# Towards the circular economy – sustainable fouling mitigation strategies in ultrafiltration of secondary effluent

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- 21 Abstract

Membrane separation is an emerging technology for secondary effluent (SE) recycling 22 23 as an alternative water source. However, SE contains secondary metabolites which form a film on membrane surfaces, leading to a decrease in hydraulic capacity. This is 24 an extensive study of the effect of fouling on UF performance, with a detailed analysis 25 of foulants composition and morphology, and the evaluation of the most effective -26 either physical or chemical – UF membrane regeneration methods. The paper also 27 investigates FNA (recycled from WWTPs) as an alternative acidic UF membrane 28 cleaning agent. In the UF-DE mode, the most effective backwashing configuration was 29 1s every 1min, where relative membrane permeability decreased by 54% after 4-h, 30 31 which indicated the presence of physically irreversible fouling after SE separation. An acidic-alkaline cleaning procedure in which the contribution of irreversible fouling was 32 13% resulted in a 100% efficiency of UF membrane regeneration. The results 33 confirmed that recycled FNA is as efficient as pure reagent-nitric acid V and that the 34 use of FNA can reduce the costs of chemical cleaning by 60%. To fit in with the idea 35 of the circular economy, we proposed a new strategy of reusing spent acidic solutions 36 as an alternative fertilizer. 37

## 38 **1. INTRODUCTION**

In recent years, the recovery of water and nutrients from wastewater, especially 39 secondary effluent (SE), has become one of the world's important parts of water 40 resource management [1,2]. Several water reclamation systems have been developed, 41 of which membrane processes recognized as energy-saving technology are the most 42 promising. The technology is efficient, helps to produce high-quality, is reagents-free, 43 and is easy to scale-transfer [3–5]. The use of multi-stage pressure-driven membrane 44 processes in the treatment of SE enables the production of water of varying qualities 45 irrigation (after ultrafiltration) to drinking standards 46 ranging from (after

ultrafiltration(UF)-nanofiltration(NF)-reverse osmosis(RO)) [2]. This dependence on 47 the hydrological conditions in a particular region makes it possible to overcome the 48 water deficit. Although these technologies offer so many benefits, membrane fouling 49 reduces membrane lifetime, thus increasing the plant's operating costs. This problem 50 mostly concerns the multi-stage, low-pressure membrane processes, such as 51 ultrafiltration (UF), the first stage of the SE treatment, where the pollutants, such as 52 colloids, organic substances, microorganisms, or inorganic substances, can 53 accumulate/adsorb not only at the UF membrane surface (reversible fouling) but can 54 also penetrate the pores (physically irreversible fouling) [6,7]. Since the removal of 55 these foulants in the UF process produces water for irrigation and significantly reduces 56 57 the membranes fouling on the further stages of the water purification [2], the optimization of the UF membrane cleaning method, including physical and chemical 58 ones, seems to be crucial to ensure the continuity of the membranes operation. 59

Mechanical cleaning – mainly hydraulic backwashing – is the commonest method for restoring membrane performance in the case of reversible fouling as it does not require a complete shutdown of the process [8,9]. It is only when mechanical removal is not sufficient that *in-situ* and *ex-situ* chemical cleaning procedures are used [10,11].

In pilot-scale installations, membranes are often backwashed with permeate streams [12,13], which usually undergo two stages of purification before they are used for backwashing. Sand filter filtration [14], coagulation [12,15], adsorption with powder activated carbon (PAC) [16], or  $O_3$  aeration [17] are some of the most used UF pretreatment methods. Still, the membrane usually requires both physical and chemical cleaning as these additional pretreatment stages are not sufficient, making it crucial to optimize both cleaning procedures, especially since there are no studies on

the effect of backwash only on ultrafiltration membranes fouling during the treatmentof SE.

The efficiency of backwashing is influenced by several factors, such as the content and 73 74 type of wastewater [13,18-21], the flow type of ultrafiltration [22], the class of membrane materials, and backwash configuration [23]. Most of the research concerns 75 backwashing performance on ceramic rather than polymeric membranes [24]. 76 Nowadays, the latter is more widely used for water treatment due to the low cost, a 77 wide variety of pore sizes, and easy processing [25]. Typically, only one backwash 78 configuration is tested [21,26,27], while studies with more than one are much rarer 79 [15,28,29]. As there are no studies related to short times and frequency of 80 backwashing, it would be necessary to check how such configurations would affect 81 ultrafiltration in a dead-end (DE) and cross-flow (CF) without SE pre-treatment. 82

Depending on the type of membrane material and pollutants causing physically 83 irreversible fouling, the chemical cleaning solutions usually contain acids (most 84 commonly used are: nitric acid V, citric acid, sulphuric acid, hydrochloric acid, or 85 phosphoric acid) [30-33], alkalines (NaOH with the addition of NaOCI and EDTA) 86 [10,34–36] or enzyme cocktails [37]. A properly selected chemical cleaning solution 87 sequence can regenerate membrane performance by almost 100% [38,39]. In modern 88 water supply systems, the selection of a chemical cleaning method ought to be cost-89 effective, and more environmentally friendly. 90

In the wastewater treatment plant (WWTP), free nitrous acid (FNA) can be produced *in-situ* through the nitritation of anaerobic sludge digestion liquor [40], which not be a solution to the problem of high ammonia concentrations in municipal and industrial wastewater [41]. Hence a better understanding of FNA biocidal and inhibitory activity against microorganisms has led to developing new FNA-based applications that

improve wastewater management technologies [42]. A few of them dedicated to 96 membrane-based processes were mainly concerned with biofouling and scaling 97 removal of RO and FO membranes [42-45]. Its potential in a pilot-scale CIP of 98 ultrafiltration membrane has not been investigated. Although UF and RO belong to the 99 same membrane separation category (pressure-driven processes), they separate 100 different contaminants, leading to different fouling forms [46,47]. Unlike RO, the UF 101 102 membrane, used in the first stage of the pressure-driven membrane processes, is more exposed to biological and organic foulants, including active sludge and its metabolites. 103 UF and RO are governed by dissimilar separation mechanisms, hence the resultant 104 105 non-identical fouling processes. Besides, FNA shows strong biocidal activity towards biofilm, which is expected in UF rather than in RO during multi-stage pressure-driven 106 membrane processes in the SE treatment. All those differences suggested that the 107 108 effectiveness of FNA in the cleaning of UF membranes is not to be taken for granted and requires a detailed study. 109

110 The circular economy package presented by the EU calls on to search for innovative disposal and treatment technologies and approaches. So far, several strategies to 111 recycle alkaline and chlorine cleaning solutions have been reported, including 112 membrane separation [48,49]. None of them have dealt with acidic membrane 113 cleaners, which are usually disposed of in the sewage system although these by-114 products contain valuable macroelements such as nitrogen in the most bioavailable 115 form of nitrates and nitrites, carbon from humic acids (organic biostimulants), and other 116 micronutrients that could be reused for fertigation. Such a simple waste management 117 118 solution constitutes a promising approach towards sustainable development and the circular economy. 119

In the present study, we have developed a novel strategy for effective UF membrane 120 regeneration after SE separation, which combines the FNA or nitric acid V-based 121 chemical cleaning and backwashing with the simultaneous reusing of waste-washing 122 streams. After an in-depth analysis of the membrane sludge composition and 123 morphology, we recognized crucial compounds which influence the most membrane 124 fouling during UF pilot treatment of real secondary effluent. Physical and chemical 125 methods to reduce fouling have been proposed including six backwashing 126 configurations each in the dead-end (DE) and cross-flow (CF) mode, and six chemical 127 cleaning approaches in the following configurations: acid-alkaline, alkaline-acid and 128 129 alkaline-enzyme-acid. Our reagents included nitric acid V [50], sodium hydroxide, sodium hypochlorite [32,51], and Filzym P1, the commercially available enzyme. This 130 study investigates for the first time FNA as an effective membrane cleaning agent after 131 ultrafiltration of secondary effluent. As a result, we propose the use of heavy metals-132 free acid washings containing valuable micro- and macroelements (N, P, and Mg) and 133 humic substances as a growth stimulator for radish sprouts. Our findings provide new 134 insights into UF membrane regeneration and by-stream recycling after SE separation 135 and correspond to circular economy assumptions. 136

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## 2. Materials and methods

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# 2.1. Characteristics of secondary effluent

The research was conducted on the actual stream of secondary effluent from the Janówek Wastewater Treatment Plant in Wrocław, Poland, which is a treatment plant of 1 000 000 population equivalent (p.e.) with full removal of nutrients carried out by the three-phase activated sludge technology. Average parameters of wastewater from February 2020 to April 2020 along with applied measuring methods are presented

- in Table 1. All measurements were repeated at least seven times, and average values
- 145 ± standard deviations were calculated.
- 146 Table 1. Characteristic composition of treated wastewater; \*a detailed description of
- the analytical methods is provided in the Supplementary Material.

Parameter	Unit	Value	Measuring method*
			spectrophotometry using
COD	mg∙L⁻¹	28.11±7.84	HACH's cuvette tests
	-		(HachLange, USA)
TOC	ma   -1	6 72 1 40	using TOC-L CSH with ASI-L
100	ing•∟ '	0.73±1.40	autosampler
Humic	ma I -1	2 05 10 41	extraction of humic substances
substances (HS)	ing•∟ •	2.05±0.41	with pentanol
Ptotal	mg∙L⁻¹	0.50±0.29	
P-PO4 <sup>3-</sup>	mg∙L⁻¹	0.34±0.24	
Ntotal	mg∙L <sup>-1</sup>	9.48±1.71	
N-NO <sub>2</sub> -	mg∙L <sup>-1</sup>	0.077±0.024	
N-NO₃⁻	mg∙L <sup>-1</sup>	5.49±1.16	
N-NH4 <sup>+</sup>	mg∙L <sup>-1</sup>	0.87±0.77	spectrophotometry using
<b>SO</b> 4 <sup>2-</sup>	mg·L <sup>-1</sup>	101±12	HACH'S CUVELLE LESIS
Cl-	mg L <sup>-1</sup>	163±15	(HachLange, USA)
Ca <sup>2+</sup>	mg L <sup>-1</sup>	75.5±12.2	
Mg <sup>2+</sup>	mg L <sup>-1</sup>	15.07±2.82	
Ă	mg·L <sup>-1</sup>	0.015±0.002	
В	mg∙L <sup>-1</sup>	0.111±0.007	
	0		using a pH-meter with a
рН		7.14±0.17	combined electrode (Elmetron,
·			Poland)
			using the multifunction
Conductivity	µS₊cm⁻¹	1190±23	instrument with conductivity
			probe (HACH, USA)
Turbidity	ΝΤΠ	1 77+1 69	using a turbidity meter (HACH,
Turblatty	NIU	4.77±1.00	USA)
			spectrophotometry using
Hardness	mgCaCO₃·L⁻¹	249±43	HACH's cuvette tests
			(HachLange, USA)
Alkalinity	mgCaCO₃ L⁻¹	204 <b>±</b> 28	according to ISO 9963-1:1994
TSS	mg·L <sup>-1</sup>	7.87±3.63	by the weighing method
As	mg L <sup>-1</sup>	<0.01	
Ba	mg•L <sup>-1</sup>	0.01	inductively coupled plasma
Cd	mg L <sup>1</sup>	<0.01	optical emission spectrometry
Ca	mg L <sup>1</sup>	70.4	(ICP-OES. Thermo Scientific
Cr	mg L	< 0.01	iCAP 7400 Duo)
Co	mg L 1	< 0.01	
Cu	mg∙L⁻¹	0.03	

Fe	mg∙L <sup>-1</sup>	0.05
Pb	mg∙L <sup>-1</sup>	<0.01
Mg	mg∙L <sup>-1</sup>	15.8
Ni	mg∙L <sup>-1</sup>	<0.01
Р	mg∙L <sup>-1</sup>	0.09
K	mg∙L <sup>-1</sup>	29.9
Na	mg∙L <sup>-1</sup>	102
S	mg∙L <sup>-1</sup>	42.2
 Zn	mg∙L <sup>-1</sup>	0.04

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2.2. 149

# **Membrane specification**

We used a commercially available W05-VC asymmetric, hydrophilic hollow fibre (Liqui-150 Flux<sup>®</sup>, USA), inside-out ultrafiltration membrane with an active layer made of 151 polyethersulfone, with an inner diameter of 0.8 mm and an active filtration area of 8.7 152 m<sup>2</sup>, and with a typical filtration flux range from 50 L·h<sup>-1</sup>·m<sup>-2</sup> to 150 L·h<sup>-1</sup>·m<sup>-2</sup>. The 153 membrane is stabilized by a spacer yarn (proprietary multifibre P.E.T. technology) 154 which is twisted around and potted with hollow fibres. The cut-off of the membrane is 155 80 kDa. The membrane can work in a dead-end (DE) and cross-flow (CF) modes with 156 a maximum working pressure of 6 bar, maximum working temperature of 40°C, and a 157 cleaning pH range of 1-13. 158

#### 159

2.3.

## The installation and conduct of experiments

160 Experiments were carried out on a fully automated pilot-scale installation located at the Wrocław Wastewater Treatment Plant. The scheme of the installation is shown in 161 Figure.1. 162



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Figure 1. Technological scheme of the installation: 1 - feed tank (secondary effluent),
2 - UF membrane module, 3 - CIP tank, 4 - retentate tank after UF and backwash tank,
5 - permeate tank after UF.

UF started with filling the feed tank (1) with secondary effluent. Then, using a pump, 167 the liquid was delivered to the UF membrane (2). UF was carried out at an initial 168 membrane pressure of 2 bar for cross-flow processes and 4 bar for the dead-end 169 mode. The operating parameters were selected based on previous research presented 170 171 in [2]. The permeate stream was directed to the UF permeate tank (5), while the retentate generated in the cross-flow mode was directed to the UF retentate tank (4). 172 The system was equipped with an additional pump for backward flushing that returns 173 a defined volume of permeate from the UF permeate tank (5) to the membrane module. 174 The following backwash configurations were investigated: 1 s every 1 min and every 5 175 min, 5 s every 5 min, 25 s every 5 min, and every 25 min; and experiments without 176 backwashing were conducted for comparison. The backflush washings were directed 177

to the UF retentate tank (4). Single UF was typically run for 4 h, except for a few in CF
where a significant decrease in flux was presented during the 14 h processes. During
backwashing, the initial pressure for cross-flow and dead-end was 2 bar and 4 bar,
respectively.

The approach proposed by Huang et al. (2021) was used the calculate the fouling resistance in the UF process at 4 bar and temperature of 20°C [52].

The calculation methods of the volumetric stream, membrane permeability, and the hydraulic reversible and irreversible resistances are detailed in the Supplementary Material. All experiments were repeated 1-6 times depending on the experiment complexity, and average values ± standard deviations were calculated.

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## 8 **2.4.** Procedure for chemical cleaning of an ultrafiltration membrane

After 4-h of the DE mode operation or when the flux decrease exceeded 70% of the 189 initial value, the membrane underwent CIP. The cleaning solution tank ((3) in Figure 1) 190 191 was filled with the appropriate solution, (depending on the procedure used as shown in Figure 2), from where the cleaning solution was fed at a pressure of 0.5 bar to the 192 UF membrane and then directed back to the CIP tank. Cleaning was carried out in 193 circulation. Each step of the cleaning lasted 30 min, except for enzymatic cleaning, 194 where two cleaning procedures were used: 90 min in circulation (C5) or 15 min in 195 circulation and 120 min of leaving the enzyme on the membrane (C6). 196

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## **CLEANING PROCEDURES**

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Figure 2. The chemical cleaning procedure consists of 4 steps for procedures C1, C2,C3, and C4, and 5 steps for procedures C5 and C6.

In this study, six chemical cleaning procedures were investigated: acid-alkaline (C1 201 and C2), alkaline-acidic (C3 and C4), and alkaline-enzymatic-acidic (C5 and C6). Their 202 203 conceptual diagrams are shown in Figure 2. In each acid cleaning step (HNO<sub>3</sub> or FNA), the pH of the starting solutions was set to 3.0. In procedures where nitric acid V (C1, 204 C3, C5, and C6) was used, the pH was set with a 20% solution of HNO<sub>3</sub>. In methods 205 using FNA (C2 and C4), a NaNO<sub>2</sub> solution with a final concentration of 200 ppm was 206 207 prepared with pH stabilisation by a 20% HNO<sub>3</sub> solution (denoted as FNA). In each procedure (C1-C6), the alkaline cleaning step (NaOH+NaOCI) proceeded identically. 208 The pH of the alkaline solution was set to 11.0 with 10% NaOH solution. A NaOCI 209 solution of 15% was added to obtain a final concentration of 200 ppm. A commercially 210

available agent Filzym P1 (Realco, Belgium) was applied for enzymatic cleaning
(procedures C5-C6). Details of the different wash types are shown in Table 2.

A regeneration rate was used to determine the effect of the methods used on the effectiveness of chemical cleaning. The calculation of the regeneration rate was presented in the Supplementary Material (SM).

Table 2. Types of chemical cleaning of the UF membrane differing in the acids used (HNO<sub>3</sub> or FNA). In each type, the initial pH of the acid solution was set to 3.0. In all alkaline cleaning steps (NaOH+NaOCI), a sodium base solution was used to set the pH equal to 11.0 with sodium hypochlorite, the concentration of NaOCI in the cleaning solution was 200 ppm.

	Type of cleaning	First step	the pH of the first solution	Penultimate step	pH of the penultimate solution	Time of unit step [min]
C1	acid- alkaline	HNO <sub>3</sub>	3.0	NaOH+ NaOCl	11.0	30
C2	acid- alkaline	FNA	3.0	NaOH+ NaOCl	11.0	30
C3	alkaline- acidic	NaOH+ NaOCI	11.0	HNO <sub>3</sub>	3.0	30
C4	alkaline- acidic	NaOH+ NaOCl	11.0	FNA	3.0	30
C5	alkaline- enzymatic- acidic	NaOH+ NaOCI	11.0	HNO₃	3.0	30 (alkaline, water, acid); 90 (circulation of enzyme)
C6	alkaline- enzymatic- acidic	NaOH+ NaOCI	11.0	HNO3	3.0	30 (alkaline, water, acid); 15 (circulation of enzyme) + 120 (enzyme on the membrane)

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#### 2.5. Management of the side stream – acid cleaning effluent

223 We tested the use of acidic solutions after (C1) and (C2) cleaning as water for plant fertigation and evaluated their phytotoxicity to radish sprouts Raphanus sativus. The 224 225 pH increased during chemical cleaning, so pH correction was not needed. For this purpose, 20 mL of liquid fertiliser containing 20, 40, 60, 80%, and 100% v/v of C1 or 226 C2 were prepared by dilution of the corresponding membrane cleaning solution with 227 ultrapure water. Ultrapure water was also used as a reference solution. Next, 24 Petri 228 dishes were prepared with 2.5 g weights of cotton wool. For each of the solutions under 229 examination, the test was carried out with 4 repetitions where 5 mL of the appropriate 230 solution was applied with an atomizer to the four wattle dishes with 25 radish grains. 231 Seed germination tests were carried out in a germinator with pink LED light in a 12/12h 232 light/dark system for 7 days. Every 2 days the seeds were rinsed with 2 mL of ultrapure 233 water. After one week, the sprouts were harvested and their length, wet biomass, and 234 concentration of chlorophylls A, B, and total were determined. The results were 235 statistically processed by Statistica software. 236

237 Methods for the determination of biomass, germ length, chlorophyll concentration, and 238 statistical methods for comparison of these parameters were reported in 239 Supplementary Materials (SM).

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## 3. Results and discussion

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# 3.1. Ultrafiltration

The ultrafiltration experiments were conducted in weekly cycles, with each process being followed by chemical cleaning of the membrane. Independently of that, the membrane was backwashed with permeate in the configuration of 5 s every 5 min. A total of 10 cycles was carried out. Figure 3A shows four selected 4-hour UF processes in the DE mode from weeks 1, 2, 9, and 10 performed to demonstrate the repeatability

of chemical cleaning. The blue bar corresponds to the flux value at the beginning and
the green bar at the end of the 4-hour filtration cycle.



Figure 3. Transport and separation properties of an ultrafiltration membrane used for the treatment of secondary effluent: (A) Membrane permeability at the beginning (blue) and in the end (green) of UF in DE mode. (B) Regeneration efficiencies of C1 and C2. (C) Retention coefficients of selected parameters at the beginning and at one of the end of UF in DE mode. The numbers 1 and 8 next to the UF processes correspond to the first and eighth-week cycle, respectively.

As can be observed in Figure 3A, the initial permeability values were close to each 257 other in every cycle. In the first experiment, the initial membrane permeability was 258 0.030±0.004 m<sup>3</sup>·h<sup>-1</sup>·m<sup>-2</sup>·bar<sup>-1</sup>. In the next cycles, permeableness was stable and 259 ranged between 0.027 and 0.028 m<sup>3</sup>·h<sup>-1</sup>·m<sup>-2</sup>·bar<sup>-1</sup>. Marked by a dashed line in Figure 260 3A, the decreases in UF permeability values in weeks 1, 2, 9, and 10 were 72%, 74%, 261 72%, and 55%, respectively, of the initial value. The final values were comparable and 262 oscillated in the range of 0.007±0.001 m<sup>3</sup>·h<sup>-1</sup>·m<sup>-2</sup>·bar<sup>-1</sup> to0.009±0.002 m<sup>3</sup>·h<sup>-1</sup>·m<sup>-2</sup>·bar<sup>-1</sup>, 263 except for the process in week 10 with the lowest decrease (55%), where the final 264 value was 0.013±0.001 m<sup>3</sup>·h<sup>-1</sup>·m<sup>-2</sup>·bar<sup>-1</sup>. For the UFs shown in Figure 3A, CIP 265

procedure C1 was used. In particular, it can be seen that the regeneration efficiency of 266 procedure C2, where FNA was applied, was almost the same as that of C1 (HNO3) 267 (Figure 3B). For the rest of the procedures (C3-C6), the permeability plots showed 268 comparable trends (Figure 7). The decrease in the permeability during UF was related 269 to the formation of filter cake [53], which was influenced mainly by the properties of the 270 secondary effluent (Table 1), especially by the content of suspended solids (TSS 271 7.87±3.63 mg·L<sup>-1</sup>). The active layer of the membrane is made of polyethersulfone, 272 which is a hydrophilic material; however, the decrease in flux size over time in DE 273 mode is similar to the decrease for a hydrophobic membrane. In CF, the flux drop 274 275 corresponds to the typical flow characteristics of a hydrophilic membrane [54].

Figure 3B shows the retention of selected compounds in the first and eighth weeks of 276 the experiment. Samples were taken one hour after the start of UF. This period ensured 277 repeatability of results and that the CIP water was thoroughly flushed out of the plant. 278 It can be seen that TSS in both cases was removed in 100% from the secondary 279 effluent. The retention coefficient for total phosphorus reached values of 45-47% and 280 for COD 37-39%. It is important to remember that phosphorus compounds and organic 281 substances (COD) are partially bound in total suspended solids [55]. Therefore, due to 282 the efficient separation of total TSS, these compound retention rates are higher than 283 those observed for other SE components. Orthophosphates, which are predominantly 284 in dissolved form, are retained to a lesser extent - 31-34%. The lowest retention 285 coefficients were obtained for humic substances (12-17%), total nitrogen (7-12%), and 286 TOC (10-11%). 287

**3.2.** Membrane fouling

The SEM-EDS was used to study the surface morphology and analyse the elemental composition of the sludge accumulated on the membrane surface after 4-h DE-UF.

SEM images (Figure S1) show that the cake structure was non-uniform, and there are 291 292 no visible crystalline phases. Due to the irregular shape and size, fouling of the membrane occurs not only on its surface in the form of a filter cake but also in the 293 pores, where substances not dissolved in the treated effluent can easily penetrate. 294 Fouling (reversible and irreversible) resistance contributed to 62% of the total 295 resistance during the UF of secondary effluent. In total fouling, the proportion of its 296 irreversible fraction was 13%. These results suggest that the SE compounds play a 297 crucial role in the formation of a reversible cake layer, but can also cause physically 298 irreversible fouling, thus chemical cleaning is required to regain full membrane 299 300 permeability.

Figure 4 shows SEM images and the distribution of elements (EDS) analysed at two 301 different positions on the UF membrane cake surface. The dominant elements both 302 atomically and by mass are carbon and oxygen. As detailed in Figure 4A and Figure 303 4B the mass content of carbon was 40.67% and 41.26%, respectively. Carbon 304 305 accounts for an even more significant proportion atomically, which was 55.25% (Figure 306 4A) and 56.10% (Figure 4B). The high content of the carbon in the examined membrane cakes was related to the presence of organic compounds, e.g. humic 307 308 substances, which were determined by FT-IR analysis (Figure 5A), and/or with microorganisms retained on the membrane. The presence of living cells was confirmed 309 by measuring ATP concentration, which was 1151±684 RLU in the secondary effluent 310 and decreased to 168±86 RLU in the permeate after UF. In turn, in the sludge collected 311 on the UF membrane, the concentration of ATP was found to be 43 271±8 052 RLU, 312 313 indicating the biomass content. Additionally, a decrease in mass (from 1.000 g to 0.6675 g) during sludge mineralisation at 550°C evidences the presence of carbon in 314 the membrane cake. Oxygen is the second most abundant element of the membrane 315

cake layer. The mass and atomic percentages of oxygen reach the values of 29.13% 316 and 29.71% (Figure 4A), and 28.97% and 29.58% (Figure 4B). Oxygen is present in 317 most organic substances as well as inorganic compounds, such as silicon oxide IV, 318 determined by XRD analysis of the membrane sludge (Figure 5B). Other elements (Na, 319 Mg, Al, Si, P, S, Cl, K, Ca, and Fe) reflected in the EDS analysis represent 30%wt. and 320 25% at. The sediment cake surface contains silicon accounting for 2.2-6.4% (on the 321 proportion of mass and atoms at Figure 4A and Figure 4B), iron, 2.2-7.4%, and 322 aluminum, 3.2-5.8%. The proportion of the phosphorus was similar to that of silicon, 323 namely 2.7-5.5%. ICP results confirm that these elements represent the largest 324 proportion in the sediment, 35.32 g kg<sup>-1</sup> (Fe), 30.00 g kg<sup>-1</sup> (P), 20.86 g kg<sup>-1</sup> (Si), and 325 17.39 g·kg<sup>-1</sup> (Al) (Table 3). 326

A smaller share in the sediment cake corresponded to metal elements of the first and 327 second group of the periodic table, like sodium (Na), magnesium (Mg), potassium (K), 328 and calcium (Ca). Their total share was in the range of 5-6% by mass and 2.6-3% by 329 330 atom. The remaining elements, non-metals, like sulphur (S) and chlorine (Cl), only represent 0.65-0.83% by mass and 1.34-1.7% by atom. ICP analysis confirmed the 331 presence of metal and non-metal elements in the membrane cake, as shown in Table 332 3, 22.52 g·kg<sup>-1</sup> (Ca), 8.86 g·kg<sup>-1</sup> (Na), 5.80 g·kg<sup>-1</sup> (K), 5.15 g·kg<sup>-1</sup> (S), 4.66 g·kg<sup>-1</sup> (Mg), 333 and 2.24 g kg<sup>-1</sup> (Zn). 334





Figure 3. SEM pictures and the distribution of elements (EDS) analysed at two different positions on the UF membrane cake surface as marked with a red frame.

Other elements, including heavy metals, like manganese (Mn), barium (Ba), copper (Cu), chromium (Cr), boron (B), lead (Pb), nickel (Ni), arsenic (As), cobalt (Co) and cadmium (Cd) were found in trace amounts. Their total content in membrane cake does not exceed 1% w/w of all the elements determined. In SE, they occur in concentrations below the method's detection limit (0.01 mg·L<sup>-1</sup>) or in concentrations close to that limit (Ba - 0.01 mg·L<sup>-1</sup>and Cu - 0.03 mg·L<sup>-1</sup>).

Table 3. Results of ICP analyses of sludge collected from the membrane surface (in  $g \cdot kg^{-1}$ ).



JJ.JZ	30.00	11.01		1 / 414	<u> </u>	6 80	616
		02	20.00	17.59	0.00	5.00	5.15
Mg	Zn	Mn	Ba	Cu	Cr	В	Pb
4.66	2.24	0.782	0.286	0.186	0.0654	0.0501	0.0388
Ni	Со	As	Cd				
0.0338	0.00634	0.00593	0.00229				
	Mg 4.66 Ni 0.0338	Mg         Zn           4.66         2.24           Ni         Co           0.0338         0.00634	MgZnMn4.662.240.782NiCoAs0.03380.006340.00593	MgZnMnBa4.662.240.7820.286NiCoAsCd0.03380.006340.005930.00229	MgZnMnBaCu4.662.240.7820.2860.186NiCoAsCd0.03380.006340.005930.00229	MgZnMnBaCuCr4.662.240.7820.2860.1860.0654NiCoAsCd0.03380.006340.005930.00229	Mg         Zn         Mn         Ba         Cu         Cr         B           4.66         2.24         0.782         0.286         0.186         0.0654         0.0501           Ni         Co         As         Cd         Cu         Cu         Cu         Cu         Bu           0.0338         0.00634         0.00593         0.00229

346

As mentioned above, FT-IR analysis confirmed the presence of organic matter, 347 especially humic substances. Figure 5A shows stretching bands of about 3200 cm<sup>-1</sup>, 348 which proves the presence of O-H groups in phenolic and alcoholic residues. These 349 groups are characteristic of humic compounds. Hydroxyl groups are also present in 350 351 sugars. The two peaks (2852 cm<sup>-1</sup> and 2921 cm<sup>-1</sup>) testify to the presence of stretching vibrations attributed to C-H bonds found in carbon chains that occur in organic 352 compounds. The presence of these bonds was also demonstrated by the presence of 353 354 characteristic bending bands with values of 1408 cm<sup>-1</sup> and 1450 cm<sup>-1</sup>. In the case of two peaks with stretching vibrations of O-H bonds falling in the range of 2500-3300 cm<sup>-</sup> 355 <sup>1</sup> and stretching C-O bonds with values of 1011 cm<sup>-1</sup> and 1232 cm<sup>-1</sup>, the presence of a 356 carboxyl group characteristic of humic compounds was confirmed. A 1232 cm<sup>-1</sup> peak 357 is attributed to the stretching vibration for the C-N bond characteristic of proteins that 358 359 may be part of the membrane deposit.



Figure 4. FT-IR (A) and XRD (B) analyses of the sludge collected from the membrane surface.

A single band at 1728 cm<sup>-1</sup> proves the presence of a C=O stretching vibration of a 363 carbonyl group, which is characteristic of proteins from a peptide bond, sugars, and 364 humic substances. The band at 1632 cm<sup>-1</sup> is related to deformation vibrations 365 366 originating from the N-H amino group (found in proteins), while the band at 1536 cm<sup>-1</sup> indicates the presence of C=C stretching bonds in the aromatic ring, characteristic of 367 humic compounds. Both the 1450 cm<sup>-1</sup> and 1408 cm<sup>-1</sup> peaks testify to the occurrence 368 of a C-C stretching vibration in the aromatic ring. An aromatic compound is also 369 evidenced by characteristic bending bands of 778 cm<sup>-1</sup> and 798 cm<sup>-1</sup>. The most 370 important functional groups in humic substances were found by FT-IR spectrum 371 analysis are carboxylic, amino, phenolic, and alcohol groups. It is assumed that humic 372 acids, which are contained in humic substances, consisting of an aromatic core. These 373 are combined with components of aliphatic structure, which is evidenced by the 374 disclosure of an amino group. 375

The putative humic acid molecule structure also contains a carbonyl group. 376 377 Macromolecular humic substances are built from the groups mentioned above, which were retained on the UF membrane in the amount of 12-17% (Figure 3B). TOC 378 decreased by 10-11% (Figure 3B), which indicates the retention of some organic 379 compounds having functional groups characteristic of e.g. humic substances. Proteins 380 were most likely removed on the membrane, as evidenced by the detection of a 381 carboxyl group and an amino group, as well as N<sub>total</sub> retention of 7-12% (Figure 3B). 382 Sugars may have been separated, as evidenced by the detection of OH and C=O 383 groups characteristic of carbohydrates. 384

The analysis of sludge from the membrane surface after UF determined the 385 compounds that contributed the most to the fouling of the membrane and thus were 386 best retained on the membrane. Although purified at the previous stages, the 387 secondary effluent contained difficult-to-fall suspended solids in the form of natural 388 organic matter (NOMs). NOMs mostly consisted of humic acids and were primarily 389 390 responsible for retaining phosphorus, aluminium, and iron ions or silica that were all identified in the solids separated by the UF membrane. Knowledge as to which 391 components cause fouling makes it possible to investigate the effectiveness of 392 methods counteracting this phenomenon. 393

394

## 3.3. Ultrafiltration membrane backwashing

Different backwash configurations were tested in the first stage by varying the backwash time and the time between successive washes, as shown in Table 4. Tests were conducted for dead-end (DE) and cross-flow (CF) filtration. Figure 6A shows the change in membrane permeability (L) during the 4 hours of the process for DE mode. As can be seen, the most significant decrease in membrane transport properties was observed for the backwash conducted for 1 s every 5 min; the permeability decrease

was more significant than that for the process without backwash. A minor decrease in
 hydraulic performance was recorded if backwashing lasted 1 s every minute.

Figure 6B shows the permeability of the UF membrane operated in the CF mode. The 403 largest decrease in hydraulic capacity (17%) in this case was observed for the process 404 without backwashing. Compared to the decreases observed in the DE mode, the 405 relatively small decrease in membrane permeability (the final flux value was 83% of 406 the initial value) was caused by the removal of a deposit from the membrane surface 407 with the retentate stream. For the other backwash configurations tested, no reduction 408 in permeability was observed, so membrane fouling occurs much more slowly during 409 the duration of UF. To determine the fouling rate on the UF membrane in the CF mode, 410 a 14-hour experiment was conducted which revealed a membrane permeability 411 decrease of 48 and 37% (Figure 6D) for 1- and 5-s backwashing every 5 min, 412 respectively. A longer backwash duration - 25 s every 5 min - produced an increase 413 in flux values related to the increase in transmembrane pressure caused by fouling. 414 415 The amount of fouling on the membrane surface was not directly proportional to the increase in pressure, resulting in an increase of the flux value in time by 30%, as shown 416 in Figure 6D. 417

Figure 6A and 6B shows that the initial permeabilities are in the range of 0.0263 to 418 0.0415 m<sup>3</sup>·h<sup>-1</sup>·m<sup>-2</sup>·bar<sup>-1</sup> for the DE mode and 0.0126 to 0.0167 m<sup>3</sup>·h<sup>-1</sup>·m<sup>-2</sup>·bar<sup>-1</sup> for CF. 419 To compare these two configurations, the percentage decrease in flux over time 420 relative to the initial flux (relative permeability  $J_p/J_{p,0}$ ) was calculated, as shown in 421 Figure 6C, DE performs much better with more frequent flushes: the smallest decrease 422 in J<sub>P</sub>/J<sub>P,0</sub> was observed for 1-second of backwash every 1 minute. For this rinse option, 423 the flux decreased by 54% after four hours of the process. On the other hand, the 424 highest permeability decrease was observed for a 1-second backwash every 5 425

minutes. The flux decreased by 75% in this case. Rinsing time also affects membrane
permeability restoration. Rinses of 25 seconds caused a noticeably smaller decrease
in permeate flux than 5-second rinses at the same five-minute frequency. The
permeate flux decreased by 59% in the former case and by 72% in the latter.

Figures 6A and 6C show, a sharp decrease in permeability for the DE mode at the 430 initial stage. The rate of decline in this index decreased as the process progressed. 431 432 The stability was related to fouling which in the first stage blocks membrane pores and causes an exponential decrease in flux. It was only in the second stage that a cake 433 layer was formed while the flux stabilised. In the beginning, the shape of the 434 permeability curve results from the intensity at which the membrane surface is being 435 blocked by the suspended solids. Then, a cake is formed on the membrane surface by 436 the retained molecules which are most likely bigger than the pore diameter and the 437 curve starts to plateau. [56,57]. 438



440

441 Figure 5. Change in membrane permeability over time at different backwash procedure 442 parameters in DE (A) and CF (B) modes in 4-h processes. (C) Changes in relative membrane permeability  $(J_p/J_{p,0})$  for DE and CF modes of operation in 4-h processes. 443 (D) Changes in relative membrane permeability  $(J_p/J_{p,0})$  in CF tests in extended cycle 444 tests in 14-h processes. 445

In CF mode, feed flows tangentially to the membrane surface, leading to a lower fouling 446 tendency than in the dead-end configuration. This means that for the low fouling rates, 447 periodic backwash can be sufficient to effectively remove membrane contamination. 448 However, usually, chemical cleaning is necessary to regenerate the membrane. A 449 450 backwashing frequency of 25s every 5 min was the only effective one in reducing both reversible and physically irreversible fouling forms in the cross-flow operation mode. 451

As a result of long-time backwashing, the sludge was decomposed and the physically irreversible fouling was desorbed from the fouled membrane, unblocking its pores. In other cases (all DE modes and other intervals in CF-UF), backflushing was ineffective in reducing membrane fouling and chemical CIP was required for the membrane to regain most of its permeability.

The impact of backwashing was assessed by determining the total permeate volume 457 obtained in 4-h DE/CF UF. Permeate losses due to backwashing were included in the 458 calculations (Table 4). As presented in our previous studies [2], membrane processes 459 are mostly applied in the treatment of secondary effluent for water recovery, which is 460 increasingly used, for example, for irrigation [58]. The backwash stream was 461 contaminated by partially flushing the sludge from the membrane and discharged to 462 the retentate tank, causing an overall permeate loss. It turned out that CF allowed the 463 collection of 3-4 times less permeate than DE did. That was related to the permeate 464 losses during backwashing, the generation of retentate, and the different operating 465 pressures of the two systems. A similar observation was made by comparing Figure 466 6A and 6B, where the ordinate axis values in the CF mode were 2-2.5 times smaller 467 than those in DE. 468

According to the results presented in Table 4, increasing the backwash time increases the permeate consumption. The same relation was observed for increasing the frequency of backwashing. Regarding the number of losses, backwashing with a shorter time and lower frequency was more efficient for DE UF due to the larger

volumes of permeate. For CF UF, the time and frequency of backwashing do notsignificantly affect the amount of final permeate volume.

Table 4. Obtained UF permeate volumes and wash losses in UF processes at different

476	backwash frequencies for DE	(4 bar) and CF (2	bar) modes.
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Flow	Backwash	Backwash	Permeate	Single
1100	tupo timo [o]	frequency	total volume	backwash
type	une [s]	[min]	[m³]	volume [cm <sup>3</sup> ]
	1	5	1.870	1000
	5	5	2.190	1250
DE	25	5	2.341	2000
DE	1	1	2.871	400
	25	25	2.424	2250
	0	-	2.193	0
	5	5	0.621	1000
CF	1	5	0.628	1250
	25	5	0.641	2000
	1	1	0.620	400
	25	25	0.663	2250
	0	-	0.621	0

#### 477

The unquestionable advantage in our research of the DE mode was the recovery of a 478 larger quantity of purified (nearly 100% of the raw material) water as permeate. This 479 mode of operation resulted in a higher accumulation of impurities on the membrane 480 surface. DE flow causes a faster build-up of membrane cake [59]. A significant 481 decrease in permeate flux occurred during the first 1-h of the process (Figure 6A). In 482 the CF mode, this decrease was not observed with such a high intensity for the same 483 time. A significant decrease in permeate flux of cross-flow only appeared after 14 484 hours. The time and frequency of backwashing do not play a crucial role in the CF 485 mode with a duration of 4-h. This is possible due to the continuous removal of most 486 deposits from the membrane surface with retentate [60]. On the other hand, the initial 487 flux of permeate in the CF mode was 2-2.5 times lower than that in DE mode, which 488

was unfavourable in terms of the amount of produced water. From this point of view, the DE mode was more advantageous. Even if the best backwash configuration was chosen in the DE mode, backwashing was not able to completely reduce fouling and restore the initial hydraulic efficiency of the membrane. When secondary effluent is passed through a UF membrane, physically irreversible fouling occurs [61]. It was necessary, hence, to apply chemical cleaning of the UF membrane to remove all the fouling-causing contaminants.

496

## 3.4. Chemical cleaning of the membrane

After a 4 h DE filtration cycle, the membrane was subjected to chemical cleaning
according to the procedures described in section 2.4.

The characteristics of the secondary effluent, which is made up of mainly organic substances [62], affect the cleaning efficiency of the UF membrane. In this study, each cleaning step, except for the enzymatic cleaning, lasted 30 min. This time allowed the residual acid or alkali collected on the membrane during UF separation to be washed away with tap water [63], which ensured stable pH in further CIP steps.



Figure 6. Degrees of recovery of membrane flux using chemical cleaning procedures:
C1 and C2 - acid-alkaline cleaning, C3, and C4 - alkaline-acid cleaning, C5, and C6 alkaline-enzymatic-acid cleaning; n.s. indicates no statistically significant differences
between the marked groups.

504

509 Figure 7 shows the recovery of membrane flux rates of the UF membrane after cleaning by each of the tested methods and the results of statistical analyses between 510 groups C1-C6. The analysis of the data presented in Figure 7 shows that the acid-511 alkaline method has better regeneration efficiency of the UF membrane than alkali-512 acid cleanings regardless of the acid used. For C1 (HNO<sub>3</sub>→NaOH) cleaning, the 513 514 efficiencies were  $101\pm8\%$ , and for C2 (FNA $\rightarrow$ NaOH) –  $103\pm5\%$ , while for C3  $(NaOH \rightarrow HNO_3) - 91\pm7\%$ , and C4  $(NaOH \rightarrow FNA) - 96\pm8\%$ . A positive effect on the 515 decomposition of multi-molecular humic acids by NaOCI [64] and the reaction of 516 517 identified silica with alkali metal hydroxides [65] was confirmed. The improvement of the recovery of membrane flux in the alkaline-acid method was achieved by introducing 518

enzymatic cleaning with Filzym P1 between cleaning with NaOH and HNO<sub>3</sub>. Filzym P1 519 520 is a mixture of enzymes with a strong oxidising character, whose role is to eliminate all organic pollutants [66]. Tests were carried out in two variants, which were either 521 flushing with the enzyme solution for 1.5 h in circulation (C5) or 15 min in circulation 522 and leaving the enzyme agent on the membrane for 2 h (C6). Only the C5 treatment 523 increased the cleaning efficiency by regenerating the membrane in 103±7%, whereas 524 525 leaving the enzyme on the membrane caused a significant decrease in cleaning efficiency. The recovery of membrane flux degree obtained in this case was 76±7%. 526

527 The Tukey test showed that for levels of p less than or equal to 0.05, 0.01, and 0.001, 528 no statistically significant differences were observed for any study groups relative to 529 the others.

Acid-alkali cleaning removed the largest amount of the contaminants from the UF 530 membrane, so it was decided to analyse solutions C1 and C2 after their usage for 531 532 membrane cleaning (Table 5). It can be stated that the ions present in the tap water used to prepare the cleaning solutions were partly responsible for the composition of 533 the spent cleaning solutions. Concentrations of ions such as sulphates, chlorides, 534 calcium, and magnesium were similar to Wrocław tap water parameters, which leads 535 to the conclusion that they partly originate from tap water and partly from removed 536 membrane foulants. During cleaning, suspended solids were washed out of the 537 membrane; the TSS content in the solutions after cleaning was 19.0 mg L<sup>-1</sup>, and 15.8 538 mg L<sup>-1</sup>, respectively, for C1 and C2 acid solutions. In the solution after acid cleaning, 539 organic compounds were primarily bound, the presence of which can be seen by the 540 increased COD values in rinses after membrane washing, 27.4 mgO<sub>2</sub>·L<sup>-1</sup> and 72.4 541 mgO<sub>2</sub>·L<sup>-1</sup>, and humic substances concentrations, 0.374 mg·L<sup>-1</sup> and 1.054 mg·L<sup>-1</sup>, for 542 C1 and C2, respectively. Nitric acid V and FNA cause slight partial dissolution of the 543

inorganic substances responsible for membrane fouling, which can be observed in the 544 545 concentrations of metals that were not present in tap water. In solution C1, iron was determined at 0.84 mg·L<sup>-1</sup>, zinc 0.51 mg·L<sup>-1</sup>, barium 0.07 mg·L<sup>-1</sup> and copper and nickel 546 0.01 mg·L<sup>-1</sup>. After FNA had been applied, these concentrations dropped to 0.12 mg·L<sup>-1</sup> 547 <sup>1</sup> for iron and 0.28 mg L<sup>-1</sup> for zinc. The differences, however, are not significant and 548 may be due to the composition of the filter cake resulting from the process. They do 549 not affect the assessment of the effectiveness of the two acids. Only the barium 550 concentration was slightly higher and amounted to 0.09 mg·L<sup>-1</sup>. The concentrations of 551 copper and nickel were below the analytical method sensitivity. Chemical cleaning also 552 flushes out the embedded microorganisms and their residues from the membrane, 553 which can be observed by ATP measurement. The ATP assay measures the biological 554 activity of microorganisms by detecting adenosine triphosphate (ATP), which is the 555 556 energy carrier in cell metabolism [67]. ATP was equal to 905 RLU after membrane cleaning C1, while 822 RLU for procedure C2. Therefore, FNA, as a green alternative 557 effectively removed the organic matter from the membrane surface, inactivated the 558 microbial cells remaining on the membrane after cleaning, and also removed fouling 559 caused by inorganic substances [45]. 560

Table 5. Physico-chemical composition of acid solutions after UF membrane chemical
cleaning by acid-alkaline method (C1 and C2).

		Acid washed	Acid washed
Parameter	Unit	nitric acid V	FNA
		(procedure C1)	(procedure C2)
COD	mgO <sub>2</sub> ·L <sup>-1</sup>	27.4	72.4
Ptot	mg∙L⁻¹	0.89	0.847
N <sub>tot</sub>	mg∙L⁻¹	67	91.5
PO <sub>4</sub> <sup>3-</sup>	mg∙L⁻¹	0.47	0.310
N-NO <sub>2</sub> -	mg∙L⁻¹	0.026	39.7
N-NO <sub>3</sub> -	mg∙L⁻¹	66.5	57.6

N-NH <sub>4</sub> +	mg∙L⁻¹	0.279	0.124
SO4 <sup>2-</sup>	mg∙L⁻¹	63.7	70.5
Cl	mg∙L⁻¹	40.6	20.9
Ca <sup>2+</sup>	mg∙L⁻¹	79.1	76.7
Mg <sup>2+</sup>	mg∙L⁻¹	15.8	14.2
Hardness	mgCaCO₃·L⁻¹	262.5	250.0
Humic substances	mg∙L⁻¹	0.374	1.054
рН		3.61	5.66
Turbidity	NTU	9.74	8.97
Alkalinity	mgCaCO₃·L⁻¹	125	250
TSS	mg∙L⁻¹	19.0	15.8
С	µS₊cm⁻¹	1056	1116
ATP	RLU	905	822
	Results of IC	CP analyses	
Р	mg∙L⁻¹	0.58	0.33
K	mg∙L⁻¹	9.17	6.74
S	mg∙L⁻¹	23.7	23.4
Na	mg∙L⁻¹	42.7	87.2
Ca	mg∙L⁻¹	80.5	76
Mg	mg∙L⁻¹	12.6	10.9
Fe	mg∙L⁻¹	0.84	0.12
Cu	mg∙L⁻¹	0.01	<0.01
Ni	mg∙L⁻¹	0.01	<0.01
Zn	mg∙L⁻¹	0.51	0.28
Ва	mg∙L⁻¹	0.07	0.09
As	mg∙L⁻¹	<0.01	<0.01
Cd	mg∙L⁻¹	<0.01	<0.01
Со	mg∙L⁻¹	<0.01	<0.01
Pb	mg∙L⁻¹	<0.01	<0.01
Cr	mg∙L⁻¹	<0.01	<0.01

563

In terms of chemical cleaning efficiency, the use of alkali-acid methods did not result in flux recovery rates as initially expected, which was evidenced by the lower flux recovery rates compared to acid-alkaline modes. The sequence, therefore, plays a decisive role in UF membrane cleaning. Acids have been proven to remove fouling caused by inorganic substances better, while alkalis reduce organic fouling more effectively [68]. Inorganic compounds are present in relatively large amounts, so acidbase methods have a slightly better effect on UF membrane cleaning. Alkaline-acid

mode performance can be improved by adding enzymatic cleaning. The use of the 571 572 alkaline-acid procedure with an enzymatic agent (Filzym P1) in the circulation proved to be as effective as the acid-base methods. The use of enzyme was justified because 573 elevated ATP values were determined in the solutions after alkaline cleaning, 574 indicating the presence of biological species [69]. However, due to the cost of the 575 576 enzyme agent and the duration of chemical cleaning, the acid-alkaline method seems to be the more profitable because this strategy ensures a 100% removal of all 577 physically irreversible fouling in a relatively short period, which extends the lifespan of 578 the membrane. 579

580 With all the ecological and economic aspects taken into account, FNA could become a competitive reagent for fouling removal. This study confirmed that FNA restored 581 membrane performance (Figure 7) and removed fouling from the membrane surface 582 and pores (Table 5) in a way comparable to nitric acid V. The replacement of 583 commercially available nitric acid V with FNA, obtained at the wastewater treatment 584 585 plant, can further increase the cost-effectiveness of cleaning as presented in Figure 8. Neither the use of HNO<sub>3</sub> nor FNA causes a technological difference in the cleaning 586 procedure, so the main cost is the purchase of the reagent (HNO<sub>3</sub>). Based on 587 588 commercially available nitric acid V, it has been estimated that using it to clean the membrane generates a cost of 0.08 € m<sup>-2</sup>. FNA is produced at the wastewater 589 treatment plant, so its cost is 0 € m<sup>-2</sup>. Using NaOH and NaOCI alkaline step generates 590 a cost of 0.05 €·m<sup>-2</sup>. Therefore, taking into consideration acid-alkaline procedure C2 591 (where recycled FNA is used), the total cost of reagents is  $0.05 \in m^{-2}$ , while for C1 592 593 (where commercially available nitric acid V is used) the total cost increases to a value of 0.13 € m<sup>-2</sup>. On a semi-pilot or pilot-scale experimental study determined differences 594 appear to be relatively small, however, with industrial installations, this will play a 595

significant role in assessing the cost-effectiveness of utilizing FNA. As Figure 8 shows, 596 597 alkaline-enzymatic-acid procedures (C5/C6) are the most expensive and the total costs increase by ~80% and ~93% compared to procedures C1 and C2, respectively. The 598 enzyme solution alone comes with a price of almost  $0.64 \in m^{-2}$ , which contrary to C1 599 and C2 seems to be highly uneconomic. More importantly, the alkaline-enzymatic-acid 600 cleaning procedure produces additional wastewater streams which is a less 601 ecologically acceptable solution than a two-step acid-alkaline method, like C2, where 602 the significant environmental benefits are gained by replacing the commercial acidic 603 reagent by FNA which is produced in-situ at the wastewater treatment plant. To fit in 604 605 with the idea of the closed circular economy, where all the waste is reclaimed, we proposed a new strategy of recycling the spent acidic solutions after membrane 606 chemical cleaning, as an alternative fertiliser (Figure 8). 607



Figure 8. Schematic diagram of sustainable UF membrane regeneration strategy after
 SE recycling with a comparison of the most effective (acid-alkaline C1, C2, and
 alkaline-enzymatic-acid C5/C6) cleaning solutions costs.

# 612 3.5. Management of the spent acidic solution after membrane chemical 613 cleaning

614 Chemical cleaning of membranes removed organic and inorganic pollutants and transferred them to the cleaning solution, enriching it with many components that can 615 be used as an alternative fertiliser. A likely limitation to the utilization of after-cleaning 616 617 solutions for plant fertigation could be their contamination with heavy metals that were identified in the membrane sludge. As can be seen, although the sludge contained a 618 considerable amount of heavy metals such as lead, cobalt, arsenic and cadmium 619 (Table 3), all these elements did not exceed detectable concentrations (0.01 mg·L-1) 620 in the acidic post-cleaning streams (Table 5) and were below permissible levels set by 621 the Food and Agriculture Organization [70]. Therefore, solutions after the application 622 of HNO<sub>3</sub> or FNA for C1 and C2 chemical cleaning of membranes could not pose a 623 threat to crop cultivation. To prove this, the phytotoxicity tests have been performed on 624 radish seeds according to the methodology described in Section 2.5. Germination tests 625 were carried out with 20, 40, 60, 80, and 100% washing agent solutions. Reference 626 (control) tests were carried out with ultrapure water. One of the most important 627 parameters determining the use of solutions after cleaning is the pH. Radish seeds 628 grow best in moderately acidic soil [71]. Both solutions had an initial pH of 3.0. Cleaning 629 flushed out most of the foulants from the membrane, which caused the pH to rise: in 630 the case of  $HNO_3$  – up to a value of 3.61, while in the case of FNA – 5.66. The final pH 631 of acid cleaning solutions remained close to the pH of soil suitable for radish cultivation. 632 The alkaline post-cleaning solutions due to the high pH (pH 8-9) have not been 633

considered as potential fertiliser. Figure 9A shows the analyses of length, wet biomass, 634 and total chlorophyll content of radish sprouts after one week of growth. Statistic 635 analysis revealed that for the seeds grown on HNO<sub>3</sub> and FNA solution, sprout lengths 636 showed a distribution different from normal, and statistically significant differences 637 were observed at a 100% concentration compared to the control group (Table S1). 638 The difference in radish sprouts length grown on 100% concentration chemical 639 cleaning (C1 and C2) and that of the control groups can be observed in Figure 9B. The 640 mean sprout length for the control groups for C1 acid solution was 2.2±0.2 cm and for 641 C2 acid solution – 2.3±0.2 cm. The mean plant lengths for the statistically significant 642 643 group (100%) relative to the control were 2.7±0.2 cm in both cases.



644

Figure 9. (A) Results of measurements of length, wet biomass, chlorophyll A, chlorophyll B, total chlorophyll, and total chlorophyll per wet biomass of radish sprouts after one week of culture on solutions after membrane cleaning with nitric acid V and FNA in groups which were dilutions of these solutions, with final concentrations of 20%, 40%, 60%, 80%, and 100%. The control group in both tests is the culture run on ultrapure water. (B) Pictures of radish sprouts after cutting one of the plates from the control group (top) and one of the plates from the 100% nitric acid solution V group(bottom).

For both HNO<sub>3</sub> (C1) and FNA (C2), the distributions of the biomass data were normal 653 data distributions, while the variances were homogeneous. Both statistically significant 654 differences were not observed as compared to the control group (Table S1). When 655 comparing C1 and C2, for each concentration, higher biomass was obtained for the 656 sprouts grown on solution C1, which was for the groups from 20 to 100% respectively: 657 1.5156±0.2284 g, 1.3165±0.1368 g, 1.2867±0.0944 g, 1.2857±0.1491 g, and 658 1.4331±0.0201 g than for sprouts grown on solution C2, which was for the same 659 dilutions: 1.1818±0.1307 g, 1.1410±0.1277 g, 1.2063±0.1501 g, 1.0965±0.0568 g, and 660 1.4000±0.1292 g, respectively. 661

Chlorophyll A, B, and total chlorophyll content per wet germ weight measured in plant 662 663 leaves on the medium with the HNO<sub>3</sub> cleaning solution (C1) showed similar trends: normal data distributions, heterogeneous variances, and no statistically significant 664 differences (Table S1). No phytotoxicity of the diluents occurred. The concentration of 665 666 total chlorophyll in the undiluted HNO<sub>3</sub> acid solution was 5.606±0.899 mg·L<sup>-1</sup>, which was lower than in the control group (5. 979±0.795 mg·L<sup>-1</sup>), but in the other groups, the 667 concentration was higher and was  $7.876\pm0.683$  mg L<sup>-1</sup>,  $7.554\pm0.512$  mg L<sup>-1</sup>, 668 7.934±0.572 mg·L<sup>-1</sup>, and 7.726±1.890 mg·L<sup>-1</sup>, respectively, for acid shares in the test 669 solution of 20, 40, 60 and 80%. Despite the lack of statistically significant differences, 670 671 we observed a favourable effect of the solutions on the chlorophyll content of the cultured sprouts in the 20-80% groups. 672

673 Measured chlorophyll A in leaves of plants on medium with solution after washing with 674 FNA (C2) showed a normal distribution of data, homogeneous variance, and

statistically significant differences in 20% and 40% concentrations relative to the 675 676 control group (Table S1). The concentration of chlorophyll A in the control group was 4.306±1.355 mg L<sup>-1</sup>, while in the 20% and 40% groups it was 5.837±0.0896 mg L<sup>-1</sup> and 677 6.283±0.589 mg·L<sup>-1</sup>, respectively. In the remaining groups, despite the lack of 678 statistically significant differences, no phytotoxicity of the solutions towards the sprouts 679 was observed, and the concentration of chlorophyll A was above 5 mg L<sup>-1</sup>. Chlorophyll 680 681 B had a distribution other than normal, and statistically significant differences only in the concentration of 40% (which was 2.510±0.651 mg·L<sup>-1</sup>) against the control (Table 682 S1)(1.715±0.413 mg·L<sup>-1</sup>). In the other groups, the concentration of chlorophyll B was 683 684 more than 2 mg·L<sup>-1</sup>. In total chlorophyll and total chlorophyll per weight of radish leaves, the data distribution was normal. The variance was homogeneous, and statistically 685 significant differences were shown in the concentration of 40% relative to the control 686 687 (Table S1). In this case, the greatest difference was visible, that is, in the control group, the mean concentration of total chlorophyll was 6.021±0.763 mg·L<sup>-1</sup> [(7.527±2.204)·10<sup>-</sup> 688 <sup>4</sup>) mg·g<sup>-1</sup>] and in the statistically significant group –  $8.793\pm1.031$  mg·L<sup>-1</sup> 689  $[(10.991\pm1.2885)\cdot10^{-4})$  mg·g<sup>-1</sup>]. In the other groups, also the concentration of total 690 chlorophyll was higher than in the control group; for a 20% solution it was 7.920±1.164 691  $mg \cdot L^{-1}$  [(9.899±1.454)·10<sup>-4</sup>)  $mg \cdot g^{-1}$ ], for 60% – 7.537±0.754  $mg \cdot L^{-1}$  [(9.421±0.943)·10<sup>-1</sup> 692 <sup>4</sup>) mg·g<sup>-1</sup>], for  $100\% - 7.299 \pm 1.159$  mg·L<sup>-1</sup> [(9.124±1.449)·10<sup>-4</sup>) mg·g<sup>-1</sup>], and the least 693 for  $80\% - 7.272 \pm 1.348 \text{ mg} \cdot \text{L}^{-1}$  [(9.090±1.686)·10<sup>-4</sup>) mg·g<sup>-1</sup>]. 694

695 Comparing the two acid solutions, it can be seen that higher chlorophyll concentrations 696 were obtained for the nitric acid V solutions used in procedure C1 for most of the 697 groups. In the statistically significant group (40% for FNA) and the 100% group, higher 698 chlorophylls concentrations were obtained for the solution after the C2 procedure. The 699 differences are not significant enough to conclusively state that one of the acids is considerably more useful in stimulating chlorophyll concentrations. Both acids have a similar effect on sprout length and weight. Growth-stimulating properties were only observed in the 100% groups. In the other groups, lengths and weights were very similar or slightly higher in both cases. No inhibition of plant growth was observed under the influence of the acid solutions. HNO<sub>3</sub> and FNA showed similar effects on radish sprouts.

706 The spent FNA solution (after cleaning C2) is richer in plant growth nutrients compared to HNO<sub>3</sub> (C1) in that it has a higher concentration of organic matter, including humic 707 substances. Still, the lower concentration of N<sub>total</sub> in the acid solution after C1 is more 708 709 beneficial because radish prefers nitrogen-poor soil [72]. The solutions also contain other micro- and macro-nutrients necessary for plant growth, mainly Ca, Na, Mg, S, K 710 and in minor amounts P, Fe, Zn, Ba and Cu, and Ni in the case of the HNO<sub>3</sub> solution 711 (C1). Plants fed with the solution cleaned with FNA (C2) grew longer sprouts. Also, the 712 HNO<sub>3</sub> solution (C1) can be used as a – slightly less effective – fertiliser. The amount 713 714 of waste produced during membrane separation of secondary effluent may be 715 decreased by adopting the presented solution. The generated washings stream can be applied as a supplement in the new fertilisation of crops. 716

## 717 **4. Conclusions**

The present study focused on the fouling and cleaning method of ultrafiltration membrane used to extract water from secondary effluent. The TSS, P<sub>total</sub>, COD, HS and N<sub>total</sub> rejection (100%, ~50%, 38%, 14% and ~10%, respectively), as well as SEM-EDS and FT-IR analysis, indicate that organic compounds, phosphorus and nitrogen macromolecules and inorganic matter (silicon oxide IV, aluminum- and iron-bearing solids) blocked the UF membrane. By carrying out the four-hour DE UF, the permeate flux dropped to 75% of the initial value, which made the mechanical (backwashing) or

chemical treatment of the membrane necessary to ensure the continuity of UF. The 725 726 most effective backwashing configuration for UF-DE was 1s every 1min, where relative membrane permeability decreased by 54% after 4-h separation. Experimental data 727 showed that the application of physical backwashing did not effectively reduce fouling 728 and, consequently, did not restore the original hydraulic efficiency of the UF membrane 729 in the DE mode. This indicates that the pollutants were not only deposited on the 730 membrane surface but also accumulated inside the membrane pores (physically 731 irreversible fouling), which made chemical treatment necessary to conduct. We 732 demonstrated that the sequence of using acidic and alkaline cleaning solutions is very 733 734 important, especially when an actual waste stream, like SE, is separated. In our case, the best effect was observed for the acid-alkaline cleaning strategy. We examined that 735 after UF of SE inorganic compounds are present in a relatively larger amount 736 737 compared to the organic matter in membrane fouling. When the acid cleaning step is performed before alkaline, membrane regeneration efficiency is higher, because acids 738 better removed inorganic compounds. Acid-alkaline (C1 and C2) method efficiency of 739 the recovery of membrane flux stood at 100%, while for alkaline-acid C3 and C4 740 procedures it stood at ~91% and ~96%, respectively. The replacement of HNO<sub>3</sub> (C1) 741 742 with FNA (C2) did not affect the acid-alkaline cleaning (giving 103±5% membrane regeneration efficiency), which opens up new possibilities for free nitrous acid 743 application in membrane-based processes. Free nitrous acid can be produced in-situ 744 in WWTP by partial nitrification of the anaerobic digestion liquor, and its utilization for 745 UF fouling mitigation is a reasonable and low-cost solution as it reduces the use of 746 747 energy and chemicals. In line with the circular economy, the acidified nitrite/nitrate solution from the chemical cleaning of the UF membrane was reused as a fertiliser 748 agent. When radish seeds were grown on the acidified nitrite/nitrate solution, the 749

r50 leaves of plants contained more chlorophyll, and the plants had longer stems and r51 greater biomass as compared to the control group. The stimulating effect of these r52 solutions on the growth and yield of radish suggests their high recycling potential as a rew acid nitrogen-rich fertiliser. The proposed new idea is in line with the conception r54 of zero waste because here entire products or by-product materials are reused or recycled.

## 756 CRediT authorship contribution statement

Krystian Czuba: Investigation, Formal analysis, Methodology, Data curation, Writing 757 - original draft, Validation, Visualization. Kornelia Pacyna: Investigation, Visualization, 758 Data curation, Formal analysis. Anna Bastrzyk: Investigation, Conceptualization, 759 Formal analysis, Writing – review & editing. Małgorzata Kabsch-Korbutowicz: 760 Writing - review & editing. Anna Dawiec-Liśniewska: Conceptualization, Formal 761 analysis, Writing - review & editing, Visualization. Przemysław Chrobot: 762 Conceptualization. Amin Shavandi: Writing – review & editing, Daria Podstawczyk: 763 Conceptualization, Formal analysis, Methodology, Supervision, Resources, Project 764 administration, Funding acquisition, Writing - review & editing. 765

## 766 Declaration of competing interest

The authors declare that they have no known competing financial interests or personalrelationships that could have appeared to influence the work reported in this paper.

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