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Molecular weight distribution of pre-treated MDF wastewater

Ismail Hakki Zengin

ismailhakkizengin@gmail.com

Yildiz Technical University Department of Environmental Engineering: Yildiz Teknik Universitesi Cevre Muhendisligi Bolumu https://orcid.org/0009-0009-4138-2467

Oruç Kaan Türk

Yildiz Technical University Department of Environmental Engineering: Yildiz Teknik Universitesi Cevre Muhendisligi Bolumu https://orcid.org/0000-0002-6473-2150

Merve Saral

Yildiz Technical University Department of Environmental Engineering: Yildiz Teknik Universitesi Cevre Muhendisligi Bolumu

Gizem Çelik

Yildiz Technical University Department of Environmental Engineering: Yildiz Teknik Universitesi Cevre Muhendisligi Bolumu

Gülin Biçe Yıldırım

Yildiz Technical University Department of Environmental Engineering: Yildiz Teknik Universitesi Cevre Muhendisligi Bolumu

Uğur Kurt

Yildiz Technical University Department of Environmental Engineering: Yildiz Teknik Universitesi Cevre Muhendisligi Bolumu

Mehmet Çakmakcı

Yildiz Technical University Department of Environmental Engineering: Yildiz Teknik Universitesi Cevre Muhendisligi Bolumu https://orcid.org/0000-0003-4784-6006

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Abstract

This study investigates the molecular weight distribution (MWD) of wastewater generated from a medium-density fiberboard (MDF) production facility to better understand the size and nature of organic pollutants and to identify suitable treatment methods. Sequential membrane filtration was performed using membranes with molecular weight cut-offs (MWCO) of 500, 150, 50, 10, and 1 kDa, and the filtrates were analyzed for key water quality parameters. Results indicated that 57% of the COD originated from particles larger than 1 µm, 72% from those larger than 0.22 µm, and 21.17% from fractions retained by the 1 kDa membrane, while only 6.43% was below this threshold after pretreatment. These findings demonstrate that the organic load in MDF wastewater is predominantly associated with suspended solids and high-molecular-weight organics. The hybrid use of microfiltration (MF) and nanofiltration (NF) membranes showed a potential to remove more than 90% of the high COD load, highlighting the feasibility of membrane-based treatment as an effective option for MDF wastewater.

1. Introduction

The wood-based panel sector includes a variety of sub-industries that produce fiberboard, particleboard, plywood, oriented strand board, and other wood panels. The wood-based panel business has seen significant growth in recent years, mostly propelled by the furniture and building industries (González-García et al., 2019; Zhou et al., 2024). According to Food and Agriculture Organization of the United Nations statistics (FAOSTAT), medium-density fiberboard (MDF) and plywood are the most commonly utilized panels in this industry (Lao & Chang, 2023; Zhou et al., 2024). MDF is a composite panel made from wood fibers that are bonded together with resin via the application of heat and pressure (Mokhtar et al., 2012). MDF is a commonly used alternative to wood because of its durability and physical characteristics. It has a diverse array of uses, including over 50% in furniture, building and flooring, interior design, and several other fields (ASTM, 2023).

MDF industry is one of the industries with high water consumption. MDF wastewater has a unique set of characteristics in that it has temperatures above 40 ^{O}C and contains suspended particles and organic matter, and intensive water use in MDF production can result in chemical oxygen demand (COD) concentrations of up to 25,000 mg/L and suspended solids (SS) concentrations of up to 9,000 mg/L (Khonakdar Dazmiri et al., 2019; Navas-Cárdenas et al., 2022). These wastewaters, which fail to meet discharge limits using conventional wastewater treatment systems, must undergo treatment using suitable procedures and circumstances to safeguard both the environment and the limited natural resources (Ghorbannezhad et al., 2016; Munoz et al., 2014).

The differences in pollutant concentrations between the influent and effluent enable us to assess the effectiveness of a treatment facility. Nevertheless, the measurement of MWD plays a crucial role in thoroughly assessing the effectiveness of specific treatment techniques and offering precise insights into the fate of pollutants in treatment facilities (Calace et al., 2001; Sophonsiri & Morgenroth, 2004; Yaman et al., 2016). According to the findings of the MWD study conducted on different treatment

procedures, it has been discovered that pollutants with a low molecular weight (< 1 kDa) are capable of being quickly degraded in biological treatment environments (Calace et al., 2001; Campagna et al., 2013). On the other hand, chemical treatment and filtering methods are more successful in eliminating contaminants with a relatively large molecular weight (> 5 kDa) (Malpei et al., 1997; Uner et al., 2006).

To the best of our knowledge, there is a lack of research into the treatment of MDF wastewaters. Due to the high temperature and the presence of higher quantities and different kinds of contaminants in MDF wastewater, it is essential to use suitable treatment procedures to reduce the harmful impacts of these pollutants on the environment. The categorization of wastewater components based on their specific molecular weights provides valuable insights into the characteristics of wastewater, facilitating the development of suitable treatment methods (Dulekgurgen et al., 2006; Leiviskä et al., 2008). In this study, the MWD of several contaminants in highly pollutant-loaded MDF wastewater examined and assessed potential treatment options based on the contaminants' types and sizes.

2. Materials and methods

2.1. Source and characterization of the feed solution

(MDF) industry is a challenging type to treat due to its high organic load and complex compounds. This wastewater contains complex organic substances such as lignin, cellulose, hemicellulose, tannins, resins, polyphenols, and oils, many of which are refractory pollutants that are not easily degradable by biological methods

The wastewater used in this study was collected from an MDF production factory located in Turkey and it was characterized by pH, conductivity, COD, sulfate, turbidity, color, TSS and total hardness analysis. The characteristics of wastewater are presented in Table 1.

Table 1
Charactersitcis of wastewater used in the study.

pH	Conductivity,	COD,	Sulfate,	Turbidity,	Color,	TSS,	Total Hardness,
	µS/cm	mg/L	mg/L	NTU	Pt-Co	mg/L	mg $CaCO_3$/L
4.61	1,603	41,422	171.02	13,310	26,420	16,510	660

2.2. Pre-treatment Procedure

Jar test experiments were conducted in the Environmental Engineering Department Laboratory at Yıldız Technical University to simulate the primary treatment stage of a full-scale wastewater treatment plant treating MDF industry effluents. Coagulation–flocculation, a widely adopted method for removing colloidal particles, color, and organic matter, was selected due to the high contaminant load and complex matrix of MDF wastewater. PACS, a high-basicity coagulant with minimal sulfate content, was chosen for its effectiveness in turbidity and color reduction, as well as its minimal contribution to

residual sulfate levels in treated water. PACS is widely applied in drinking water production, municipal and industrial wastewater treatment, and process water systems. In this study, it was applied using a stock solution prepared at a concentration of 1.273 mg/mL. The jar test conditions were designed to reflect practical operational parameters, allowing for the results to be scalable to real-world treatment systems.

Jar test experiments were conducted to determine the optimal coagulant dosage and mixing/contact conditions. PACS was tested at concentrations of 100, 500, 1,000, and 2,500 mg/L. For each test, 500 mL of wastewater was placed into beakers, and the pH was adjusted to 6.0–7.0 using 1 N NaOH or 1 N H_2SO_4 before coagulant addition. The coagulation stage was performed by rapid mixing at a velocity gradient of 100 s^{-1} for 5 minutes, followed by flocculation at 20 s^{-1} for 25 minutes. Subsequently, settling was allowed for 30, 60, and 90 minutes to observe the effects of sedimentation time.

Following sedimentation, 100 mL of supernatant was transferred into two 50 mL Falcon tubes and centrifuged at 3000 RPM for 2, 3, 4, and 5 minutes to evaluate the influence of centrifugation time on solid–liquid separation. Taking into account chemical dosing efficiency, energy input, and pollutant removal performance, the experimentally optimized pre-treatment conditions were identified as 1,000 mg/L PACS dosage, 90 minutes of settling, and 3 minutes of centrifugation contact time.

2.3. Lab Scale Membrane Filtration Setup

MWD experiments were conducted using a lab-scale membrane filtration setup, located in Yildiz Technical University's Environmental Engineering Laborator, which consists of a vertical flow filtration unit made of stainless steel from the Sterlitech brand, a nitrogen gas tank, a pressure gauge, a magnetic stirrer, a precision balance, and a computer. After placing the feed water into the filtration unit, the unit was positioned on the magnetic stirrer, which was used throughout the filtration process to maintain homogeneity. In this pressure-operated system, the pressure was kept constant using nitrogen gas, an inert gas, and the weight of the filtrate was recorded with a precision balance connected to a computer, enabling the calculation of flux. The laboratory-scale vertical flow membrane filtration setup is shown in Fig. 1.

The properties of the membranes used in the MWD study are provided in Table 2.

Table 2
Properties of the membranes used in the study.

Manufacturer	Type	Pore Size	Material	Permeability (L.m^2.hr/bar)
NADIR RM MP005P 1016	MF	0.05 µm	PES	> 300
NADIR RM UP 150P 1060	UF	150 kDa	PES	> 286
NADIR RM UH 050 P	UF	50 kDa	PESH	> 85
Sterlitech YMCQSP3001	UF	10 kDa	PES	85/30 Flux (GFD)/psi
Sterlitech YMGESP3001	UF	1 kDa	Polyamide	18/400 Flux (GFD)/psi

Before performing the MWD experiments, a pre-treatment with PACS was implemented due to the adhesive properties of MDF wastewater that were induced by the resin. The wastewater was subsequently filtered through cartridge filters with pore sizes of 5, 1, and 0.22 microns, respectively. Membranes with molecular weight cutoffs of 500, 150, 50, 10, and 1 kDa were operated at pressures of 1, 1, 2, 4, and 8 bar, respectively. A peristaltic pump was employed to sustain circulation in the cartridge filters during the filtration process.

2.4. Analysis

The specific water quality parameters that are given in Table 3 were carried out to characterize the raw MDF wastewater and the effluents from the MWD study. These analyses were performed using standard methods to ensure accurate and reliable results.

Table 3
Water quality analysis conducted in the study.

Analysis	Method	Material
COD	Standard Methods, 5220 C	Closed Reflux
Conductivity	Standard Methods, 2510	Conductivity Probe
pH	Standard Methods, 4500 H^+	pH Probe
Sulfate	Standard Methods, 4500 $SO4^{2-}$	Spectrophotometric
Total Hardness	Standard Methods, 2340 C	Titration
TSS	Standard Methods, 2540 D	Filtration Setup
Turbidity	Standard Methods, 2130 B	Spectrophotometric

3. Results and discussion

3.1. Water Quality Results

The COD parameter is one of the most commonly used water quality indicators for estimating the amount of oxidizable organic matter in wastewater. It is a critical parameter that provides essential insights into water quality, as it is essential to measure the concentration of organic pollutants in the effluent in order to evaluate the performance of the treatment facility. Figure 2 reveals that a substantial proportion of COD originates from large particulate and colloidal matter.

Specifically, the > 5 μm size fraction, which includes wood fibers and resin particles, alone accounts for approximately 55% of the total COD. Furthermore, the colloidal fractions in the 1–0.22 μm and 0.22–0.05 μm ranges contribute approximately 15% and 9.5% of the COD, respectively. Collectively, these findings indicate that over 80% of the COD is associated with suspended or colloidal organic substances larger than ~ 0.05 μm. In contrast, the contribution of dissolved organic matter—represented by low molecular weight fractions—is relatively limited, accounting for only about 18% of the total COD. Indeed, all fractions below 0.05 μm (including those ≤ 150 kDa) comprise merely one-fifth of the total COD. This distribution suggests that the organic load in MDF wastewater is predominantly composed of particulate or high-molecular-weight polymeric compounds, whereas the contribution from mid-sized molecules (150–10 kDa) is minimal.

The turbidity parameter is an important indicator in wastewater for evaluating water quality due to its ease of measurement and significance. Turbidity is caused by suspended solids, organic matter, microorganisms, colloids, and other pollutants that reduce water clarity. Assessing turbidity is crucial for determining water quality, evaluating treatment efficiency, and protecting public health. As shown in Fig. 3, the particle size fractions contributing to the turbidity of MDF wastewater reveals that the majority of turbidity originates from large particles and colloidal-sized substances. In particular, the suspended solids larger than 5 μm account for approximately 40% of the total turbidity, while fine colloids in the 1–0.22 μm range contribute a similar proportion of around 40%. Medium-sized particles (5–1 μm) are responsible for about 9% of the turbidity, and very fine colloids in the 0.22–0.05 μm range account for approximately 11%. The contribution of particles smaller than 0.05 μm (50 nm) is negligible (~ 0%). This distribution clearly indicates that over 90% of the turbidity is caused by suspended and colloidal matter larger than 0.22 μm, while dissolved molecules do not contribute to turbidity.

Monitoring the color parameter is essential for wastewater treatment and the protection of water quality in receiving environments. Color is caused by the presence of organic and inorganic compounds, dissolved organic substances, heavy metals, and dyes in the water. The distribution of the color parameter across various molecular weight and particle size fractions reveals the dimensional characteristics of color-causing substances in MDF wastewater. According to the Fig. 4, color intensity primarily originates from large and colloidal-sized materials. Particles larger than 5 μm (e.g., visibly suspended colored solids) account for approximately 27% of the total color, while fine colloidal matter in the 1–0.22 μm range contributes around 26%. Additionally, the 5–1 μm range contributes 12.5%, and the 0.22–0.05 μm (50–220 nm) fraction adds about 16.7%.

These values indicate that approximately 82% of the color in the wastewater stems from suspended solids or colloidal structures larger than 0.05 µm. In contrast, the contribution of smaller, dissolved color-causing molecules is relatively low. Dissolved high molecular weight compounds in the 0.05 µm – 150 kDa fraction account for only about 11% of the color, while the remaining lower molecular weight fractions (150–50 kDa, 50–10 kDa, 10–1 kDa, and < 1 kDa) together explain merely ~ 6–7%. The majority of the color in MDF wastewater originates from polymeric or particulate large organic molecules—likely lignin derivatives, tannin aggregates, or fine wood fibers. Small molecules, on the other hand, contribute negligibly to color. This distribution supports the understanding that substances such as humic acids and tannins typically impart color to water in the form of high molecular weight aggregates.

Another important parameter in wastewater treatment and membrane filtration is sulfate. High sulfate concentrations in wastewater can cause corrosion, leading to damage to infrastructure. Under anaerobic conditions, sulfate-reducing bacteria can reduce sulfate to hydrogen sulfide gas, which is associated with foul odors and toxic effects. In membrane filtration, high sulfate concentrations can accumulate on the membrane surface in the presence of calcium and magnesium, reducing filtration efficiency and shortening the membrane's lifespan. This also leads to more frequent backwashing, increasing operational costs.

The size of the membrane pore is directly correlated with the removal of sulfate, as illustrated in Fig. 5. The 1 kDa membrane was the most effective in removing sulfate. Pathogens, bacteria, and suspended particulates can be eliminated by UF membranes; however, they are incapable of eliminating dissolved ions such as sulfate. Nevertheless, NF membranes are capable of removing divalent ions, including sulfate. The membrane, which is situated in a transition zone between UF and NF, is capable of removing sulfate due to its 1000 Da MWCO.

Conductivity is a critical parameter in membrane filtration and wastewater treatment, as it quantifies the capacity of water to conduct electrical current and represents the total concentration of dissolved ions. Conductivity is frequently used to monitor the membrane process's efficiency in membrane filtration. Membrane clogging or damage is indicated by an increase in conductivity in the filtrate (Yang et al., 2019).

The conductivity removal efficiencies of the pressure-driven membranes employed in this study, which have varying pore diameters, are restricted, as illustrated in Fig. 6. The highest conductivity removal efficiency of 29.5% was attained using a 1000 Da membrane, as the conductivity value decreased in tandem with the decrease in pore size.

Membrane processes may result in the formation of deposits on the membrane surface due to total hardness, which is caused by the presence of calcium and magnesium ions. This can clog the membrane pores, thereby reducing permeability and removal efficiency. Consequently, total hardness is a critical water quality parameter in membrane processes. (Lee, 2000; Shirazi et al., 2010). As shown in Fig. 7, it is evident that total hardness cannot be effectively removed with only pre-treatment (coagulation with PACS). Similarly, sufficient hardness removal was not achieved with cartridge filters or

MF membranes. MF membranes are ineffective in the elimination of hardness due to their inability to remove dissolved ions. In addition, it has been noted that UF membranes (150, 50, and 10 kDa) are ineffective in the removal of hardness. Nevertheless, the efficiency of hardness removal was enhanced to 45% when a membrane with a 1 kDa MWCO was employed.

3.2. Membrane Characteristics

Contact angle, SEM, EDS, and ATR-FTIR analyses were implemented to monitor the modifications in the morphological characteristics of the membranes' surfaces subsequent to filtration.

ATR-FTIR analysis is commonly used to identify and characterize inorganic and organic compounds. The ATR-FTIR spectra in Fig. 8 illustrate the modifications in the surface properties of the membranes employed in the MWD study (150 kDa, 50 kDa, 10 kDa, 1 kDa) subsequent to filtration. The S = O bands are represented by the peaks observed at 1150 and 1240 cm^{-1}, whereas the benzene ring stretching vibrations in the 1500 cm^{-1} region are the characteristic peaks of PES membranes (Koloti et al., 2018).

The peak at 3314 cm^{-1} is attributed to hydroxyl groups (O-H) that are derived from moisture or protective compounds. It is observed that these peaks become less pronounced after filtration. It is estimated that the decrease in the intensity of these peaks is due to the adsorption of organic matter onto the membrane surface, leading to interactions with hydroxyl groups during filtration. The peaks in the 3100 – 2850 cm^{-1} wavelength range correspond to aromatic and aliphatic C–H stretching vibrations, which are typically observed in PES membranes (Yang et al., 2019).

The graphs in Fig. 9 illustrate the time-dependent changes in the flux of the membranes used throughout the MWD study. In each membrane experiment, the system was operated for at least 6 hours, and the volume of filtrate was recorded using a precision balance and transferred to a computer for flux calculations. For the PES MF membrane with a 500 kDa MWCO, the initial flux was 400 LMH ($L/m^2.h$), but it dropped sharply within 60 minutes and stabilized around 20 LMH. This significant drop in flux is believed to result from large organic molecules in the wastewater accumulating on the membrane surface and clogging the pores. The formation of a cake layer on the membrane surface is consistent with the SEM images presented in Fig. 12. The SEM images marked with a) show that a cake layer formed on the surface of the dirty membrane (right) compared to the clean membrane (left).

The membrane with a 150 kDa MWCO had an initial flux of 120 LMH, which decreased rapidly within one hour to stabilize at 10 LMH. Although a cake layer was also observed on this membrane, it was less pronounced than on the 500 kDa membrane. The SEM images marked with b) in Fig. 11 confirm this observation, clearly showing the accumulation of contaminants on the surface of the dirty membrane compared to the clean membrane.

For the membrane with a 50 kDa MWCO, the initial flux was 75 LMH, which steadily decreased to stabilize at 12 LMH. While the drop in flux was likely due to potential clogging on the membrane surface

and pores, it was less pronounced compared to the first two membranes. This is attributed to the larger pore sizes of the first two membranes, which retained larger contaminants and reduced the pollution load in the wastewater. The membrane with a 10 kDa MWCO started with an initial flux of 50 LMH, which gradually decreased to 15 LMH. Notably, the membrane with a 1 kDa MWCO experienced the least drop in flux, starting at 10 LMH and remaining stable around 6 LMH throughout the 6-hour operation. Overall, when evaluating the flux graphs of all membranes, the general trend observed is a drop in initial flux during the first hour, followed by a more stable continuation thereafter. The greater decrease in flux observed in membranes with high MWCO is attributed to the fact that the majority of organic pollutants in MDF wastewater consist of large organic compounds and colloidal particles. These larger substances are retained by the high MWCO membranes, leading to a reduction in the pollution load as they are unable to pass through the membrane.

Figure 10 illustrates the changes in contact angles before and after filtration for membranes with different MWCOs used in the MWD analysis. Measuring the contact angle is important as it provides insight into the hydrophilicity or hydrophobicity of the membrane surface. From the table, it can be seen that the contact angle of the membrane with a 500 kDa MWCO increased after filtration.

This increase in the contact angle is likely due to the adsorption of hydrophobic organic compounds present in the wastewater onto the membrane surface. Studies have shown that the accumulation of hydrophobic organic matter on the surface can enhance the hydrophobicity of the membrane (Gao et al., 2011). A significant decrease in the contact angles was observed for the membranes with MWCOs of 50, 10, and 1 kDa after filtration. This notable reduction is believed to result from the accumulation of hydrophilic compounds present in MDF wastewater on the membrane surfaces. Compounds with hydrophilic structures, such as proteins and polysaccharides, can adsorb onto the membrane surface and increase its hydrophobicity (Madaeni & Mansourpanah, 2004).

The EDS data reveal the elemental distribution of the membranes used in the MWD study before and after the treatment of MDF wastewater. This analysis allows for the identification of the types of pollutants that can accumulate or adsorb onto the membrane surfaces.

Table 4 illustrates that the clean membranes consist of carbon (C), oxygen (O), and sulfur (S) elements, which originate from the structure of PES membranes. After filtration, aluminum (Al), silicon (Si), calcium (Ca), magnesium (Mg), chlorine (Cl), and sodium (Na) elements were detected on the membrane surfaces. Additionally, an increase in the amount of carbon (C) and a decrease in the amount of oxygen (O) were observed on almost all membranes. This suggests that the cake layer observed in the SEM images in Fig. 11 is formed by the accumulation of organic pollutants, salts, and other inorganic materials.

Table 4
The elemental distribution analysis of the surfaces of the membranes used in the MWD study.

Pristine			**Fouled**		
Element	**Weight, %**	**Atomic, %**	**Element**	**Weight, %**	**Atomic, %**
500 kDa					
C K	39.51	46.52	C K	52.73	60.6
O K	60.49	53.48	O K	44.05	38.01
			Al K	1.21	0.62
			Si K	0.53	0.26
			Ca K	1.48	0.51
150 kDa					
C K	45.9	57.24	C K	50.54	60.35
O K	37.2	34.82	O K	39.32	35.25
S K	12.31	5.75	Na K	0.47	0.29
			Mg K	0.91	0.54
			S K	4.86	2.17
			Ca K	3.91	1.4
50 kDa					
C K	54.25	66.4	C K	54.41	64.17
O K	27.43	25.2	O K	35.38	31.32
S K	18.32	8.4	Na K	0.71	0.44
			Mg K	0.39	0.23
			S K	6.81	3.01
			Cl K	0.33	0.13
			Ca K	1.98	0.7
10 kDa					
C K	54.66	66.85	C K	51.89	63.19
O K	26.9	24.7	O K	32.25	29.48
S K	18.45	8.45	Na K	1.49	0.95

Pristine			Fouled		
Element	**Weight, %**	**Atomic, %**	**Element**	**Weight, %**	**Atomic, %**
500 kDa					
			Mg K	0.39	0.24
			S K	11.4	5.2
			Cl K	0.13	0.05
			Ca K	2.45	0.89
1 kDa					
C K	59.06	70.08	C K	63.85	73.03
O K	26.25	23.38	O K	26.69	22.92
S K	14.7	6.53	S K	9.46	4.05

4. Conclusion

This study provides the first comprehensive molecular weight distribution (MWD) analysis of highly pollutant-loaded medium-density fiberboard (MDF) wastewater. Sequential membrane filtration, combined with pre-treatment using PACS, revealed that the organic load is predominantly composed of particulate and colloidal fractions larger than 0.05 µm, accounting for over 80% of the total COD. Only a small proportion of organic matter was present in the low-molecular-weight fraction (< 1 kDa), indicating limited biodegradability and the necessity for advanced treatment processes.

The results indicate that a hybrid MF–NF treatment scheme can achieve over 90% COD removal from MDF wastewater, offering a practical solution for managing this challenging industrial effluent. Understanding the MWD not only provides insight into pollutant characteristics but also guides the selection of pretreatment and advanced membrane processes. These findings are expected to support the design and optimization of pilot- and full-scale treatment systems. Future studies should focus on validating hybrid membrane configurations under real operating conditions and assessing their long-term performance and economic feasibility. Overall, this work establishes a critical scientific basis for optimizing advanced treatment solutions for a challenging and under-researched industrial wastewater type.

Declarations

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Figures

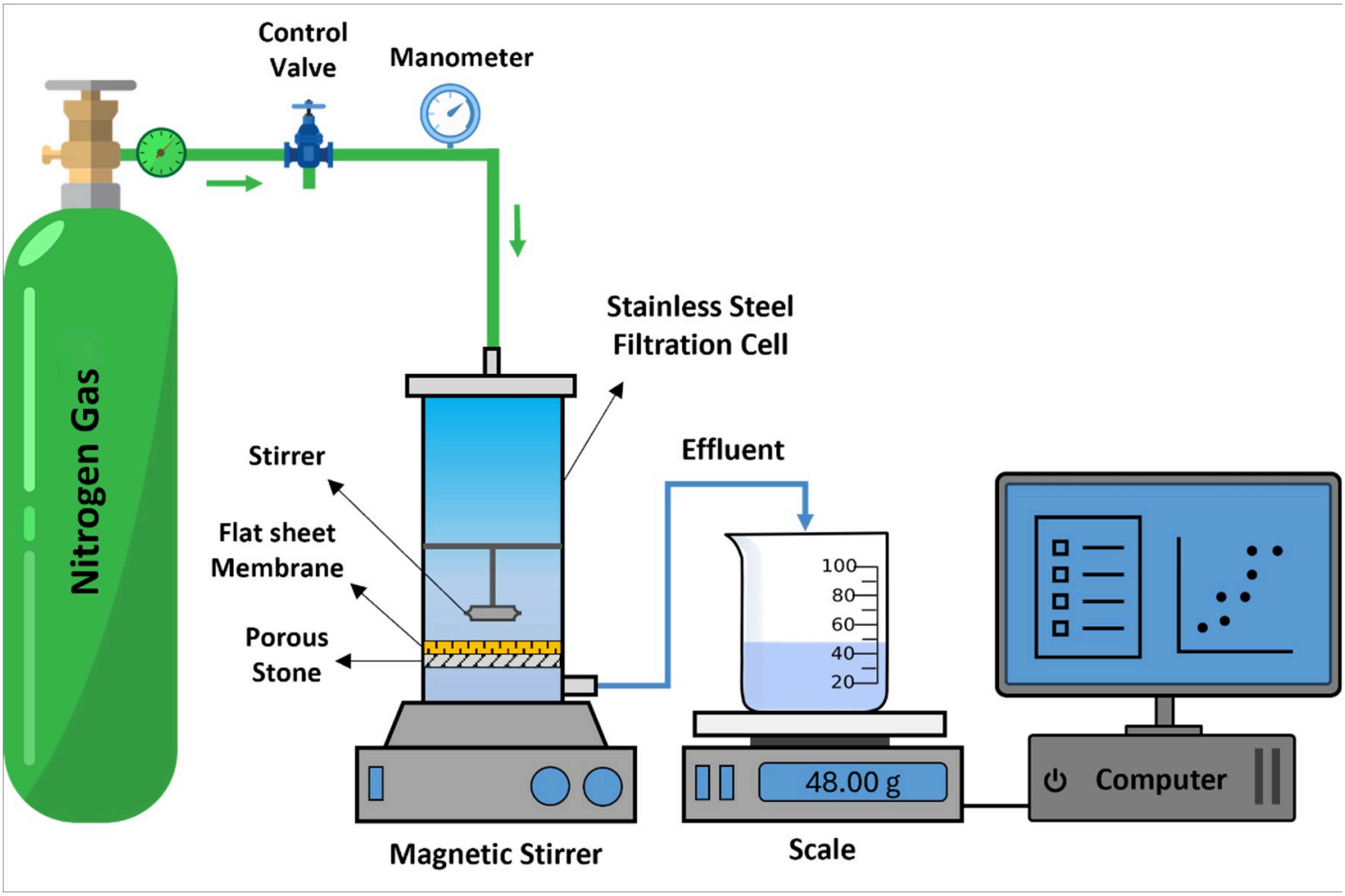


Figure 1

Shematic diagram of lab-scale membrane filtration setup

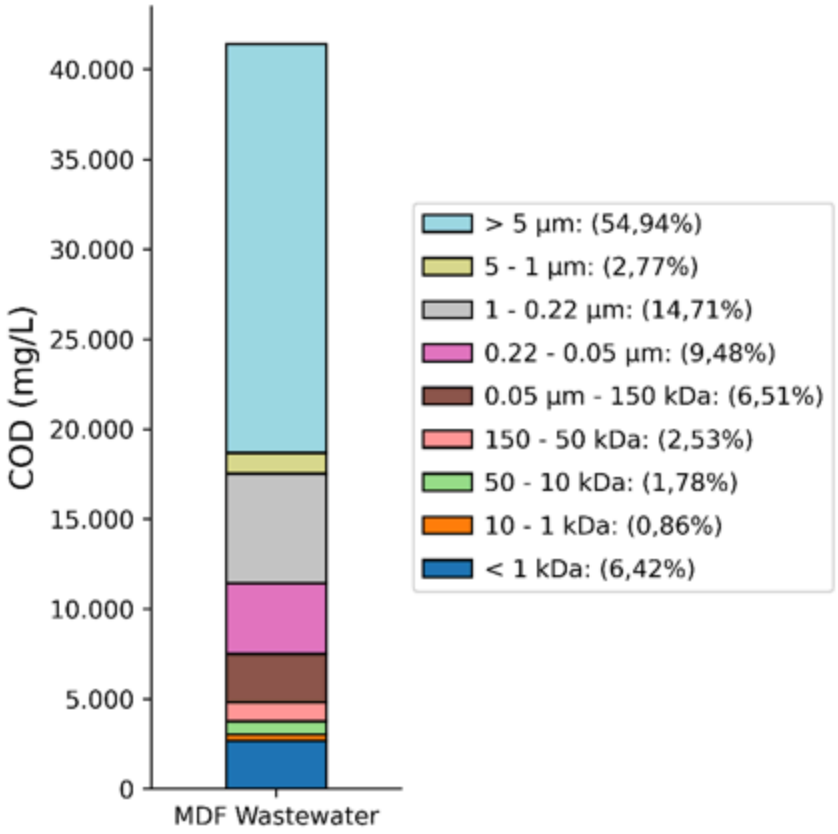


Figure 2

Molecular weight distribution of COD in MDF wastewater

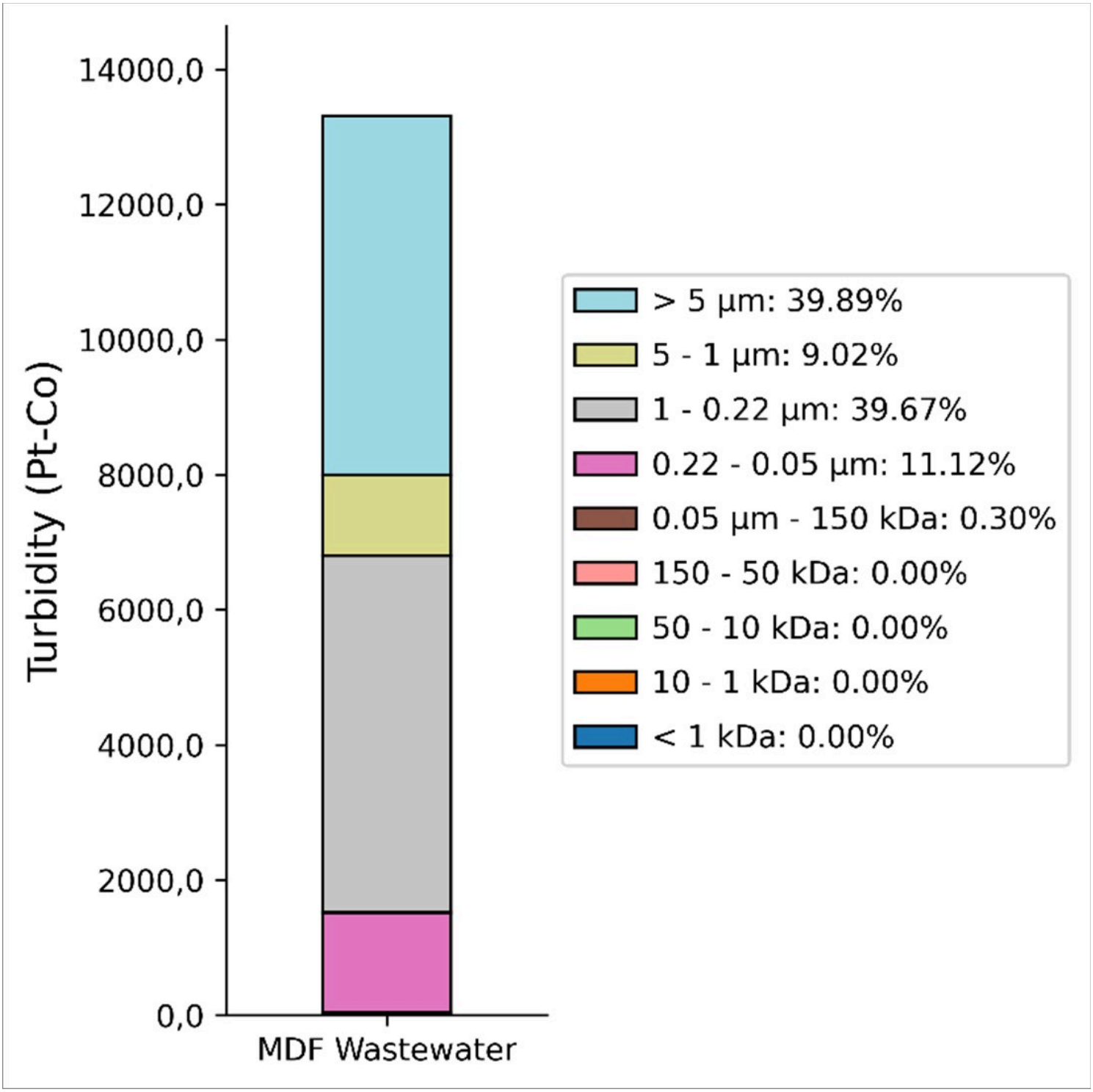


Figure 3

Molecular weight distribution of turbidity in MDF wastewater

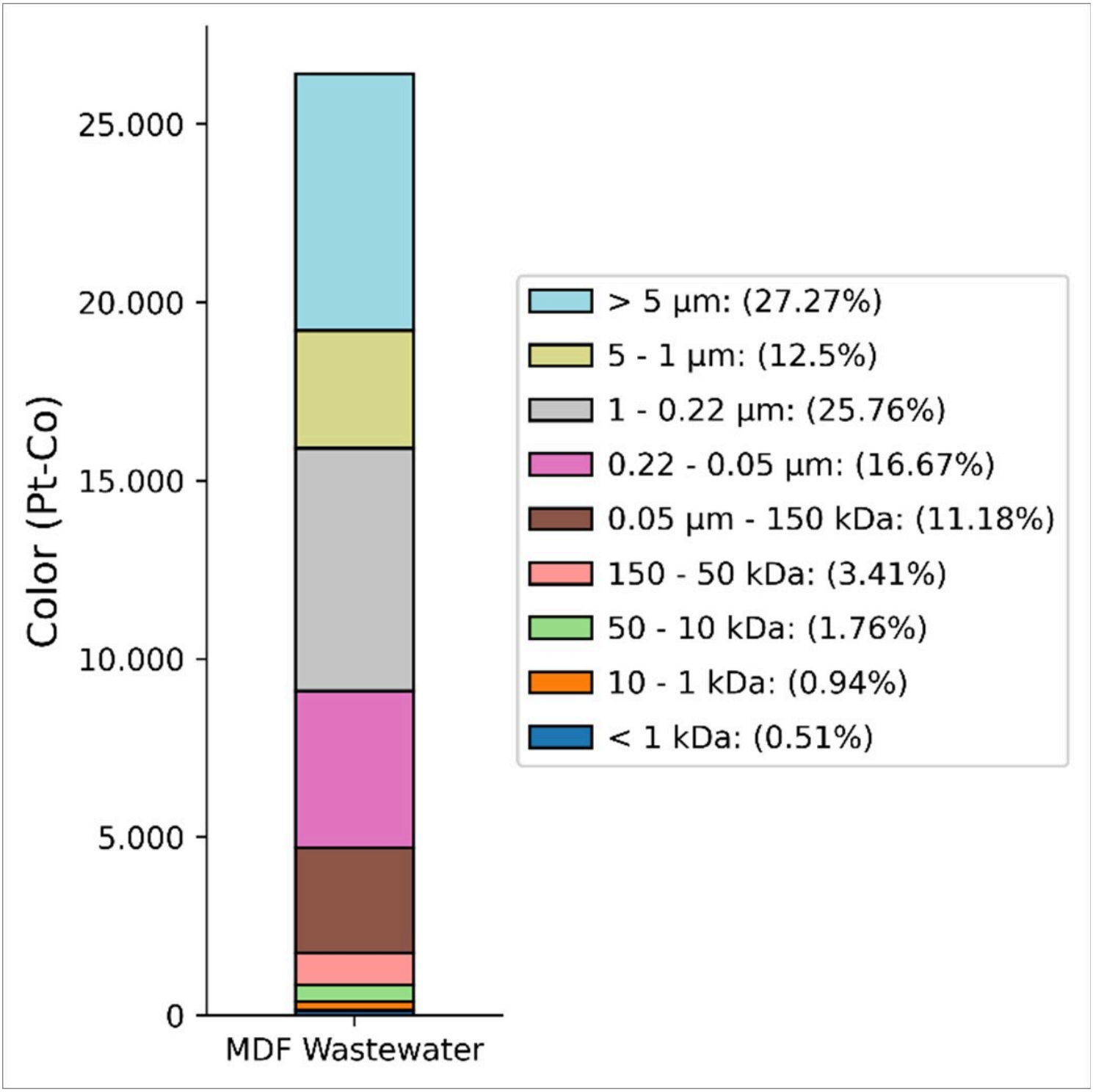


Figure 4

The color values of the filtrates obtained in the MWD study and the color removal efficiencies of the membranes

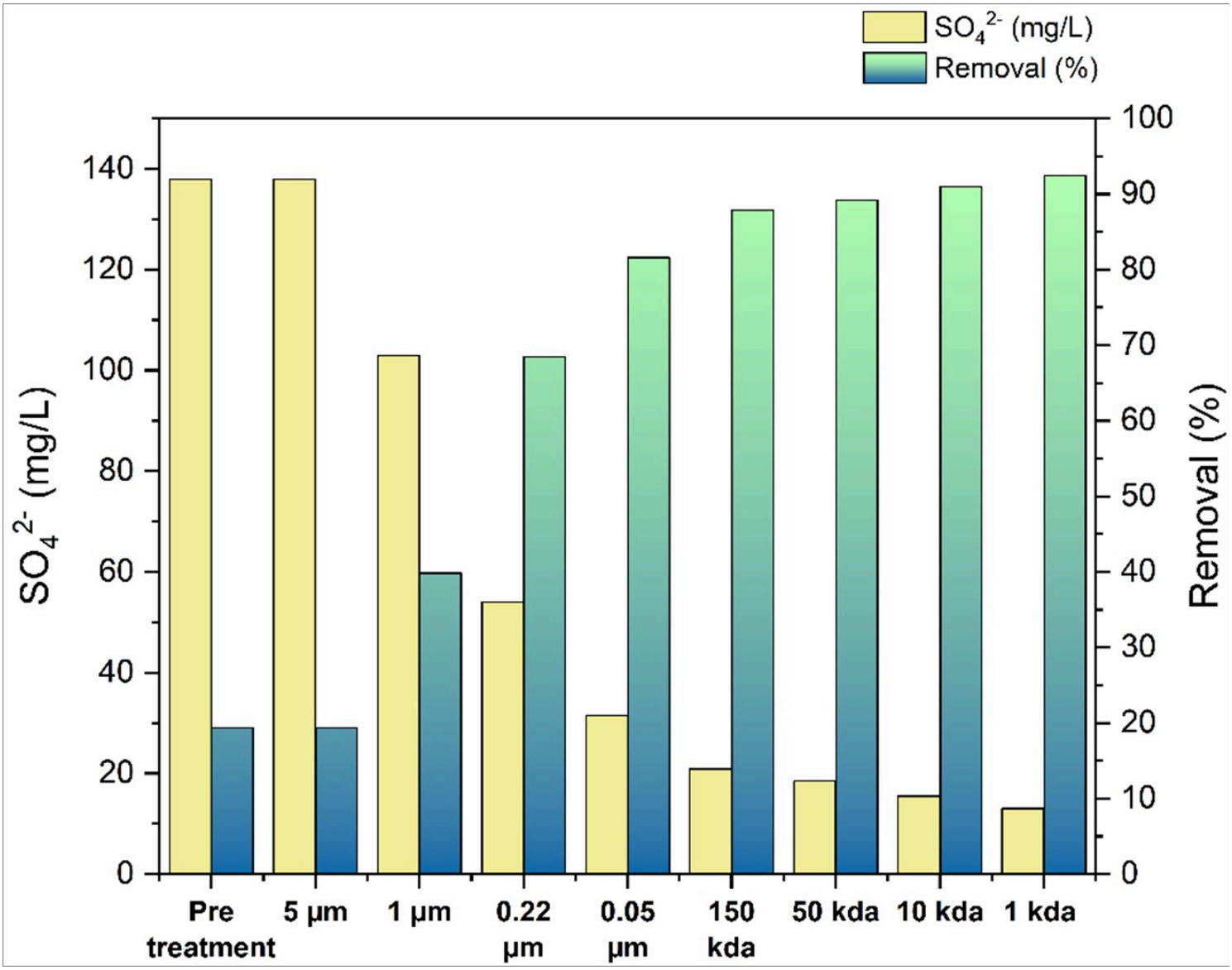


Figure 5

The sulfate values of the filtrates obtained in the MWD study and the cumulative sulfate removal efficiencies of the membranes

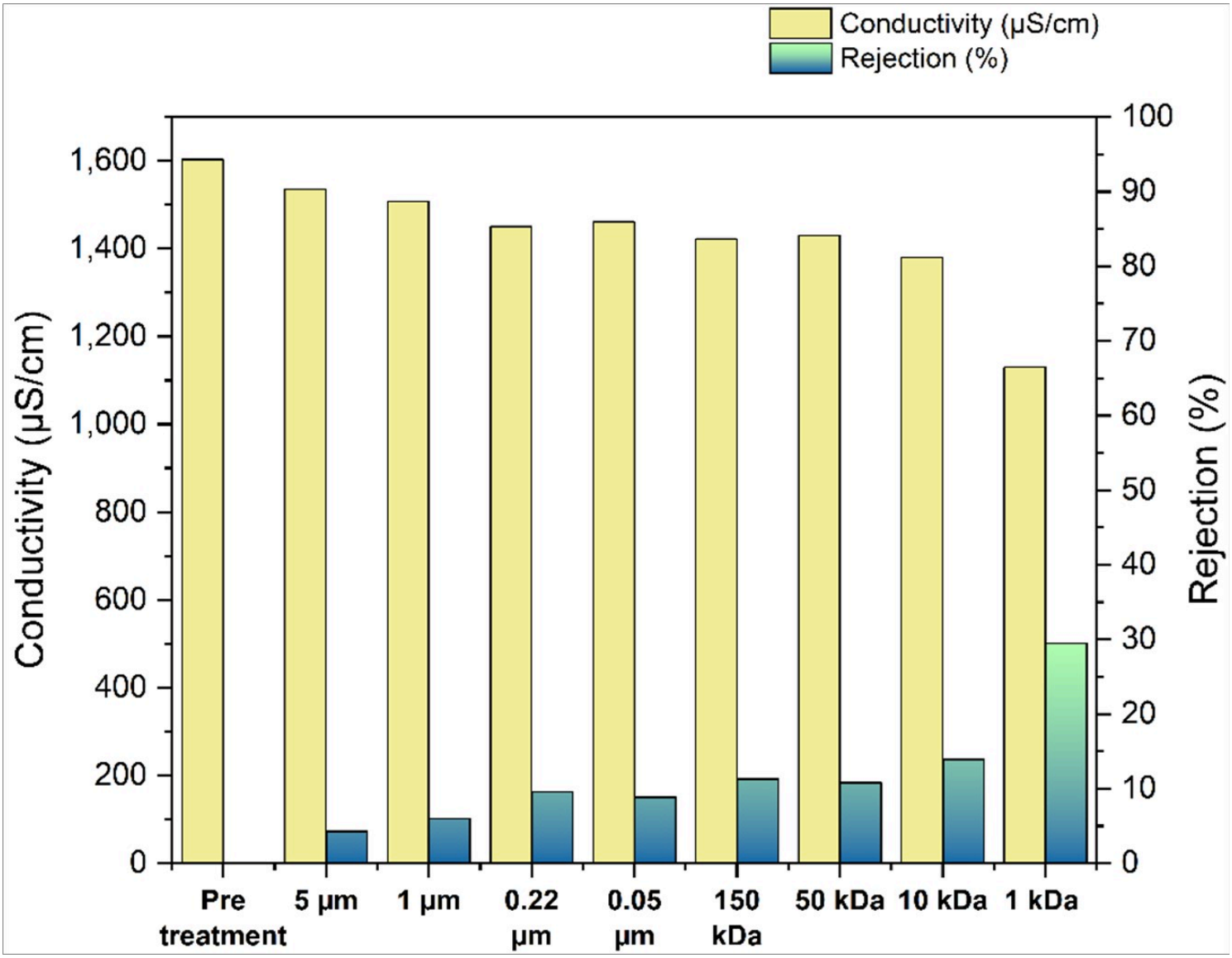


Figure 6

The conductivity values of the filtrates obtained in the MWD study and the cumulative conductivity rejection efficiencies of the membranes

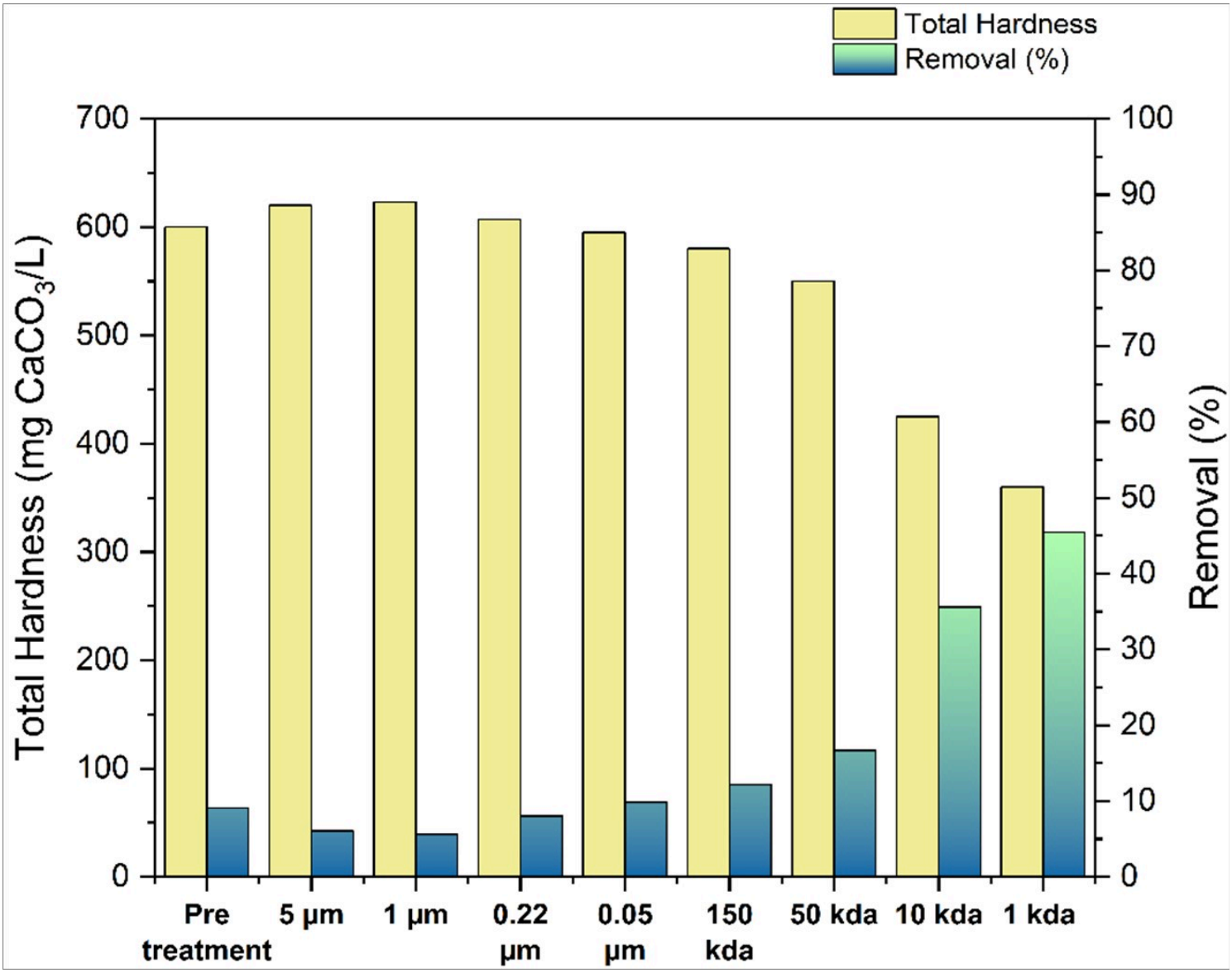


Figure 7

The total hardness values of the filtrates obtained in the MWD study and the cumulative total hardness removal efficiencies of the membranes

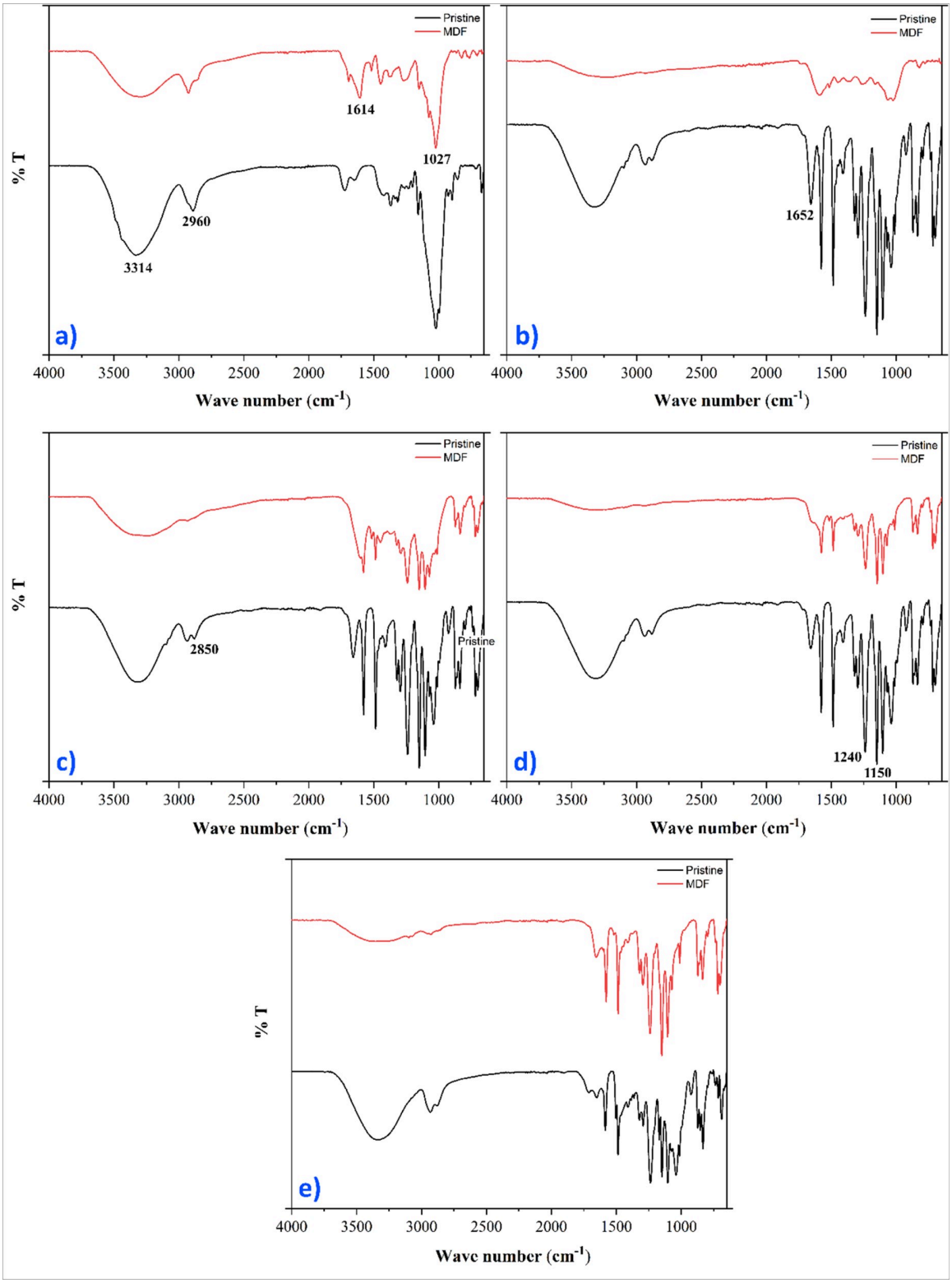


Figure 8

The ATR-FTIR spectra of the membranes used in the MWD study are as follows: a) 500 kDa; b) 150 kDa; c) 50 kDa; d) 10 kDa; e) 1 kDa.

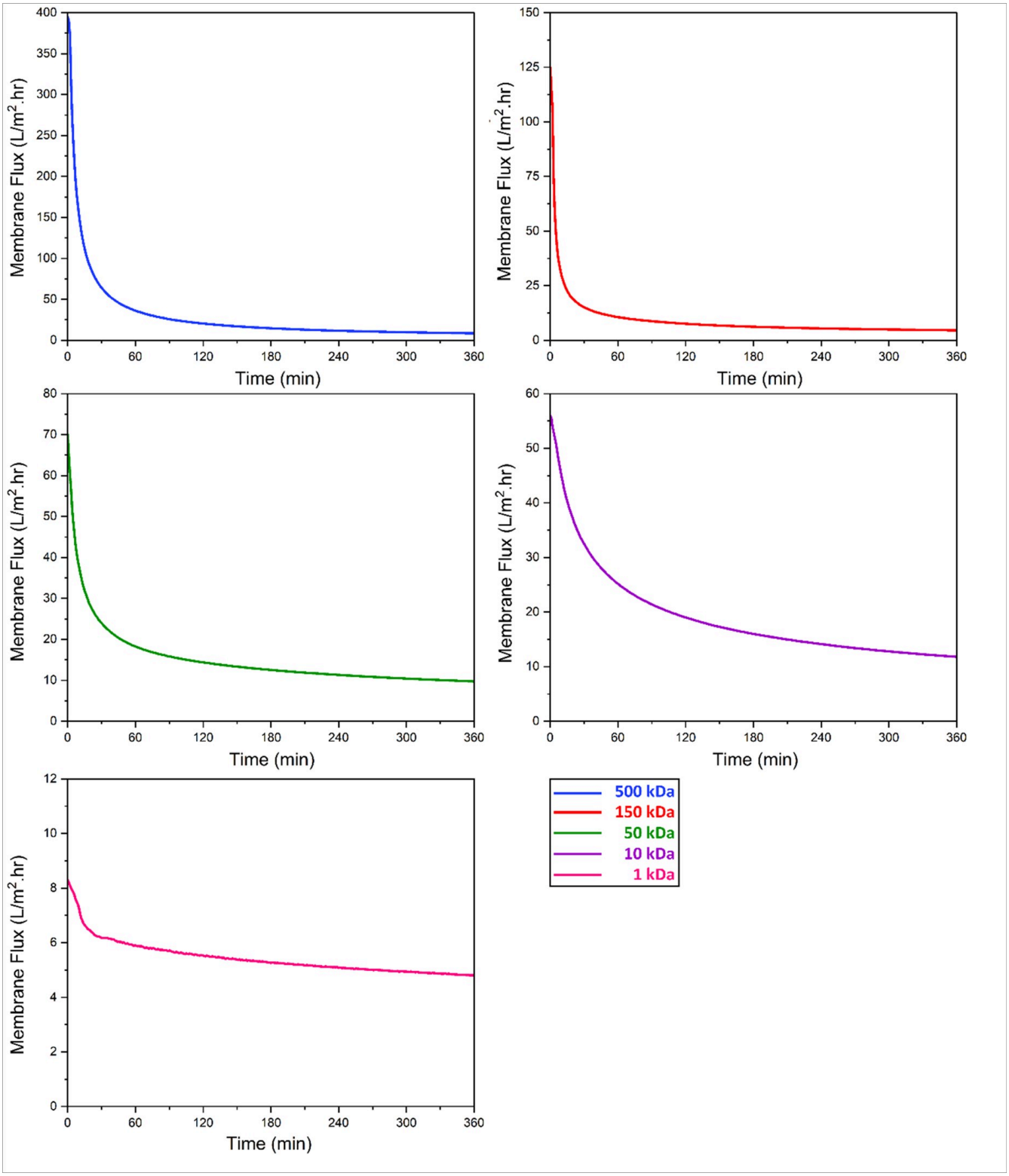


Figure 9

The time-dependent changes in the flux of the membranes used in the MWD study.

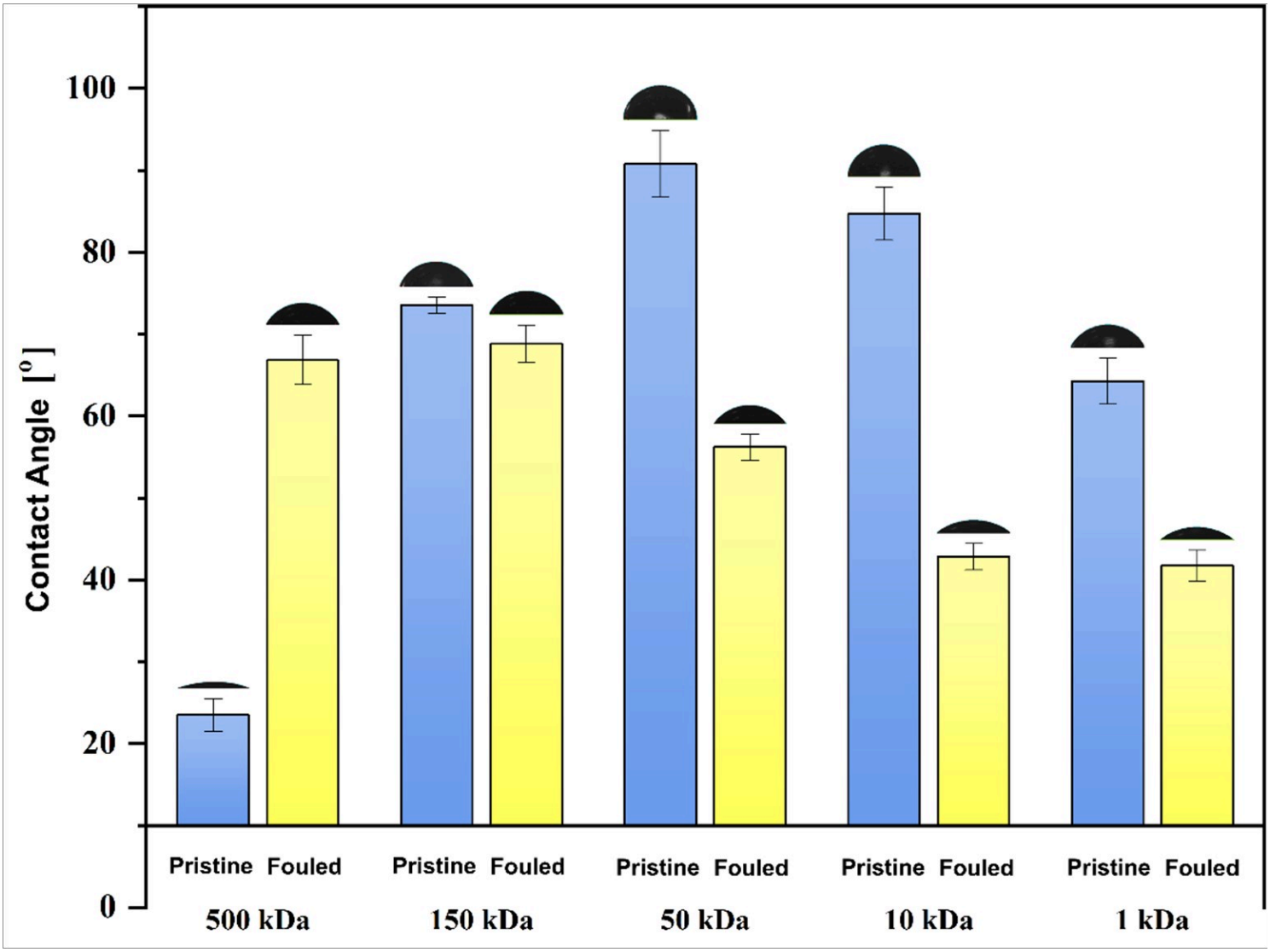


Figure 10

The changes in the contact angles of the membranes used in the study after filtration.

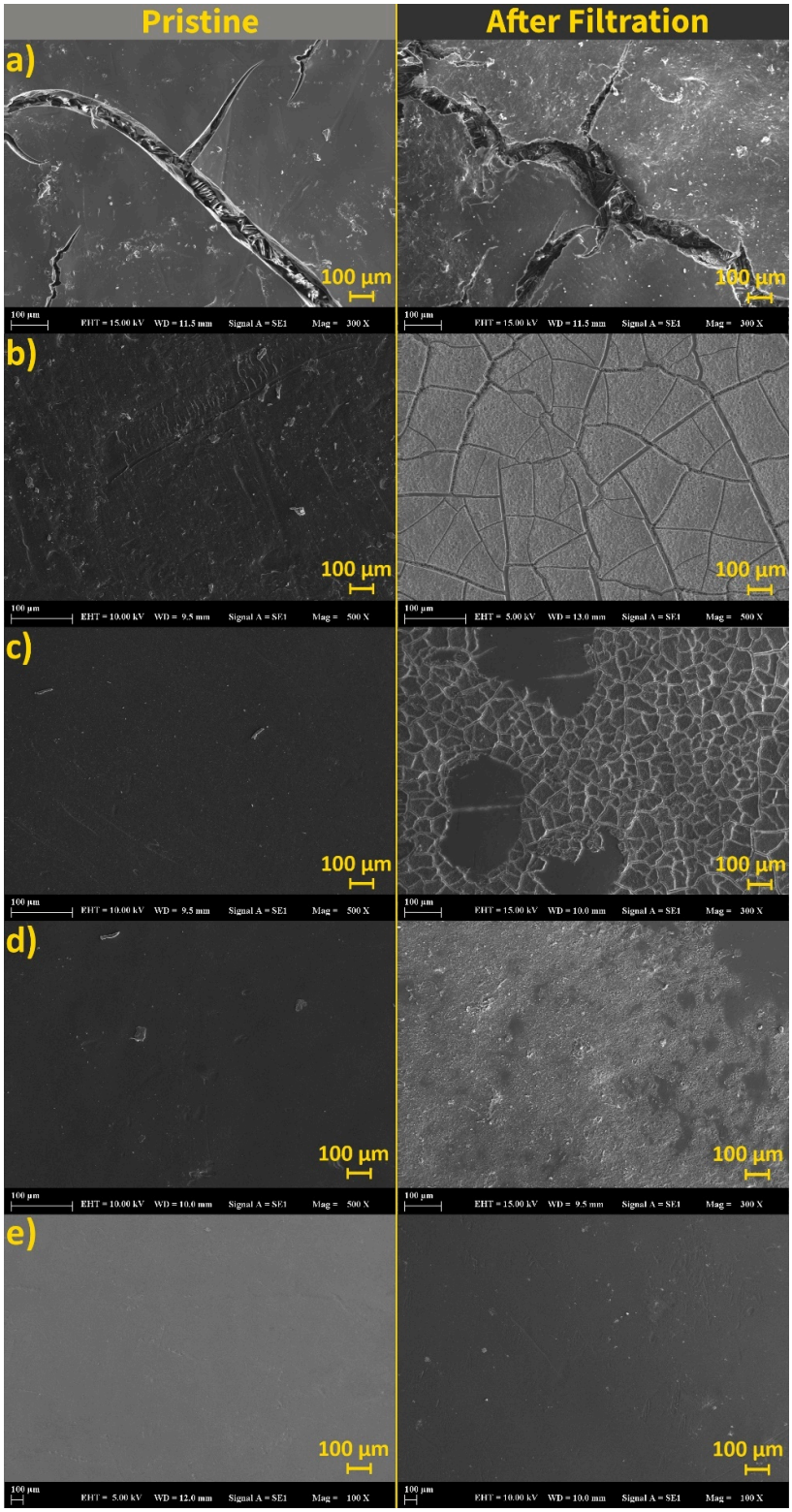


Figure 11

The SEM images of the membranes used in the MWD study: a) 500 kDa; b) 150 kDa; c) 50 kDa; d) 10 kDa; e) 1 kDa.

Supplementary Files

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