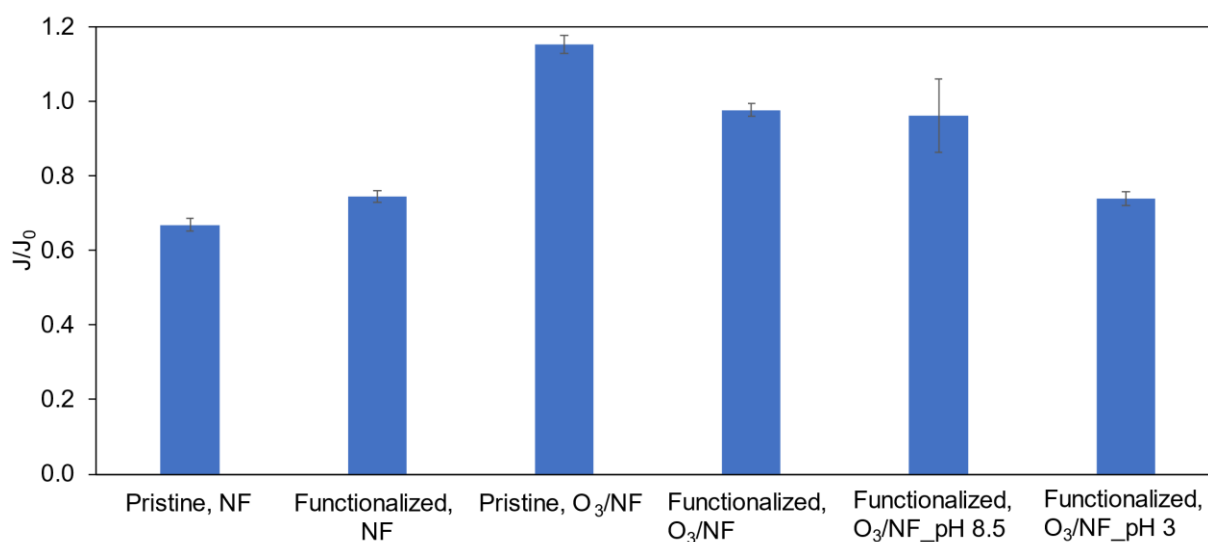
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360 Determination of intermediate decomposition products is very important from practical
 361 point of view, since the oxidation of organic compounds in many cases led to formation more
 362 complex and toxic compounds than the initial pollutants (Miralles-Cuevas et al. 2017). These
 363 compounds can reduce the efficiency of the NF process and/or affect the toxicity of the
 364 permeate (Miralles-Cuevas et al. 2017). These issues are discussed in the further paragraphs.

365

366 3.4. Membrane performance during IBU removal

367 The idea of proposed system, i.e. the hybrid ozonation-NF process, was the degradation
 368 of ibuprofen by ozonation and the separation of the products decomposition by the membrane
 369 in order to obtain a purified product (permeate). Nevertheless, intermediates formed during the
 370 process and undecomposed IBU could effectively block the pores of the membrane, thus
 371 reducing the efficiency of the filtration process was observed (Karnik et al. 2005). Figure 6
 372 presents the normalized permeate flux decline after 2 h of removal of the model PhAC
 373 depending on the feed composition and pH.



374

375 Figure 6. Normalized permeate flux decline after 2 h of removal of the ibuprofen depending on
 376 the feed composition and pH.

377

378 The largest decrease of the permeate flux was measured in the case of **NF** with the using of
 379 pristine membrane, probably due to blocking the pores of the membrane by IBU molecules
 380 presented in the feed. Interestingly, a slight increase in the permeate flux was also observed for
 381 this membrane during ozonation. It could be caused by the electrostatic interaction between the
 382 PhAC molecules and the hydrophilic surface of the pristine membrane, which separation layer
 383 was made of TiO₂ (Zhao et al. 2018; Hossain et al. 2019). On the other hand, in the case of **NF**
 384 of the ibuprofen solution through a functionalized membrane, a decrease in the permeate flux
 385 by 25% after 2 hours of the process was observed. During catalytic ozonation, the flux
 386 practically did not decrease (only 2% after 2 h) (Fig. 6), which was reflected in the
 387 decomposition of ibuprofen from the beginning of the experiment (Fig. 3b). A slight decrease
 388 could have been influenced by the residual undecomposed ibuprofen or the intermediate
 389 products of catalytic ozonation. Since the catalyst was coated on ceramic membrane for
 390 simultaneous proceeding of catalytic ozonation and membrane separation process, the
 391 membrane foulants could be timely decomposed before their accumulation on the membrane
 392 surface or within its pores (Zhang et al. 2016). In the presence of salt (pH 8.5) the decrease of
 393 the permeate flux was negligible as well (4% after 2 h). On the other hand, during the removal
 394 of ibuprofen at the feed pH of 3, a 26% decrease in the permeate flux was noted after 2 h of the
 395 experiment (Fig. 6). These results were also reflected in the degree of decomposition of the
 396 model PhAC. Moreover, the obtained results may also be the result of electrostatic interactions

397 between ibuprofen molecules and the membrane surface. It is well established that, the pH of
398 the solution is a crucial parameter which has a significant effect on the $\cdot\text{OH}$ formation and
399 organic pollutant properties related to decomposition (Dalrymple et al. 2007). Since the pH was
400 adjusted at 8.5, the IBU degradation increased, due to the formation higher amount of OH
401 radicals, whereas the reverse situation occurred for pH 3 (Kezzim et al. 2017). And this, in turn,
402 was reflected into the values of the observed permeate flux.

403 It is worth noting that the membrane did not reject inorganic salts presented in the
404 feed due to their lower molecular weights than MWCO of NF membrane applied in the
405 experiments (200 Da). Initial conductivity of the feed solution was about 1720-1732 $\mu\text{S cm}^{-1}$
406 for samples with inorganic salts both at pH 3 and 8.5. After 2 h of process in the permeate
407 conductivity varied from 1918 to 2215 $\mu\text{S cm}^{-1}$ and in the feed was 1952 - 2287 $\mu\text{S cm}^{-1}$. The
408 higher value of the feed and permeate conductivity in relation to the treated solution was most
409 likely due to the presence of intermediate products of ibuprofen decomposition. Such low salts
410 rejection, expressed in a high conductivity, by ceramic NF membrane was obtained as well by
411 Fujioka et al. (Fujioka et al. 2018).

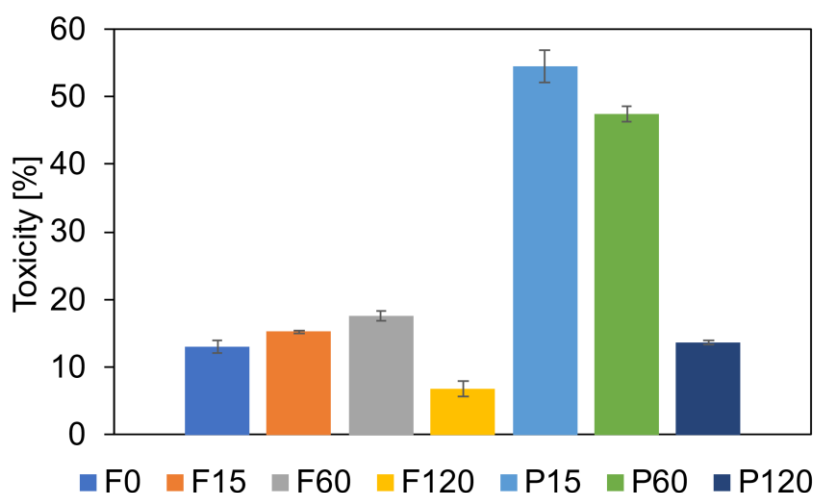
412

413 3.5. Ecotoxicity study during IBU removal

414 Toxicity testing is a very important method to evaluate the effectiveness of treatment
415 technologies. The solutions exhibit different toxicity effects expressed by microorganisms
416 mortality rate. The Microtox® test applied in this experiment is a well-established test
417 measuring the acute toxic impact on the bacteria *Aliivibrio fischeri*. The exposure time of the
418 bacteria with the samples was 15 min and the luminescence analysis was then performed. The
419 toxicity evolution was expressed in terms of percentage of luminescence inhibition. The
420 samples for which the results are less than 20% are considered as non-toxic, between 20 and
421 50% as low-toxic, and above 50% as toxic (Persoone et al. 2003). In case of the treated solutions
422 under acidic pH and in the presence of inorganic salts all samples were characterized as toxic
423 regardless of process time (99.99% of toxicity) (data not presented). The obtained results were
424 caused by such low pH. The most common stressor, which had an impact on the
425 microorganisms is high osmotic pressure of the feed. In the acidic environment the wall cell of
426 bacteria was disrupted and bacteria cell died, what affected on the observed toxicity.
427 In turn, in the present of salts under alkaline conditions the initial feed did not exhibit toxicity
428 (13%) (Fig. 7). During the O_3/NF process some increasing of toxicity of treated feed was noted,
429 nevertheless the samples still were non-toxic. After 15 and 60 minutes the toxicity was 15 and
430 18%, respectively. Finally, at the end of the process toxicity of F120 sample was two times

431 lower than F0, i.e. 7 vs. 13% (Fig. 7). Opposite situation for permeates was noted. The permeate
 432 after 15 minutes exhibited high toxicity (54%). The applied treatment led to decrease of the
 433 permeate toxicity to about 47% after 60 minutes of the experiment (Fig. 7). These results
 434 indicate that the presence of the other feed components, i.e. by-products, which passed through
 435 NF membrane affected the toxicity values (Quero-Pastor et al. 2014; Miralles-Cuevas et al.
 436 2017). The course of changes of mortality suggests that although the efficiency of degradation
 437 was high (Fig. 3b), the formation of by-products of oxidation was still faster than their complete
 438 removal. Finally, at the end of the process treatment the permeate (product of treatment process)
 439 was characterized as non-toxic. The toxicity was the same like in case of the initial feed
 440 solution. The ecotoxicity of IBU (10 mg L^{-1}) towards alga *Selenastrum capricornium* cultures
 441 and for optimal pH (8.5-9) and stirring of the system for 20 min during ozonation was studied
 442 by Quero-Pastor et al. (Quero-Pastor et al. 2014). No toxic effect of PhAC on the model
 443 organism was noted at the beginning of the treatment process. However, after the stirring and
 444 pH adjustment, the percentage inhibition visible increased, in results of formation of hydroxy-
 445 ibuprofen metabolite. Moreover, at concentration of IBU 10 mg L^{-1} , a higher toxicity due to
 446 oxidative process proceeding was found (Quero-Pastor et al. 2014).

447



448

449 Figure 7. Toxicity of treated solution during hybrid catalytic ozonation-NF process under pH
 450 8.5 and in the presence of inorganic salts. F0 - initial feed, F15, F60, F120 - feed samples
 451 collected after 15, 60 and 120 minutes of the process, P15, P60, P120 - permeate samples
 452 collected after 15, 60 and 120 minutes of the process.

453

454 3.6. Economic aspects of IBU removal in the O_3/NF system

455 The cost of proposed treatment process is mainly related to the energy of ozone
456 generation and NF. Nevertheless, it should be emphasized that the costs of novel treatment
457 technologies depend mostly on the type of process and design configuration proposed, therefore
458 it is difficult to compare the costs of various technologies properly. For instance, the application
459 of O₃ at low doses is economically effective and less expensive than Granular Activated Carbon
460 (GAC) (Pistocchi et al. 2022). The ozonation is considered as a promising method for increasing
461 the efficiency in microbial load and pharmaceutical reductions with moderate treatment costs
462 (Zagklis et al. 2022). For ozonation systems it was reported that the cost of treatment of 1 m³
463 of secondary effluent is 0.03 EUR (Chys et al. 2018, Zagklis et al. 2022). According to Choubert
464 et al. (Choubert et al. 2017) in France it is 0.1-0.2 EUR m⁻³ depending on the size of the plant,
465 operating conditions and the supply chain of reagents. In some publication it was reported that
466 the energy consumption (kWh) of catalytic ozonation and filtration in the cross flow system for
467 Lake Lansing water was 3.032*10⁻³ and 6.2*10⁻⁴, respectively, calculated for 1000 L of treated
468 water with O₃ dose of 20 µg s⁻¹ (Wang et al. 2017b). Taking into the calculation the price of 1
469 kWh as 0.2126 EUR (mean price in Europe), the cost of such system is 0.0008 EUR m⁻³.
470 Assuming the energy consumption of 0.3 kWh m⁻³ of treated water in case of ozonation and 1
471 kWh m⁻³ for NF (Rizzo et al. 2019), the presented hybrid O₃/NF system required 0.0011 EUR
472 m⁻³. This cost is lower than the values reported in the abovementioned literature (Choubert et
473 al. 2017, Chys et al. 2018, Zagklis et al. 2022), however, it must be noted that the system was
474 not optimized and the investigations were carried out in the laboratory scale installation. Such
475 low value could also result from using functionalized catalytic membrane, which significantly
476 improved decomposition efficiency (Pistocchi et al. 2022). For comparison, Zagklis et al.
477 (Zagklis et al. 2022) stated that chlorination and UV irradiation are characterized by the lowest
478 treatment costs (0.004 EUR m⁻³). The cost of photocatalytical TiO₂/UV treatment of 1 m³ of
479 water containing 0.8 mg L⁻¹ total organic carbon was 0.44 USD, whereas in case of 8.0 mg L⁻¹
480 total organic carbon it was 0.81 USD (Basile et al. 2018). On the other hand, the cost of phenol
481 degradation, calculated on a basis of degradation rate constants, was significantly higher, i.e.
482 2285 USD m⁻³, than that of trichloroethylene degradation (3.99 USD m⁻³) (Basile et al. 2018).
483 In case of membrane bioreactors (MBR) the treatment cost varied from 0.10 to 0.68 USD m⁻³
484 (Gao et al. 2022). A ketoprofen decomposition in a submerged photocatalytic membrane reactor
485 generated cost of 13-24.4 USD m⁻³ order⁻¹, depending on applied conditions (Szymański et al.
486 2023c).

487

488 *3.7. A comparison of proposed system with other techniques dedicated to IBU removal*

489 The literature survey reported other techniques dedicated to IBU removal. Among them
490 there are photolysis (Yan and Song 2014), non-thermal plasma treatment (Zeng et al. 2015),
491 UV/H₂O₂ (Liu et al. 2017) and UV/O₃ (Mehrjouei et al. 2020) hybrid processes, Fenton (Zhang
492 et al. 2019), membrane separation processes (Ganiyu et al. 2015, Arefi-Oskoui et al. 2019) as
493 well as adsorption (Silva et al. 2023). It was found that the application of single non-thermal
494 plasma treatment led to quite fast IBU degradation (91.7% in 80 min), however, the
495 mineralization was very low (ca. 30%) (Zeng et al. 2015). In general, the main drawback of
496 such technology is low ability to mineralize ibuprofen and its by-products. Shu et al. (2013)
497 studied the degradation of IBU in concentration of 10-40 mg L⁻¹ with addition of 25 or 50 mg
498 L⁻¹ H₂O₂ at neutral pH in the reactor equipped with an inner Hg lamp (200-320 nm). By
499 increasing of hydrogen peroxide concentration, the ibuprofen removal was 1.6-fold greater.
500 Nevertheless, H₂O₂ due to its strong reactive potential creates a high toxicity of treated solution
501 (Szymański et al. 2018b). A hybrid O₃/H₂O₂ system is the most widely investigated among
502 hybrid ozonation techniques, despite high toxicity of reagents (Mehrjouei et al. 2020). It has
503 been applied for pure and natural waters, hospital wastewater and wastewater treatment plant
504 effluents (Brillas 2022). The first recognized research involving O₃/H₂O₂ system for IBU
505 removal is work of Zwiener and Frimmel (2000). They treated 2 µg L⁻¹ of ibuprofen in pure
506 water and river water (total organic carbon concentration was 3.7 mg L⁻¹) and pH 7.5 by
507 application of 0.4-1.8 mg L⁻¹ of H₂O₂ and tank reactor under continuous supply of 1-5 mg O₃
508 L⁻¹. After 10 min of ozonation, 99% of ibuprofen removal was achieved for 1.8 mg H₂O₂ L⁻¹
509 and 5 mg O₃ L⁻¹. In order to remove ibuprofen Fenton-based processes were applied as well.
510 However, they have two main drawbacks, i.e. process optimum at pH near 3 and generation of
511 a large amount of sludge rich in iron hydroxides, which requires post-treatment step
512 (Chehrenegar et al. 2016). An interesting and novel technique of IBU removal based on
513 adsorption has been proposed by Silva et al. (Silva et al. 2023). External magnetic field caused
514 the adsorption of IBU on magnetic beads of alginate/polypyrrole/ZnFe₂O₄ (Alg/PPy/ZnFe₂O₄)
515 in the amount of 108.2 mg g⁻¹ in 70 min. Despite high efficiency of this method, there is a
516 necessity of adsorbent regeneration. Our research group investigated a photocatalytic
517 membrane reactor utilizing membrane distillation, equipped with capillary polypropylene
518 membrane in order to remove the ibuprofen, naproxen and diclofenac from water or wastewater
519 (Mozia et al. 2016). It was found that the efficiency of the treatment process was strictly
520 dependent on the feed composition, and the key factors that influenced the photodegradation of
521 the IBU were inorganic ions, organic compounds and turbidity.

522 The method described in this article is undoubtedly very effective for removing
523 ibuprofen (99% after 15 min) and obtaining a non-toxic permeate. In addition, the simultaneous
524 conducting of catalytic ozonation and NF significantly reduces the time needed for its removal.
525 Nevertheless, tests with a real matrix are required.

526 All applied treatment technologies depend on the feed matrix and required degree of
527 purification. Then, the type of process and design configuration are proposed. Hence, the
528 comparison of the technologies and clear indication of the best method for ibuprofen removal
529 is complex.

530

531 **Conclusions**

532 A removal of ibuprofen in a hybrid ozonation-NF system equipped with catalytic
533 ceramic membrane was investigated. The permeability of the pristine and functionalized
534 membranes were determined to be 7.6 and 10.1 L m⁻² h⁻¹ bar⁻¹, respectively for pure water. The
535 application of ozone caused slight decrease of pristine membrane permeability to value 7.1 L
536 m⁻² h⁻¹ bar⁻¹, and for catalytic membrane no influence of O₃ was observed. It was found that
537 high effectiveness of decomposition of pharmaceutical occurred even in the present of inorganic
538 salts and pH 8.5. During the first 15 min of the experiment, the removal of IBU was equal to
539 75%, and after 90 min it reached the value of 99%. Significantly lower degradation of ibuprofen
540 under acidic pH was observed, i.e. 41% and 89%, after 15 min and 120 min, respectively. This
541 was associated with the low amount of OH radicals formed from ozone. The highest permeate
542 flux decline was noted in the presence of salts and at pH 3 as well (26% after 2 h of process).
543 Under alkaline conditions and in the absence of salts the flux decreasing was negligible due to
544 fast decomposition of ibuprofen (4% and 2%, respectively). In case of the process with
545 inorganic salts and under pH 8.5 the O₃ consumption was the highest during whole time. Three
546 by-products, i.e. 2-(4-(1-Hydroxy-2-methyl propyl)phenyl) propanoic acid, 2-(4-
547 Isobutylphenyl) ethanoic acid and 4-Isobutylacetophenone were detected during ozonation,
548 which had an influence on the acute toxicity towards *Aliivibrio fischeri*. The initial feed was
549 assigned as non-toxic. The applied treatment resulted in an increase of toxicity in the case of
550 permeate, which was attributed to the formation of more intermediates, which passed through
551 the membrane upon NF. Nonetheless, it was found that the product of O₃/NF process (i.e.
552 permeate) was non-toxic at the end of the process (after 2 h). Finally, it can be concluded that
553 the hybrid ozonation-NF system thanks to synergistic effects induced by contaminant oxidation
554 and rejection using catalytic ceramic membrane showed excellent performance towards the
555 elimination of ibuprofen, promoting its efficient removal (98%) and also decreasing its toxicity.

556 This configuration will be tested with a real wastewater treatment plant effluent so as to deeply
557 investigate the beneficial effect of this coupling on fouling dynamics.

558 The results in the present manuscript demonstrated that proposed O₃/NF system can be
559 considered as useful for ibuprofen removal. Nevertheless, further studies are still needed before
560 taking advantage of their potentiality at industrial level. First of all, the investigations with
561 application of real matrices should be considered and economical assesment of proposed system
562 in a pilot plant scale should be carried out. Coupling of catalytic ozonation and NF process is a
563 promising solution, due to the potential rejection of small molecules and fast degradation of
564 organic compounds, including by-products, with a very good membrane performance. Despite
565 the fact that ceramic membranes are more expensive than organic ones, they are characterized
566 by high potential for catalytic ozonation, since they exhibit strong resistance to ozone and a
567 catalytic layer could be easily deposited on their surface. Future work should be focused as well
568 on finding the optimal conditions of the process in order to reduce the treatment costs, especially
569 related to the using of low amount of ozone. It could be obtained e.g. by application of the
570 ozonation contactor.

571

572 **Ethical Approval**

573 Not applicable

574

575 **Consent to Participate**

576 Not applicable

577

578 **Consent to Publish**

579 Not applicable

580

581 **Availability of data and materials**

582 The datasets used and/or analysed during the current study are available from the corresponding
583 author on reasonable request.

584

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748 **Competing Interest**

749 The authors declare that they have no known competing financial interests or personal
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751

752 **Author contributions**

753 Kacper Szymański: conceptualization, designed the experiments, conducted the research and
754 analysed the data, funding acquisition, writing and editing; Sylwia Mozia: conceptualization,
755 revised the project; Andre Ayrál: review and editing; Stephan Brosillon: review and editing;

756 Julie Mendret: supervision, writing, review and editing. All authors read and approved the final
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