Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2021.27882

243 (2021) 116–122
December

Removal of organic compounds in the pretreatment of a brackish industrial waste stream

Ewa Łobos-Moysa*, Edyta Kudlek

Department of Water and Wastewater Engineering, Faculty of Power and Environmental Engineering, Silesian University of Technology, Gliwice, Poland, email: ewa.lobos-moysa@polsl.pl (E. Łobos-Moysa)

Received 14 September 2021; Accepted 7 October 2021

ABSTRACT

The paper discusses the treatment of brackish wastewater (1,000 mg Cl-/L), which also contained a high concentration of organic compounds (1,576 mg O2/L as COD) and was characterized by high toxicity. Wastewater treatment was carried out in the following systems: microfiltration (MF), coagulation, coagulation/ultrafiltration (UF), coagulation/UF/nanofiltration (NF). Flat polymer membranes with PES and polyamide-TFC were used in the tests. The removal of impurities was as follows: The pre-treatment carried out by MF or by coagulation was to protect the next stages of treatment, i.e. UF and NF. In both cases, similar effectiveness were obtained, respectively: 33.3% (TOC), 33.9% (COD), 66.9% (colour) and 26.6% (TOC), 21.7% (COD), 41.4% (BOD), 64.2% (colour). Due to the decrease in flux during MF, coagulation was used as the first stage of brackish wastewater treatment. This process was carried out with the use of aluminum compounds at a dose of 1.5 g/L and the following parameters: rapid mixing (2 min), slow mixing (20 min), and sedimentation (20 min). The wastewater pre-treated in this way was treated in UF followed by NF, achieving high efficiency: 93.7% (TOC), 83.7% (COD), 98.3% (BOD), 99.24% (colour), and 79.8% (IC).

Keywords: Industrial wastewater; Brackish wastewater; Membrane pressure techniques; Coagulation

1. Introduction

Industrial wastewater is not only a hazardous waste, which destroys the whole environment, but it can be a source of valuable raw materials, which could be reused. An important challenge for environmental engineering is not only the search for methods that can effectively reduce the volume of the generated wastewater stream but also allow for the partial or complete reuse of several components occurring in those streams [1]. The reuse of those components is only possible after their separation from the water matrix, which can contain both organic and inorganic compounds [2]. Fractionation of such medium without changing its properties and the appropriate treatment of waste streams is the proper neutralization of industrial wastewater and fully fits into the assumptions of the circular economy.

One of the most popular methods and often used in the industry are membrane techniques [3]. This fractionation method does not require the addition of chemicals and changing the physicochemical properties of the wastewater streams. Membrane techniques can be successfully used in the treatment of industrial wastewater, because:

- They allow for the generation of two separate steams: a concentrated organic compounds stream with a minimum amount of mineral additives and a concentrated mineral compounds stream slightly contaminated with organic compounds.
- They allow obtaining clean water for the industry by the use of multi-stage membrane processes, in which the last stage of treatment is reverse osmosis (RO), electrodialysis (ED), or membrane distillation (MD).

* Corresponding author.

One of the most difficult to treat is brackish wastewater, which is produced in a wide variety of industries, such as crude oil extraction and processing, coal extraction, food, pharmaceutical, and textile industries. Brackish wastewater may also be generated in landfills out of waste from iron ore and rare earth metals mining and in municipal landfills. Such wastewater contains often large amounts of organic and mineral compounds. The concentration of salt ions in this specific water matrix is usually greater than 20 g/L and can in some cases reach the value of 150 g/L [4]. Lefebvre and Moletta [4] indicated that the cheapest wastewater treatment technology consists of single biological processes or a combination of physicochemical/biological treatment. However, the physicochemical composition of brackish wastewater can sometimes exclude the use of biological processes and force the use of membrane technologies. The first and most important step in the treatment of brackish wastewater by the use of membrane techniques, such as multi-stage pressure membrane filtration, is the pre-treatment. The pre-treatment leads to a reduction in the load of organic pollutants reaching the first stage of membrane filtration. These contaminants can negatively affect the filtration process itself and increase the costs of the process through more frequent cleaning of the used membranes and a negative impact on the membrane material. Therefore, various pre-treatment methods are used. The pre-treatment can be carried out using classical chemical methods like the coagulation process, or in-depth oxidation processes combining the action of several chemical reagents. For example, the coagulation process by the use of anionic polyacrylamide can be used as an effective pre-treatment method of wastewater from crude oil extraction and processing [5]. The use of nanofiltration at the next treatment stage for this wastewater stream resulted in a decrease in the permeate flux and an increase in salt retention depending on the molar mass of the polyacrylamide anion [6]. The use of advanced oxidation processes as a pre-treatment of salt-containing wastewater in the coal chemical industry can reduce the concentration of organic compounds, measured as COD to 50–80 mg/L before it enters the reverse osmosis membrane [7]. Whereas, chemical softening, ion exchange, and nanofiltration are used to reduce the divalent ion concentration to less than 50 mg/L for high hardness salt-containing wastewater [7].

Another solution for the treatment of water streams containing organic and mineral compounds are hybrid simultaneous processes. Such processes are generally conducted in reactors, which allow for a simultaneous action of biodegrading microorganisms and ion-exchange membranes [8]. This solution allows for the reduction of the COD value by 72%–94% and the removal of salinity ranging from 21% to 84%. A flow-through coupled system of electro-Fenton and electrosorption processes was designed for purification and desalination of high-salinity organic wastewater from the pharmaceutical industry [9]. This system allowed for a significant decrease of the COD and TN and salinity values, which were reduced by 96.5%, 98.2%, and 46.2%, respectively.

Another important topic is the coal-mine water desalination to produce water for human consumption or salt production [10] while remembering that also other industrial wastewater can be a source of reclaimed water and additionally a source of raw materials in the circular economy.

The research aimed to select the appropriate process of pre-treatment of brackish wastewater containing a significant amount of organic to neutralize the wastewater and possible fractionation to recover raw materials and water.

2. Materials and methods

2.1. Characteristic of brackish wastewater

The effluent used was collected from an enterprise located in the Silesian Voivodeship from a storage reservoir. The composition of the wastewater was very variable in terms of the content of organic and mineral pollutants. Table 1 shows the characteristics of this wastewater. We expect that this real wastewater may contain decomposition products of plastics, chemical substances, and mixtures, hence it is characterized by a high COD and at the same time low BOD_5 and toxicity towards vascular plants. In further research, this wastewater will also be subject to qualitative and quantitative analysis using a chromatograph to select organic compounds hazardous to the environment and human health.

2.2. Treatment methods and experimental procedures

The coagulation and flocculation of wastewater were carried out in glass reactors with a volume of 3 L. In preliminary tests, aluminium compounds were used as coagulants at doses ranging from 0.5 to 2 g/L. The process was carried out in 4 replications. Although coagulation with this compounds can also be carried out at pH > 7. In our case, the optimal effect was obtained at pH < 7.1. The dose of 1.5 g/L was selected as the optimal for further research. Rapid mixing (2 min) and slow mixing (20 min) were preceded by a pH correction to 7.0. After sedimentation (20 min), the treated wastewater was subjected to the membrane processes.

Based on preliminary studies on this type of wastewater pre-treatment, the MF membrane with a pore size of 0.1 μm was selected. Also, MF 0.3 μm and UF 10000 Da membranes, were examined. The microfiltration and ultrafiltration

Table 1
Characteristic of brackish wastewater

Parameter	Value
Total organic carbon (TOC), mg C/L	687–764
Chemical oxygen demand (COD), mg O_2/L	1,283–1,576
Biochemical oxygen demand (BOD_5), mg O_2/L	290–311
BOD_5/COD	0.2
pH	8.2–8.3
Conductivity, mS/cm	11.9–12.4
Salinity, mg NaCl/L	7,100–7,900
Chloride, mg Cl^-/L	1,000–2,000
Inorganic carbon (IC), mg C/L	1,155–1,311
Colour, mg Pt/L	2,600

processes were carried out on a plate membrane module SEPA CF-NP by GE Osmonics (USA) equipped with flat-sheet microfiltration or ultrafiltration membranes. The characteristics of the membranes are presented in Table 2. The active filtration surface of the membrane placed in the membrane cell was 0.0155 m^2. The membrane operated in a cross-flow mode with recirculation of the concentrate to the feeding tank. The transmembrane pressure was set at 0.5 MPa and the cross-flow velocity was kept at the level of 1.0 m/s. The process was carried out to collect 33% of the initial volume of the feed.

The nanofiltration process was conducted in a steel filter module with a capacity of 400 cm^3. The active membrane filtration surface area was 0.0038 m^2. The process was conducted in a dead-end filtration mode at a transmembrane pressure of 2.0 MPa. The process was carried out to collect 50% of the initial volume of the feed. The characteristics of the nanofiltration membrane are presented in Table 2.

2.3. Analysis methods

The effectiveness of wastewater treatment was assessed based on general organic pollutant indicators, i.e. total organic carbon (TOC), COD, and BOD_5, the content of mineral compounds: inorganic carbon (IC), conductivity and salinity, as well as physical parameters: color and toxicological tests.

The TOC and IC concentrations were measured by the use of the TOC-L analyser by Shimadzu Corporation (Kioto, Japan). The TOC value was calculated as the difference between the total carbon concentration TC and the IC. COD and colour were analyzed using the UV-VIS Spectrophotometer Pharo 300 Spectroquant® by Merck KGaA (Darmstadt, Germany). The multifunction meter CPC-511 (Elmetron, Poland) was used to measure pH, conductivity and salinity.

The toxicity of this wastewater stream was established by the use of the *Lemna minor* growth inhibition test. Detailed information about the test procedure was given in previous works [11]. The test indicated changes in the green parts of the indicator plants and an inhibition in the process of their growth. Based on the rate of these changes, it is possible to determine: high toxicity, toxicity, low toxicity, or no toxicity.

3. Results and discussion

3.1. Effectiveness of brackish wastewater treatment in systems integrated with membrane techniques

In studies on the fractionation of brackish wastewater, following single pre-treatment processes i.e.: MF or coagulation (as stage 1), combined coagulation and UF (stage I and stage II), and multi-stage processes i.e.: coagulation and UF followed by NF (stage I, stage II and stage III) were used.

In the initial research, membrane filtration was used to pre-treat brackish wastewater containing a large amount of organic compounds. The COD value of the brackish wastewater was up to 1576 mg O_2/L, and BOD_5 value was up to 311 mg O_2/L. Such a low BOD_5 value and BOD_5/COD ratio at the level of 0.2 shows, that the sewage is not susceptible to biological treatment. An additional problem in wastewater treatment was the presence of ion chloride, which was found to fluctuate significantly, i.e., from 1,000 to 2,000 mg Cl^-/L. During the research, the average chloride content was 1,000 mg Cl^-/L, salinity ranged from 7,100 to 7,900 mg NaCl/L and conductivity from 11.9 to 12.4 mS/cm.

The permeate obtained after the filtration by the polymer MF flat sheet membranes was characterized by a lower content of organic impurities, i.e. a reduction of TOC from 687 to 458 mg/L, COD from 1,283 to 848 mg O_2/L and a significant colour change was achieved (Figs. 1, 2 and 5). A slight IC removal from 1,153 to 1,044 mg/L was also marked (Fig. 4). Although the wastewater did not contain suspended solids, it was not turbid, but had an intense colour (2,600 mg Pt/L). The physicochemical composition of this type of water stream causes difficulties with the flow in the early stages of the filtration process. The flux decreased from 9.55×10^{-3} m^3/m^2 s to 2.86×10^{-3} m^3/m^2 s in 5 min. Despite the conduction of the process in the cross-flow mode, the pollutants contained in the wastewater quickly caused the fouling phenomenon. Therefore, in further research, the use of membrane filtration as a method of wastewater pre-treatment was abandoned.

The salinity content can affect the membrane fouling formation in a variety of ways. Such a difference was demonstrated during studies on the effect of NaCl on this phenomenon during ultrafiltration of humic acid and bovine serum albumin [12]. A high concentration of NaCl promotes the humic acid fouling formation.

Coagulation was used as an alternative pre-treatment method. The test results are shown in Figs. 1 – 5. Using a chemical process – coagulation and physical separation process – microfiltration, a comparable pre-treatment effect was obtained, i.e. a reduction in TOC from 764 to 561 mg/L, COD from 1,576 to 1,234 mg O_2/L, BOD_5 from 290 to 170 mg O_2/L and a significant colour change.

3.2. Effect of coagulation on the effectiveness of brackish wastewater treatment by membrane filtration methods

Coagulation is used as a preliminary treatment and may precede processes characterized by higher selectivity. The advantages of industrial wastewater coagulation include: commonly known process mechanisms, simple operation, process compactness, while the most serious disadvantages include the formation of large amounts of sludge [13]. Another process that can be considered in the case of saline water or sewage is electrocoagulation [14].

In our case, coagulation successfully replaced microfiltration. Parameters such as TOC and colour were removed at a similar level during microfiltration and coagulation and were equal to respectively 33.3% and 26.6% for the TOC removal and, 66.9% and 64.2% for the reduction in the colour value (Table 2). With the assumed parameters, the influence of coagulation as a pre-treatment on the subsequent stages of membrane filtration was assessed. There was no negative impact of wastewater components on the course of filtration in the second and third stage of treatment, or on the UF and NF membranes themselves, as was the case with MF in the first stage. At the second stage,

Table 2
Characteristics of tested membranes at the following stages of wastewater treatment

Membrane type	Material	Pore size/Cut-of	Symbol	Stage
Microfiltration membrane	PES	0.1 µm	MF	I.
Ultrafiltration membrane	PES	10,000 Da	UF10kDa	II.
	PES	5,000 Da	UF5kDa	II.
Nanofiltration membrane	Poliamide-TFC	300 Da	NF300Da	III.

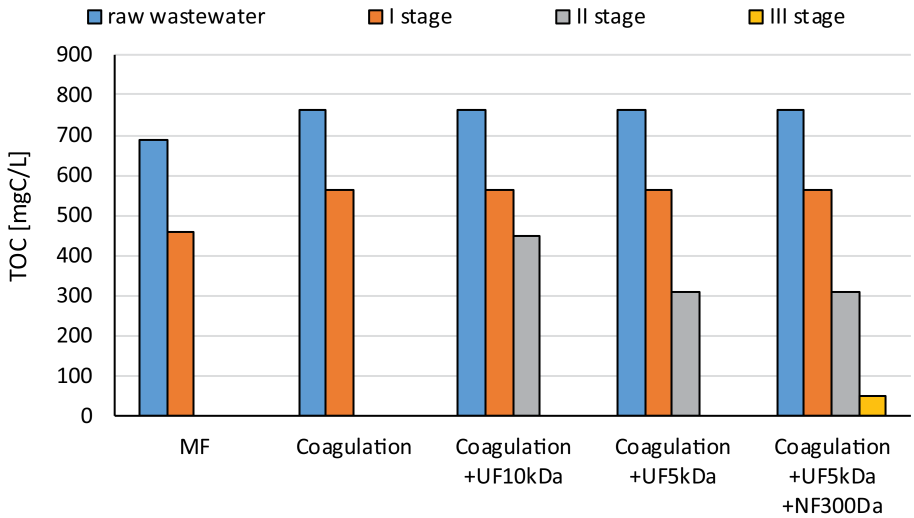

Fig. 1. TOC content in raw and treated brackish wastewater after single and integrated processes.

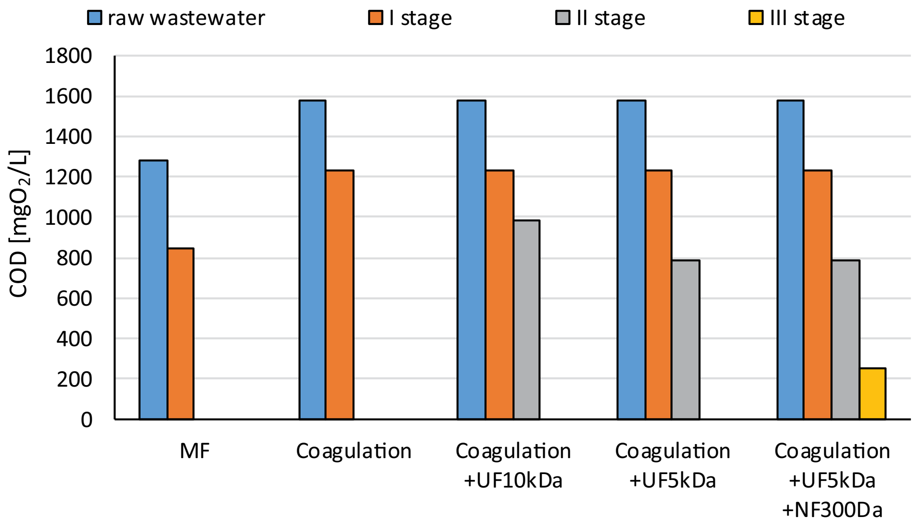

Fig. 2. COD in raw and treated brackish wastewater after single and integrated processes.

different purification efficiency was obtained depending on the applied UF membrane, i.e., 10 or 5 kDa. For parameters describing the content of organic substances such as TOC and COD, the efficiency was twice as high during the process conducted with the 5 kDa membrane than with the 10 kDa membrane. For example, 33.3% removal of the TOC was noted for the 5 kDa membrane and only 14.9% of TOC was removed by the 10 kDa membrane. Whereas the COD was reduced by the 5 kDa membrane by 28.3% and by the 10 kDa membrane a 15.7% reduction was observed. On the other hand, the colour of sewage was reduced by 23.2% and 15.4%, for the 5 and 10 kDa membrane respectively.

Throughout the purification process Coagulation/UF5 kDa/NF300 Da, very high efficiencies were obtained,

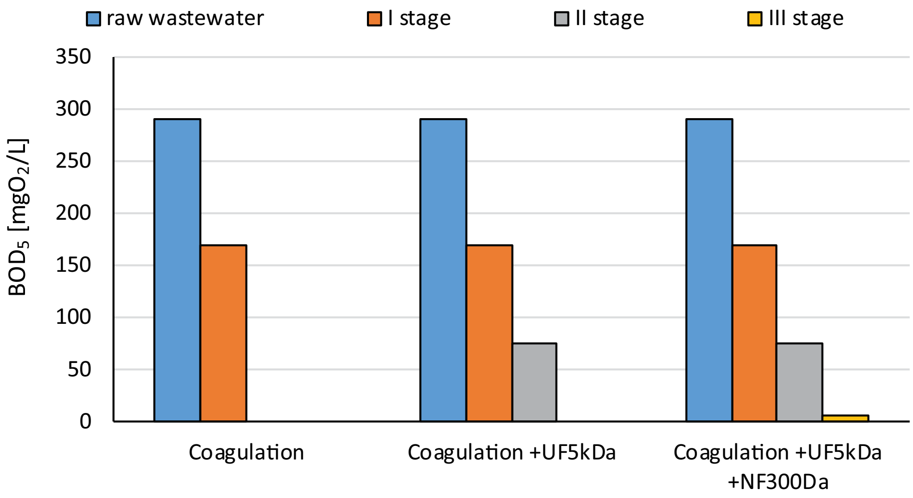

Fig. 3. BOD_5 in raw and treated brackish wastewater after single and integrated processes.

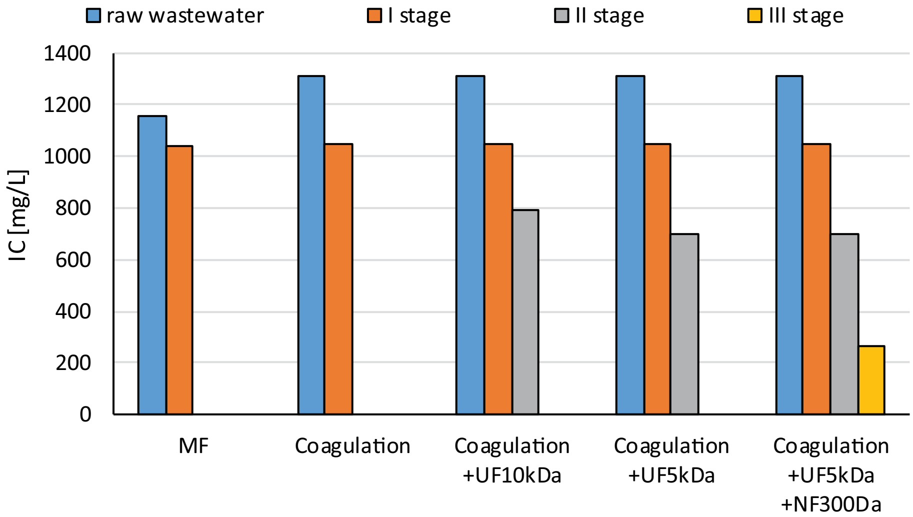

Fig. 4. IC content in raw and treated brackish wastewater after single and integrated processes.

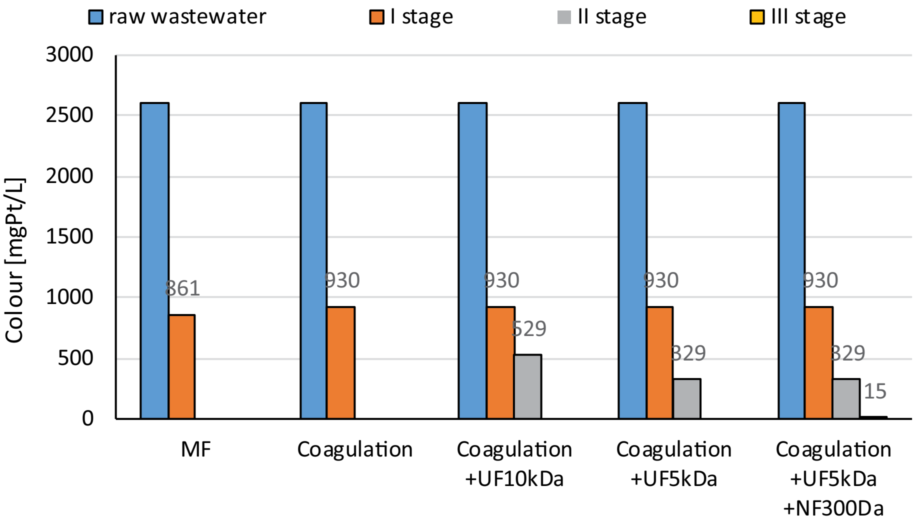

Fig. 5. Colour in raw and treated brackish wastewater after single and integrated processes.

Table 3
The effectiveness of brackish wastewater treatment

Parameter	MF	Coagulation	Coagulation +UF10kDa	Coagulation +UF5kDa	Coagulation +UF5kDa +NF300Da
TOC	33.3%*	26.6%	26.6%	26.6%	26.6%
			14.9%	33.3%	33.3%
			∑ = 41.5%	∑ = 59.9%	33.9%
					∑ = 93.9%
COD	33.9%	21.7%	21.7%	21.7%	21.7%
			15.7%	28.3%	28.3%
			∑ = 37.4%	∑ = 50.0%	33.7%
					∑ = 83.7%
BOD_5	-	41.4%	–	41.4%	41.4%
				32.8%	32.8%
				∑ = 74.2%	24.1%
					∑ = 98.3%
Colour	66.9%	64.2%	64.2%	64.2%	64.2%
			15.4%	23.2%	23.2%
			∑ = 79.6%	∑ = 87.4%	12.0%
					∑ = 99.4%

* The effectiveness was calculated with reference to the wastewater before treatment

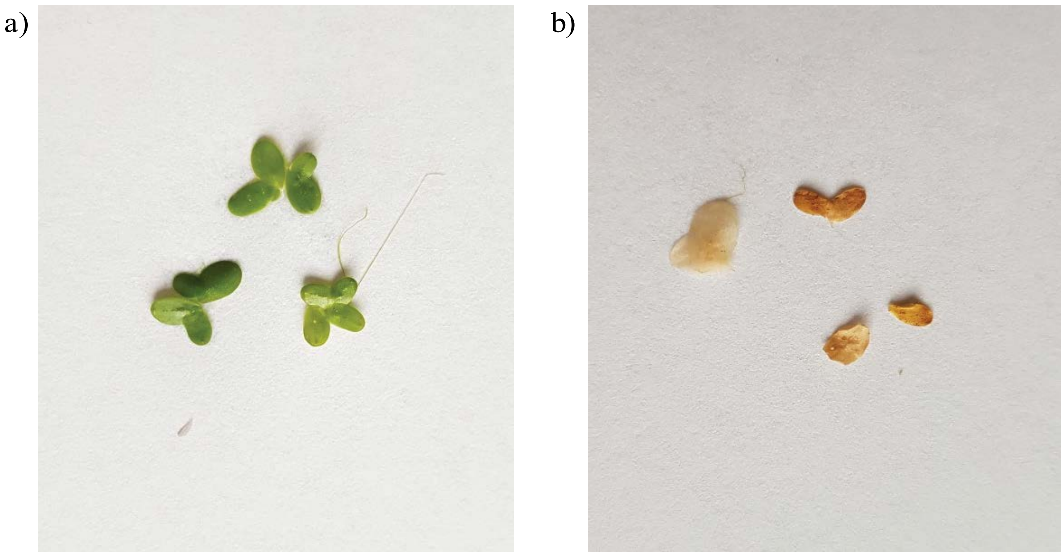

Fig. 6. Changes in the appearance of duckweed during the toxicological test: (a) reference sample and (b) after 2 days of test duration.

i.e., TOC 93.7%, COD 83.7%, BOD_5 98.3%, colour 99.4% and IC 79.8% (Table 3). Treatment of industrial wastewater is expensive and appropriate water management is important, e.g. reuse treated wastewater for industrial purposes or for irrigation of green spaces. The treated wastewater must meet certain requirements. Despite a significant reduction in parameters determining organic compounds, the stream contained large amounts of chlorides, i.e. 855 mg/L. The proposed stages of pre-treatment and treatment of the investigated wastewater were aimed at appropriate preparation of the feed before desalination of wastewater in membrane processes, i.e. reverse osmosis (RO), but also such a final process may be membrane distillation (MD) or electrodialysis (ED) [15,16]. Currently, RO is a common desalination process due to modular design changes and energy recovery [17,18]. The combined system containing ED-NF-MD was used for highly effective desalination of water from oilfields [19]. A very high water recovery of 99.8% was obtained.

When desalinating brackish water, special attention should be paid to anions: nitrates, iodides, bromides and fluorides, and cations: arsenic, boron, chromium, copper, cadmium and lead [16,20].

The implementation of multi-stage membrane filtration UF/NF, preceded by the coagulation process, caused the formation of three waste streams, which were characterized by significantly different physicochemical properties and a stream of clean water, which can be reused in the industrial plant. Even though the waste streams were still toxic, it is possible to treat them chemically to recover valuable components, which will be used on the premises of an industrial plant. In the case of our wastewater, the following wastes were obtained: coagulation sludge, UF concentrate, and NF concentrate. Such a separation of pollutants will in turn allow a different approach to these waste streams. The toxicity of all streams assessed based on the changes in the appearance of duckweed was at a very high level. Changes in the green part of the plants were observed after the second day of the test duration for all streams (Fig. 6). This confirms the negative influence of the components of the streams on living organisms. The UF concentrate, which contains mainly organic compounds and is highly toxic, can be treated for example using advanced oxidation processes such as the Fenton reaction, UV/Fenton, UV/H_2O_2, to obtain pure water [9,21]. The NF concentrate can be treated in the Fenton process using low doses of reagents, which guarantee the decomposition of organic compounds. While the mineral fraction can be extracted by chemical precipitation. The treatment of brackish wastewater and the management of waste streams resulting from this treatment becomes an important issue in the circular economy.

A further optimization of the Coagulation/UF/NF system for the treatment of wastewater containing both organic and mineral compounds could be done by the use of NF membrane with low fouling characteristics [22].

4. Conclusions

In order to select an appropriate method of treating brackish wastewater containing a high concentration of organic compounds (1,576 mg O_2/L as COD), high concentration of mineral compounds (1,000 mg Cl^-/L) and toxic organic compounds, coagulation and membrane filtration (MF, UF and NF) were used. The obtained results allowed for the following conclusions regarding pre-treatment:

- using a membrane with pore size 0.1 μm and coagulation with aluminium compounds, similar effects of pre-treatment of brackish wastewater were obtained; the colour of the wastewater was reduced by 66.9% and 64.2%, respectively,
- the obtained coagulation efficiency was satisfactory (26.6% of TOC, 21.7% of COD, 41.4% of BOD and 64.2% of colour removal) and allows for a high degree of removal of organic and mineral impurities during multistage treatment: coagulation/UF/NF.

A high degree of removal of organic and mineral compounds was obtained during studies on the treatment of brackish wastewater in the system: coagulation/UF5kDa/NF300Da, i.e.: 93.7% (TOC), 83.7% (COD), 98.3% (BOD), 99.24% (colour) and 79.8% (IC). As a result of the treatment, the resulting concentrates were also toxic, but they can be treated with methods that are optimal for them.

Acknowledgements

This work was supported by Ministry of Science and Higher Education Republic of Poland within statutory funds, 2021.

References

[1] U.V. Shenoy, Enhanced nearest neighbours algorithm for design of water networks, Chem. Eng. Sci., 84 (2012) 197–206.
[2] V.V. Ranade, V.M. Bhandari, Industrial Wastewater Treatment, Recycling, and Reuse, Butterworth-Heinemann, 2014.
[3] X. Zheng, Z. Zhang, D. Yu, X. Chen, R. Cheng, S. Min, J. Wang, Q. Xiao, J. Wang, Overview of membrane technology applications for industrial wastewater treatment in China to increase water supply, Resour. Conserv. Recycl., 105 (2015) 1–10.
[4] O. Lefebvre, R. Moletta, Treatment of organic pollution in industrial saline wastewater: a literature review, Water Res., 40 (2006) 3671–3682.
[5] D. Zhao, J. Song, J. Xu, S. Yu, J. Liu, Y. Zhu, Z. Gu, G. Liu, Behaviours and mechanisms of nanofiltration membrane fouling by anionic polyacrylamide with different molecular weights in brackish wastewater desalination, Desalination, 468 (2019) 114058.
[6] R. Zhang, W. Shi, S. Yu, W. Wang, Z. Zhang, B. Zhang, L. Li, X. Bao, Influence of salts, anion polyacrylamide and crude oil on nanofiltration membrane fouling during desalination process of polymer flooding produced water, Desalination, 373 (2015) 27–37.
[7] J. Shi, W. Huang, H. Han, C. Xu, Review on treatment technology of salt wastewater in coal chemical industry of China, Desalination, 493 (2020) 114640.
[8] Y. Kim, B.E. Logan, Simultaneous removal of organic matter and salt ions from saline wastewater in bioelectrochemical systems, Desalination, 308 (2013) 115–121.
[9] Y. Chai, P. Qin, Z. Wu, M. Bai, W. Li, J. Pan, R. Cao, A. Chen, D. Jin, C. Peng, A coupled system of flow-through electro-Fenton and electrosorption processes for the efficient treatment of high-salinity organic wastewater, Sep. Purif. Technol., 267 (2021) 118683.
[10] M. Turek, P. Dydo, R. Klimek, Salt production from coal-mine brine in NF-evaporation-crystallization system, Desalination, 221 (2008) 238–243.
[11] E. Kudlek, M. Dudziak, The impact of selected organic micropollutants on water ecosystems, Inż. Ekol., 18 (2017) 83–90.
[12] W. Cai, Z. Gao, S. Yu, M. Lv, Y. Shi, J. Wang, New insights into membrane fouling formation during ultrafiltration of organic wastewater with high salinity, J. Membr. Sci., (2021), doi: 10.1016/j.memsci.2021.119446.
[13] S. Vishali, S. Sakthivel, R. Karthick, V.S. Gowsigan, A sustainable approach for the treatment of industrial effluent using a green coagulant *Cassia fistula* vs. chemical coagulant, Desal. Water Treat., 196 (2020) 189–197.
[14] F.Y. AlJaberi, S.A. Ahmed, H.F. Makki, Electrocoagulation treatment of high saline oily wastewater: evaluation and optimization, Heliyon, 6 (2020) e03988, doi: 10.1016/j.heliyon.2020.e03988.
[15] K. Mitko, A. Noszczyk, P. Dydo, M. Turek, Electrodialysis of coal mine water, Water Resour. Ind., 25 (2021) 100143.
[16] M. Bodzek, Membrane separation techniques – removal of inorganic and organic admixtures and impurities from water environment – review, Arch. Environ. Prot., 45 (2019) 4–19.
[17] A. Alkaisi, R. Mossad, A. Sharifian-Barforoush, A review of the water desalination systems integrated with renewable energy, Energy Procedia, 110 (2017) 268–274.
[18] D. Karimanzira, How to use wind power efficiently for seawater reverse osmosis desalination, Energy Power Eng., 12 (2020), doi: 10.4236/epe.2020.129031.
[19] S. Zhao, S. Hu, X. Zhang, L. Song, Y. Wang, M. Tan, L. Kong, Y. Zhang, Integrated membrane system without adding chemicals for produced water desalination towards zero liquid discharge, Desalination, 496 (2020) 114693.
[20] M. Turek, P. Dydo, J. Trojanowska, A. Campen, Adsorption/co-precipitation-reverse osmosis system for boron removal, Desalination, 205 (2007) 192–199.
[21] R. Brüninghoff, Advanced Oxidation Processes. Materials and Technology for Saline Wastewater Treatment, University of Twente, 2020.
[22] C. Bartels, M. Wilf, W. Casey, J. Campbell, New generation of low fouling nanofiltration membranes, Desalination, 221 (2008) 158–167.