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Impact of Advanced Oxidation Products on Nanofiltration Efficiency

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Abstract: The aim of the work was to determine the influence of salicylic acid (SA) oxidation products on the effectiveness of their further removal in the membrane filtration process. Two commercial polyamide-based polymer membranes, HL (GE Osmonics) and TS80 (TriSep™), were used and characterized by SEM microscopic analysis, contact angles, and free surface energy. The products of salicylic acid oxidation, 2,3- and 2,5-dihydroxybenzoic acid and catechol, were determined and their impact on the removal of unreacted salicylic acid in the nanofiltration process was investigated. It was also checked to what extent and why they were retained or not by the membranes. The results of the research have shown that the main product of salicylic acid oxidation, 2,3-dihydroxybenzoic acid, has a negative impact on the retention of salicylic acid in the nanofiltration stage, while the other product, catechol, improves SA retention. The determined values of contact angles correlate well with solubility (S) of the tested compounds, which increases in the following order $S_{SA} < S_{2,3-DHBA} < S_{CAT}$, while the contact angle of the membrane decreases. Nevertheless, it has been shown that some oxidation products can penetrate the environment due to poorer membrane separation properties of these products.

Keywords: nanofiltration; AOPs (advanced oxidation processes); wastewater; salicylic acid; membrane characterization

1. Introduction

The results of studies reported in the literature show a fairly common presence of pharmaceuticals in drinking water [1–6]. Classical water treatment techniques are generally inadequate for the removal of pharmaceuticals. Combined treatment techniques, such as advanced oxidation processes (AOPs) and membrane separation (in particular nanofiltration), are technologies for possibly complete removal of these pollutants. However, the oxidation products may go through the membrane and influence the retention degree of pollutants [7].

Salicylic acid and its derivatives are often used in the pharmaceutical, cosmetic, and food industries for food preservation. Salicylic acid, as a key ingredient in many skin care products, is regularly detected in wastewater and surface waters, being the so-called pharmaceutical pollution [8,9]. Its concentration in the tested samples taken from different sources ranges from a few to even 977 ng/L [10,11]. This aromatic organic compound is toxic to organisms that live in water. Salicylic acid is a product of the decomposition of aspirin (acetylsalicylic acid), one of the most widely used medicines in the world. At ambient temperature, acetylsalicylic acid is slowly hydrolyzed to salicylic acid and acetic acid [12,13].

Therefore, it is very important to develop appropriate methods to remove salicylic acid from the environment and to degrade this dangerous, biologically active compound. Particularly promising are advanced oxidation and membrane filtration. The nanofiltration process enables effective separation of dissolved low molecular weight substances, such as divalent inorganic salts and organic molecules. The aim of the process is to separate hazardous contaminants on the membrane, that is, to obtain a clear filtrate and concentrate containing the retained substances. The methods of advanced oxidation are used to chemically modify oxidized molecules. The integration of both methods allows us to use their positive features while reducing disadvantages.

Advanced oxidation processes provide chemical modification of hazardous substances to non-toxic forms, while membrane filtration ensures removal of substrates and their oxidation products from water. As a result of combining both methods, a pure filtrate and concentrate containing oxidized products of hazardous materials are obtained.

Salicylic acid (SA) is characterized by high reaction rate with OH radical ($5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$). Reaction products are stable, which makes it possible to perform their qualitative analysis easily [14]. Main products resulting from the reaction of salicylic acid with hydroxyl radicals are 2,3-dihydroxybenzoic acid (2,3-DHBA), 2,5-dihydroxybenzoic acid (2,5-DHBA), and catechol [9,15]. Karnik [15] successfully determined two products of the oxidation of salicylic acid with ozone, that is, 2,3-DHBA and 2,5-DHBA, with 2,3-DHBA being the dominant reaction product. Chen et al. [9] obtained a similar result in the process of salicylic acid oxidation with Fenton reagent and UV/H₂O₂. The main product was 2,3-DHBA, while 2,5-DHBA and catechol were produced in small amounts.

Filtration processes are widely used in many areas of life, in the food and pharmaceutical industries, as well as in environmental protection [3,16–19]. However, the cost of these processes is high which is related, among other things, to the high sensitivity of membranes to pollutants.

The effectiveness of retention of a given compound in the membrane filtration process depends on many factors, for example, chemical structure and membrane properties, structure, charge and molecular weight of the compound being removed, and its affinity for the membrane. In the research dedicated to the removal of pharmaceuticals in the membrane filtration process, three mechanisms of their removal have been identified [20], that is, retention of molecules due to their size—the molecule diameter must be significantly larger than the membrane pore diameter, hydrophobic interaction (adsorption of particles on the membrane), and electrostatic repulsion.

The initial adsorption efficiency gradually decreases and then stabilizes, when the process reaches equilibrium state [1]. After reaching the equilibrium state, adsorption can have a disadvantageous effect on retention because it has been shown that adsorbed compounds can dissolve in the active membrane layers, then diffuse through the polymer and finally desorb to the membrane layer on the filtrate side [21]. In addition, desorption of adsorbed compounds to the membrane from the filtrate side may also occur if the compound concentration in the feed water is lower than the equilibrium concentration [22].

Comerton et al. [1] studied the effect of various factors on the adsorption of chemical compounds on a polymer membrane. They found that there was a correlation between the solubility of a given compound and its adsorption on the membrane. Adsorption would increase with decreasing water solubility and increasing hydrophobicity of the tested compound. Karnik et al. [13] showed that the use of membrane filtration at pH from 2.5 to 3 did not cause a significant decrease in the concentration of salicylic acid. This suggests that salicylic acid is not adsorbed on the membrane surface at low pH (2.5–3). In the initial stage, the concentration of salicylic acid in the filtrate decreased, then after reaching the minimum, it grew slightly. This may be due to the fact that after this time, the available sorption sites on the surface and/or within the membrane have become saturated.

An important factor affecting the efficiency and separation mechanism is the charge of the membrane surface. The tests have shown that thin-film polymer composite membranes are negatively charged at neutral pH due to deprotonation of acidic functional groups on the membrane surface [23–28] (Figure 1).

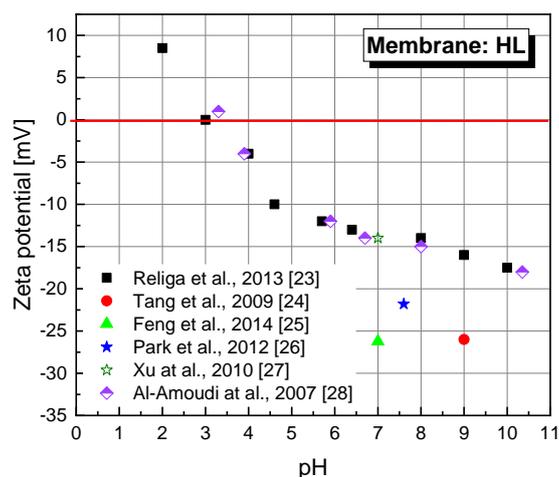


Figure 1. Dependence of zeta potential of the HL membrane on pH of the medium presented by different authors; [23] - Zeta potential of the membrane surface was determined by streaming potential, 1 mM KCl; [24] - Zeta potentials of the membrane were determined from streaming potential measurements in a background electrolyte of 10 mM NaCl; [25] - Zeta potential of the membrane was determined at pH 7.0 and 25 °C in a 1 mM/L KCl solution, using streaming potential equipment; [26] - Zeta potential of the membrane was determined at pH 7.0 and 25 °C in a 1 mM/L KCl solution, using streaming potential equipment; [27] - Zeta potential measured at pH 7 in 10 mM KCl solution.

Acidic functional groups are deliberately introduced during the preparation of the membrane in order to increase its selectivity and permeability. Filtration efficiency is usually lower for positively charged (basic) particles of medicines, while the highest efficiency is obtained for pharmaceuticals that are negatively charged (acidic) [20].

Another membrane property that has a significant impact on the mechanism of separation of organic compounds is its hydrophilicity/hydrophobicity. A parameter that makes it possible to determine the degree of hydrophobicity of a given surface is its contact angle. In the literature, the HL membrane is considered to be one of the most hydrophilic [24,29–31]. In most works, the contact angle, determined by the embedded drop method with the use of pure water as a medium, for this membrane ranges from approx. 27 to approx. 36° [24–26,31]. However, there are reports that the HL membrane is much more hydrophobic. Al-Amoudi et al. [32] stated that their HL membrane had a contact angle of 56.7°. Park et al. [29] in their earlier work determined the contact angle for the DESAL HL membrane as equal to 50.9°.

Integration of advanced methods, such as nanofiltration/reverse osmosis and advanced chemical oxidation using ozonation, O₃/UV, H₂O₂/UV, and O₃/H₂O₂, are currently the latest research direction, allowing for a complete solution to the problem of biologically active substances commonly found in waters around the world. The great majority of works are focused on achieving the most effective removal of initial compounds using the methods of advanced oxidation and membrane techniques (nanofiltration/reverse osmosis) without a deeper analysis of what is happening to their degradation products [33–39]. The influence of oxidation products on the performance and yield of the membranes has not been studied so far. Therefore, the aim of this work was to determine the impact of oxidation products of salicylic acid on the effectiveness of its further removal in the membrane filtration process.

2. Materials and Methods

2.1. Reagents and Chemicals

Salicylic acid (SA) and 2,3-dihydroxybenzoic acid (2,3-DHBA), 2,5-dihydroxybenzoic acid (2,5-DHBA), and catechol (CAT) standards were purchased from Sigma Aldrich. The initial solutions of the above compounds were prepared by dissolving 1000 mg of pure substance in pure deionized

water and kept in a refrigerator for 24 h. Target solutions used in the studies were obtained from dilutions prepared in this way. Table 1 summarizes the concentrations of solutions of the chemical compounds used in the studies. In order to observe the effect of oxidation products on the filtration of salicylic acid and all the phenomena occurring during the filtration process, including changes in the contact angle and FSE (free surface energy), the higher substrate concentrations were used.

Table 1. Concentrations of solutions of chemical compounds used in the studies.

Compound	CAS	Molar Concentration (mol/L)	Mass Concentration (mg/L)	Molar Mass of Compound (g/mol)
SA	69-72-7	5×10^{-4}	69.06	138.12
2,3-DHBA	303-38-8	3.24×10^{-4}	50.0	154.12
CAT	120-80-9	3.24×10^{-4}	35.72	110.1

A 30% solution of hydrogen peroxide was used in the oxidation with UV/H₂O₂. To 3700 mL of the solution, 1.2 mL of H₂O₂ was added (which constituted a molar concentration of 2.86×10^{-3} mol/L).

The catalase solution was prepared by pouring about 1 g of dry catalase with 25 mL of deionized water. After saturating the solution with catalase, it was filtered on a soft paper filter, and the solution prepared in this way was kept in a refrigerator. To each sample containing unreacted hydrogen peroxide, 50 µL of catalase solution was added per 10 mL of the sample.

2.2. Experimental Set Up

2.2.1. UV/H₂O₂ Oxidation

The oxidation process was carried out using UV/H₂O₂. The reaction was carried out in a tubular reactor with a volume of 3.5 L, presented schematically in a previous paper [7]. The solution was mixed by forced circulation of liquid in a closed circuit using a peristaltic pump. The reactor was made of glass; in its axis an inner quartz tube was installed with two UV lamps (monochromatic— $\lambda = 254$ nm) with total power of 22 W. 30% hydrogen peroxide was added at the beginning of the reaction, and its dose in most cases was 2.86×10^{-3} (mol/L). 10 mL of solution samples were collected every 10 min. 50 µL of catalase solution was immediately added to each sample taken in order to decompose residual hydrogen peroxide and stop the reaction. The samples were kept in a refrigerator at 4 °C for no longer than 24 h.

2.2.2. Membrane Filtration

The process of nanofiltration was carried out using the cross-flow method at a constant liquid flow, 2 L/min at 30 °C, within the system. The tests were carried out at a pressure of 1.0 MPa. The output volume of sewage was 3 L, and the solution was concentrated to a volume of 1.5 L (1:2). The scheme of the filtration system was shown in a previous paper [7].

Two flat sheet nanofiltration membranes, HL and TS80, with an area of about 314 cm² were selected for the tests; their parameters are given in Table 2.

Table 2. Parameters of the tested membranes.

Characteristics	Membrane Type	
	HL	TS80
Use	Water softening, Purification of industrial waters, wastewater decolorization	Water softening, Wastewater treatment, food industry, other industrial processes
Polymer	Thin film (composite: Piperazine-based polyamide, microporous polysulfone as a carrier layer) [23,25,40,41]	Polyamide
pH range	3–9	2–11
MWCO * (Da)	150–300	~150
Retention	98.0% (MgSO ₄)	99.0% (MgSO ₄)/80–90% (NaCl)
Typical flow rate L/(m ² ·h MPa)	96	45
Pressure range	4 MPa [42]	
Temperature range	Max. 50 °C	Max. 45 °C
Surface	Smooth, roughness (RMS **) 10 nm [24,43]	RMS 89 nm [1]
Manufacturer	GE Osmonics	TriSep™

where: * MWCO—Molecular weight cut-off (Da); ** RMS—Root Mean Squared roughness.

The HL membrane manufactured by GE Osmonics used for nanofiltration is made of a semi-aromatic polyamide based on piperazine [30,44]. The TS80 membrane is a TriSep™ product and is made of polyamide. A brand new membrane was used in each experiment. Every membrane was subjected to 1.5 MPa pressure for 50 min at ambient temperature (25–29 °C) during the filtration of pure deionized water. After 50 min, the pressure was reduced to 1.0 MPa, and the flow rate of the filtrate was measured for 10 min at 30 °C.

Experimental results are expressed in terms of the retention by the membrane of the compounds used in the present work. Retention is determined by employing the substance concentration in the permeate with reference to a representative value of substance concentration in the retentate solution, as follows:

$$R = \left(1 - \frac{C_P}{C_R}\right) \times 100\% \quad (1)$$

where C_P and C_R are the concentrations of a specific compound in the permeate and retentate, respectively.

2.3. Analytical Methods Used

2.3.1. HPLC—High-Performance Liquid Chromatography

Quantitative determination was performed using the Agilent 1290 Infinity Rapid Resolution Liquid Chromatography System (RRLC) coupled to an Agilent 6460 triple quadrupole mass spectrometer. The liquid chromatographic system was equipped with a binary pump, thermostatted column compartment, auto-sampler, and ultraviolet diode-array detector. Chromatographic separation was achieved on a Poroshell 120 StableBond SB-C18 column (2.7 μm, 150 mm (length) × 3 mm (diameter)) (Agilent Technologies, Santa Clara, CA, USA). The column temperature was maintained at 40 °C, and the injection volume was 20 μL. The mobile phase (delivered at 0.9 mL/min) consisted of solvent A, 0.1% (v/v) formic acid in water, solvent B, and methanol. The quantitative assessment was made using a nine-point calibration curve ranging from 1 to 250 μg/mL for each compound.

2.3.2. SEM Microscopic Analysis

The SEM microscopic examination was performed on a TESCAN VEGA3 scanning electron microscope (Tescan, Czech Republic). A magnification of 20,000 \times was used to study the surface topography of membranes.

2.3.3. Determination of Contact Angle and Free Surface Energy (FSE)

The contact angle was studied by the goniometric method using a PGX Goniometer (FIBRO Systems, Sweden). The tests were carried out at 22.4 ± 2 °C and relative air humidity $35 \pm 2\%$.

Contact angles for each test were determined using three standard liquids:

- Diiodomethane, DIM ($\gamma_L = 50.80$ mJ/m²: $\gamma_L^{LW} = 50.80$ mJ/m², $\gamma_L^+ = 0$ mJ/m², $\gamma_L^- = 0$ mJ/m²)
- Water, W ($\gamma_L = 72.80$ mJ/m²: $\gamma_L^{LW} = 21.80$ mJ/m², $\gamma_L^+ = 25.50$ mJ/m², $\gamma_L^- = 25.50$ mJ/m²)
- Formamide, F ($\gamma_L = 58.00$ mJ/m²: $\gamma_L^{LW} = 39.00$ mJ/m², $\gamma_L^+ = 2.28$ mJ/m², $\gamma_L^- = 39.60$ mJ/m²)

Based on the determined contact angles, free surface energy γ_S of the membrane was calculated using the Acid-Base method, identifying the proportion of dispersion component γ_S^{LW} and acid-base component γ_S^{AB} in total free surface energy ($\gamma_S = \gamma_S^{LW} + \gamma_S^{AB}$).

2.3.4. Zeta Potential Measurements

The streaming potential measurements were carried out with the SurPASS Electrokinetic Analyzer using the adjustable gap cell (Anton Paar GmbH, Austria). The maximum pressure difference was set at 25–30 kPa to assure the laminar flow. For each measurement, two pieces of the membrane (20 mm \times 10 mm) were precisely cut and installed pairwise in the adjustable gap cell separated with a 100 μ m—thick spacer. The 1 mM NaCl solution was used for the zeta potential measurements.

3. Results and Discussion

3.1. UV/H₂O₂ Oxidation

First, experiments with UV/H₂O₂ oxidation of selected compounds were carried out. Figure 2 shows the dependence of the concentration of salicylic acid (SA). UV radiation alone caused a slight decrease in the concentration of salicylic acid constituting 10% of the initial value. Hydrogen peroxide at a concentration of 2.86×10^{-3} mol/L introduced into the system caused considerable acceleration of salicylic acid decomposition. Increasing the dose of hydrogen peroxide to 7.15×10^{-3} mol/L resulted in further acceleration of salicylic acid decomposition. After 30 min, an 80% reduction of the tested compound was obtained, whereas, after 60 min, salicylic acid remained in trace amounts.

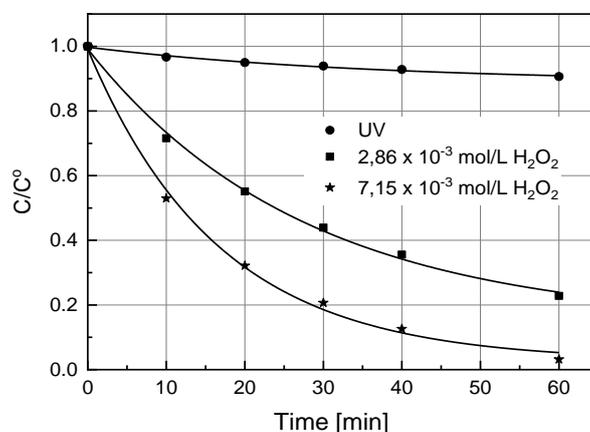


Figure 2. Salicylic acid concentration changes with oxidation time at different H₂O₂ doses, temperature 25 °C.

On the basis of the HPLC analysis, the concentrations of oxidation products of salicylic acid, subjected to UV/H₂O₂, were identified and determined. These products were further subjected to nanofiltration. The tests were performed at a dose of H₂O₂ equal to 2.86×10^{-3} mol/L after 60 min of exposure of salicylic acid to oxidizing agents. Three intermediates were identified whose concentrations are summarized in Table 3. As a result of the reaction of 75% salicylic acid, 14.8 mg/L of 2,3-dihydroxybenzoic acid (2,3-DHBA), 5.1 mg/L of catechol, and trace amounts of 2,5-dihydroxybenzoic acid (2,5-DHBA) were obtained. Figure 3 shows structural formulas of salicylic acid and identified products of its oxidation.

Table 3. Concentrations of salicylic acid and its oxidation products after 60 min of oxidation with UV/H₂O₂; H₂O₂ dose = to 2.86×10^{-3} mol/L, temperature 25 °C.

Compound	SA	2,3-DHBA	2,5-DHBA	Catechol
Concentration (mg/L)	17.5	14.8	trace amounts	5.1
Molar concentration (mol/L)	1.27×10^{-4}	0.96×10^{-4}	–	0.46×10^{-4}
Degree of conversion (%)	75	19.2	–	9.2

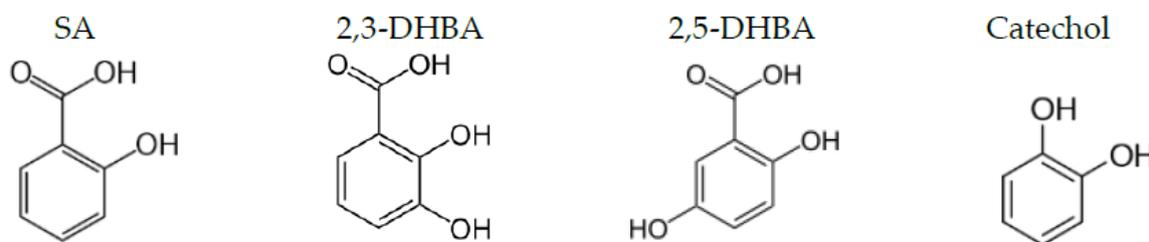


Figure 3. Structural formulas of salicylic acid and identified products of its oxidation.

The results are consistent with the results published by other researchers [9,13]. Based on the analysis of the concentration of the resulting products and the degree of salicylic acid conversion, it was estimated that oxidation products, such as 2,3 DHBA, 2,5-DHBA, and catechol, constitute about 40% of all oxidation products.

3.2. Nanofiltration

The nanofiltration process was carried out using two polyamide-based polymer membranes: HL and TS80. Figure 4A shows retention coefficients of salicylic acid for varying degrees of concentration of the initial solution (white bar) on the HL membrane. The measurements were taken at the beginning of the process (zero degree concentration), obtaining 500 mL of filtrate from 3000 mL of the initial bath (concentration degree 1/6), and analogously—obtaining 1000 mL of filtrate (concentration degree 1/3) and 1500 mL of filtrate (concentration degree 1/2). Figure 4B,C show the concentration of salicylic acid in the concentrate and filtrate, respectively, depending on the degree of initial bath concentration. Figure 5 presents the results obtained with the TS80 membrane.

Salicylic acid retention in the initial reaction step was 37.6% and gradually decreased to 22.8%. Salicylic acid is characterized by a relatively low molecular weight (138.12 g/mol). The molecule of this acid does not contain additional spatial substituents besides the carbonyl group. The HL membrane is characterized by MWCO (Molecular weight cut-off) in the range of 150–300 (Da). It should be noted that the tests were carried out at native pH of the solution, that is, pH = 3.5. The dissociation constant of salicylic acid is $pK_a = 2.97$. It is known from the literature that HL membrane at this pH has a zeta potential close to zero [23–28] (Figure 1). However, the results of some studies indicate that the DESAL HL membrane can be negatively charged at pH 3 (ca. -10 mV, measurements with 10 mM KCl, [45]). The low molar mass of salicylic acid which is lower than the MWCO and unfavorable conditions for electrostatic repulsion cause low retention of salicylic acid. One of the phenomena that seem to

be important in the first stage of the filtration is the adsorption of salicylic acid molecules on the membrane. For the adsorption process, there is a gradual decrease in the filtration efficiency because molecule retention on the membrane by sorption is a short-time incident. Molecules move through the membrane along its pores and pass into the filtrate. Probably the sorption process can take place until active areas of the membrane surface are saturated and then, after 1/3 degree of concentration, the retention percentage is constant on both membranes (Figures 4A and 5A). Figure 6 shows the dependence of the filtrate flux on filtration time. In the case of the HL membrane, a very small filtrate flux decrease was observed, approx. 5% at pH = 3.5.

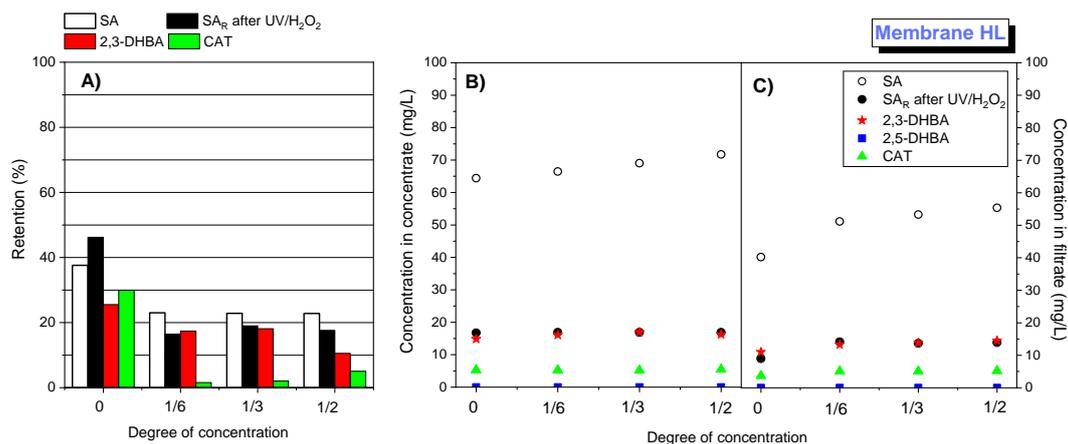


Figure 4. (A) Dependence of retention on the degree of initial bath concentration; (B) dependence of concentration of salicylic acid and products of its oxidation in the concentrate on the degree of initial bath concentration; (C) dependence of concentration of salicylic acid and products of its oxidation in the filtrate on the degree of initial bath concentration; HL membrane, pressure 1.0 MPa, temperature 30 °C. Abbreviations: SA- salicylic acid; 2,3-DHBA- 2,3-dihydroxybenzoic acid; 2,5-DHBA- 2,5-dihydroxybenzoic acid; CAT- catechol; SA_R-residual salicylic acid after UV/H₂O₂.

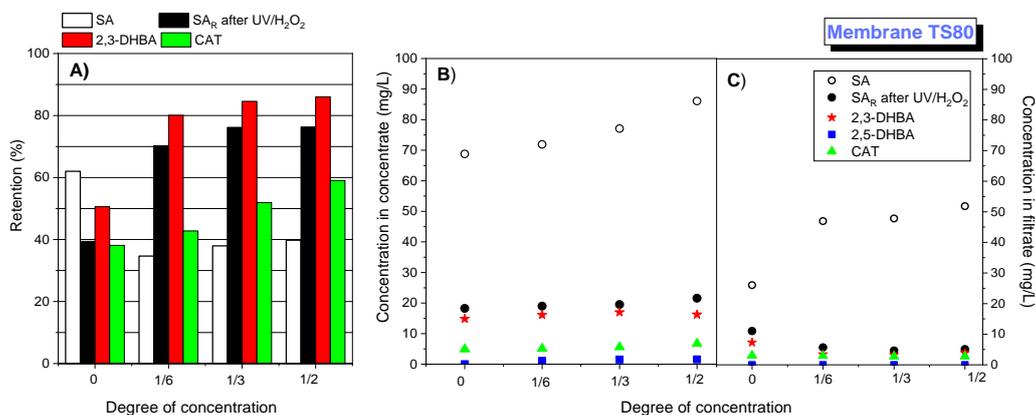


Figure 5. (A) Dependence of retention on the degree of initial bath concentration; (B) dependence of concentration of salicylic acid and products of its oxidation in the concentrate on the degree of initial bath concentration; (C) dependence of the concentration of salicylic acid and products of its oxidation in the filtrate on the degree of initial bath concentration; TS80 membrane, pressure 1.0 MPa, temperature 30 °C. Abbreviations: SA- salicylic acid; 2,3-DHBA- 2,3-dihydroxybenzoic acid; 2,5-DHBA- 2,5-dihydroxybenzoic acid; CAT- catechol; SA_R-residual salicylic acid after UV/H₂O₂.

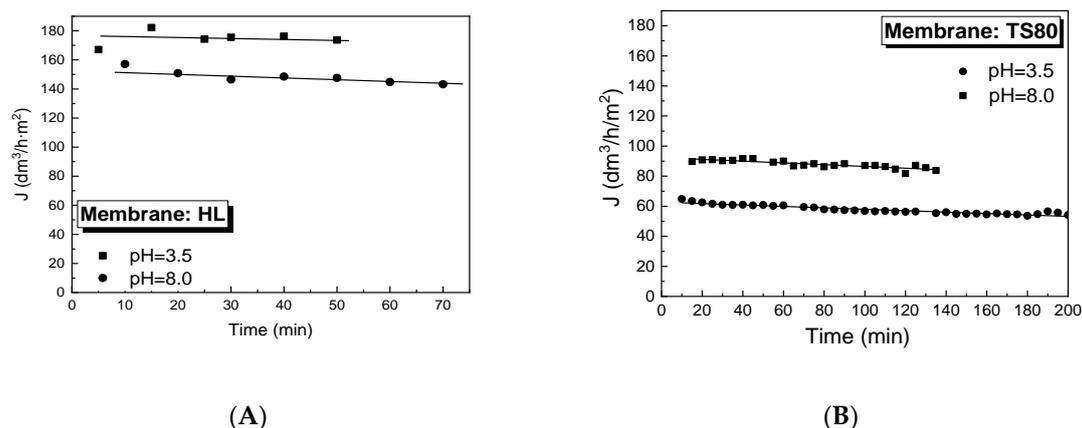


Figure 6. Dependence of filtrate flux on the filtration time: (A) for HL membrane; (B) for TS80 membrane; pressure 1.0 MPa, temperature 30 °C.

In the case of the TS80 membrane, the salicylic acid separation efficiency was evidently higher. Figure 5A shows the retention of salicylic acid (white bar) depending on the degree of initial solution concentration. Figure 5B,C show the concentration of salicylic acid in the concentrate and filtrate, respectively, depending on the degree of concentration. The salicylic acid retention in the initial stage was 62.2% and gradually decreased to 39.8%. Higher retention may result from the fact that the TS80 membrane is more compact (MWCO 150 Da) and rougher (RMS (Root Mean Squared roughness) 89 nm) than the HL membrane [1]. Higher filtration efficiency may result from the fact that the TS80 membrane is negatively charged at pH 3 [45]. For the TS80 membrane, the filtrate flux was lower than for the HL membrane (Figure 6). It was observed that at pH 3.5, the filtrate flux decline was slightly higher than for the HL membrane, amounting to about 11%. Figure 7 presents SEM micrographs with a magnification of 20,000 \times prepared using an electron scanning microscope. On the basis of microscopic images, it can be concluded that the TS80 membrane has more undulated and uneven surface than the HL membrane. The HL membrane is characterized by a smooth surface, as evidenced by the micrograph shown in Figure 7A. Its RMS roughness has been determined by other researchers as about 10 nm [30,43]. It should be taken into account that retention of oxidation products on the TS80 membrane, in particular, 2,3 DHBA, is much higher than for pure SA, in contrast to the HL membrane. This phenomenon is discussed further.

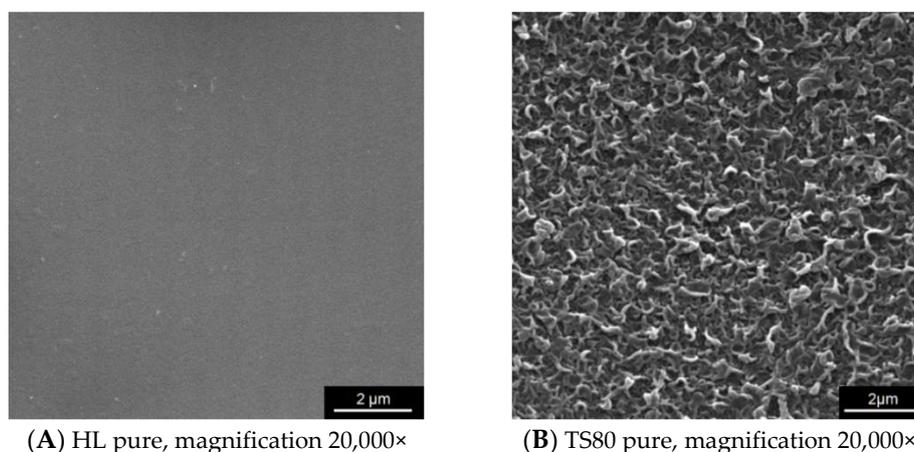


Figure 7. SEM microscopic images of selected membranes at 20,000 \times : (A) HL pure, magnification 20,000 \times ; (B) TS80 pure, magnification 20,000 \times .

The HL and TS80 membranes were characterized by similar values of the contact angle. The contact angle for the HL membrane was 59.0° (for water), while for the TS80 membrane was 53.4° (for water). Both membranes can be classified as hydrophilic.

3.3. Retention of Oxidation Products

As a result of the investigation with the use of the HL membrane for nanofiltration of oxidized salicylic acid solutions, it was found that one of the oxidation products, namely 2,3-dihydroxybenzoic acid, showed similar retention coefficients to salicylic acid, while the other product, catechol, showed very low retention ability on the membrane (Figure 4A). Probably this was due to the fact that the structure of 2,3-dihydroxybenzoic acid was not different from that of salicylic acid molecules, with the exception of the attached $-OH$ group in the ortho position, while in catechol molecules, the $-COOH$ group was replaced by $-OH$ during SA oxidation. Similar results were obtained for the TS80 membrane, for which an analogous comparison of results is shown in Figure 5A. Also, in the case of this membrane, it was observed that the main oxidation product, 2,3-DHBA, had similar retention coefficients as SA, while the efficiency of separation of catechol molecules on the TS80 membrane was much worse than that of the above-mentioned compounds.

This is important from the point of view of environmental protection. Using integrated methods of advanced oxidation and nanofiltration processes for removing dangerous pollutants from wastewater, it should be noted that despite a significant decomposition of the starting compound, we can allow the emission oxidation products whose chemical structure and low molecular weight contribute to the low efficiency of separation on the membrane. Although catechol is a biodegradable compound, it has been shown that there is a risk that some more dangerous oxidation products may penetrate the permeate in water treatment processes. Therefore, such research should be carried out, and potential risks resulting from the integration of advanced oxidation and membrane techniques should be analyzed.

3.4. The Influence of Oxidation Products on the Retention of Residual Salicylic Acid

In the case of the HL membrane, it was observed that, at the beginning of the filtration process, there was a slight increase in the retention of undecomposed salicylic acid in the reaction mixture compared to the retention of pure salicylic acid solution. After concentrating the solution to 1/6 of the initial volume, a slight but permanent deterioration of the separation efficiency of the membrane for this acid was observed. A small but noticeable decrease of salicylic acid retention in the reaction mixture was reported compared to the pure salicylic acid solution.

In the case of the TS80 membrane, a marked improvement in the filtration efficiency of salicylic acid was observed in the presence of its oxidation products (Figure 5). During the concentration of the initial solution, retention of salicylic acid and its oxidation products clearly increased. The TS80 membrane is more compact (lower MWCO value) and rougher than the HL membrane, which can contribute to more efficient retention of oxidation products. This may be particularly important for low molecular weight oxidation products, for example, glyoxylic, maleic, fumaric, malic, oxalic, and tartronic acids, which on passing through the membrane can be blocked inside the membrane pores, gradually contributing to improved separation of the tested compounds on the membrane.

In the next stage of research, an experiment was carried out by adding 2,3-DHBA at a concentration of 3.24×10^{-4} mol/L (50 mg/L) to SA solution and catechol at a concentration of 3.24×10^{-4} mol/L (35.72 mg/L) to the other SA solution. The solutions prepared in this way were nanofiltered on the HL membrane, and then calculated retention coefficients of salicylic acid were compared with the values obtained for pure SA solution. The results are shown in Figure 8.

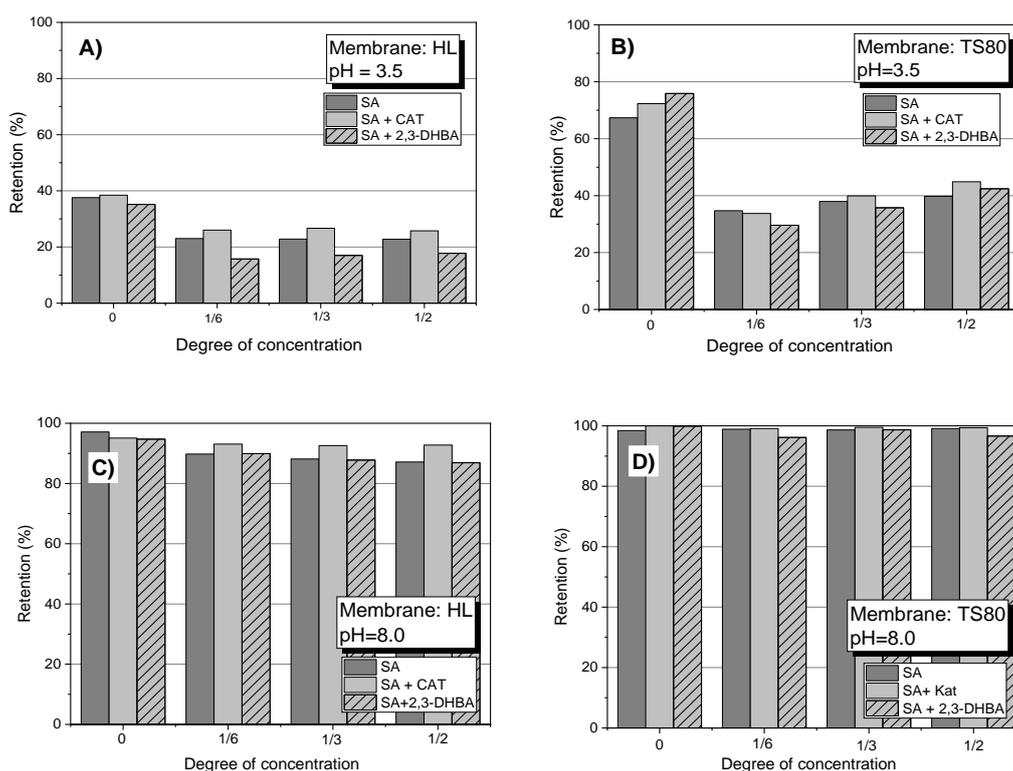


Figure 8. Retention coefficients of salicylic acid in the presence of 2,3-DHBA (2,3-dihydroxybenzoic acid) and catechol (CAT) at pH = 3.5 and pH = 8.0. SA- salicylic acid.

If results for the HL membrane at pH = 3.5 are considered, it is found that 2,3-dihydroxybenzoic acid had a negative impact on the retention of salicylic acid, which is evidenced by a slight decrease in the retention coefficient of this acid in the presence of 2,3-DHBA (Figure 8A). Despite the low molecular weight of salicylic acid which is lower than the MWCO, apart from the adsorption phenomenon, the size exclusion mechanism and the interference effect of oxidation products may affect the SA separation process. 2,3-DHBA can be a competitive compound to the active sites of the membrane, causing weaker adsorption of SA on it. The tests showed that the retention coefficients of 2,3-DHBA in the above experiment were close to the coefficients for salicylic acid and ranged from 20 to 28% depending on the concentration of the initial solution (results not shown in the Figures).

In the case of the TS80 membrane, the negative effect of 2,3-DHBA is visible only in the first stage of the process (Figure 8B). In the final stage, with a concentration of 1:2, the presence of both oxidation products improved SA retention coefficients. This may be due to the fact that in the initial stage, the adsorption process dominates, while during the concentration, the separation through spatial blocking and electrostatic repulsion becomes dominant. In the case of TS80 membrane, at pH 3, the membrane surface is charged negatively (ca. -20 mV, measurement with 10mM KCl, [45]), and consequently, the effect of electrostatic interaction should be taken into account. The results are consistent with Figure 5. During concentrate concentration, higher SA retention coefficients were obtained compared to pure SA solution.

If the results for pH = 8.0 are considered, it is found that 2,3-DHBA did not affect the salicylic acid separation process (Figure 8C,D). This may be due to the fact that at pH = 8, the mechanism of separation by electrostatic repulsion dominates. With this mechanism, the oxidation products do not compete with the starting substrate.

It was observed that in the case of catechol, there was a tendency to improve the SA retention coefficient regardless of the type of membrane and pH. This may be due to the fact that catechol is blocked inside the pores of the membrane, reducing the voids, while not blocking the active sites on the membrane surface.

Table 4 summarizes the pH and conductivity values of the concentrate and filtrate during the filtration process on the HL membrane. The conductivity of the SA solution concentrates ranged from 153 to 165 $\mu\text{S}/\text{cm}$. The presence of 2,3-DHBA caused an increase in the conductivity of the SA solution ranging from 208 to 251 $\mu\text{S}/\text{cm}$. 2,3-DHBA had a slightly higher acidity ($\text{pK}_a = 2.91$) than SA due to the presence of an additional OH group in the aromatic ring. The presence of two acids in the solution caused weaker dissociation (the conductivity of the SA + 2,3-DHBA mixture was lower than the sum of the values obtained for pure solutions of these acids). The poorer dissociation of SA could, to a certain extent, influence the effectiveness of its separation on the membrane. The presence of catechol had no effect on the conductivity of concentrates and filtrates. This was due to the low dissociation of catechol ($\text{pK}_a = 9.45$). Solutions containing catechol had a slightly higher pH.

Table 4. The pH and conductivity of concentrates and filtrates obtained during filtration on the HL membrane.

Concentration ratio	Concentrate		Filtrate	
	pH	Conductivity, $\mu\text{S}/\text{cm}$	pH	Conductivity, $\mu\text{S}/\text{cm}$
		Salicylic acid		
0	3.52	153	3.83	77
1/6	3.54	158	3.56	118
1/3	3.51	163	3.53	139
1/2	3.52	165	3.54	140
		Salicylic acid + 2,3-DHBA		
0	3.43	206	3.60	142
1/6	3.43	231	3.46	208
1/3	3.43	248	3.46	220
1/2	3.43	251	3.46	221
		Salicylic acid + Catechol		
0	3.67	150	4.04	69
1/6	3.70	161	3.78	138
1/3	3.69	168	3.76	141
1/2	3.69	177	3.76	151

Piperazine-based polyamide membranes, which include the HL membrane, have a charge on their surface as a result of the presence of amino and carboxyl groups. Typical membranes of this type have an isoelectric point within pH 3–4 [23,28]. At lower pH, amine groups are activated (ammonium ions are formed), which causes a positive charge on the membrane surface. At pH above 3–4, carboxyl groups of the polyamide are dissociated, resulting in a negative charge. Zeta potential studies revealed that the membrane used for SA filtration showed a significant decrease in the negative charge on the membrane surface (at pH 5.2, zeta potential was -2.5 mV, at pH 7.9, it was -7.0 mV) as compared to the pure HL membrane (Figure 1). The presence of 2,3-DHBA in the SA solution caused a further shift towards positive values of the zeta potential. This may be due to the fact that the acidity of carboxyl groups of SA and 2,3-DHBA is greater than that of carboxyl groups on the membrane surface. In the case of a system in which a stronger and weaker acid is present, the H^+ ions combine with the weak acid residues and neutralize the negative charge. This could explain a decrease in the amount of negative charge of the HL membrane used for the filtration of SA and SA + 2,3-DHBA. The membrane used for filtration of the SA + catechol mixture has very similar characteristics of the dependence of zeta potential on pH as for the pure membrane, only to a small extent are the values shifted towards positive values, suggesting that the presence of catechol neutralizes the effect of salicylic acid on the membrane surface. One of the probable reasons may be the formation of hydrogen bonds between the molecules of SA and catechol, resulting in better separation of SA during filtration. Further research is necessary in this respect because, at pH = 3.5, catechol interacts poorly with the membrane surface

passing through it virtually unaffected. It can be assumed that at pH = 8, catechol may improve SA retention because its presence contributes to the increase in hydrophilicity of the membrane (Table 5), thereby increasing the driving force of electrostatic repulsion.

Table 5. Average values of contact angle for three standard liquids and free surface energy of pure HL membrane and membrane after salicylic acid filtration.

No.	Sample	Contact Angle Θ , deg.			Free Surface Energy FSE, mJ/m ²		
		Θ_W	Θ_F	Θ_{DIM}	γ^{LW}	γ^{AB}	γ
1	HL membrane before filtration–pure	59.0	51.6	34.8	42.1	1.2	43.3
2	HL membrane after salicylic acid filtration	75.9	71.3	47.6	35.6	6.9	42.5
3	HL membrane after filtration of oxidized salicylic acid	48.6	51.1	45.1	37.0	0.0	37.0
4	HL membrane after filtration of salicylic acid and 2,3-DHBA mixture	66.4	55.1	33.8	42.6	1.6	44.2
5	HL membrane after filtration of salicylic acid and catechol mixture	55.1	49.7	36.5	41.3	0.3	41.6
6	HL membrane after filtration of water and H ₂ O ₂ (0.324 mL/L)	59.6	44.5	34.8	42.1	4.1	46.3

wetting liquids: Water (W), formamide (F), diiodomethane (DIM).

3.5. Determination of Contact Angles and Free Surface Energy

The contact angle and free surface energy (FSE) were determined for the HL and TS80 membranes. For the HL membrane, extended tests, including measurement of the above-mentioned parameters for the pure membrane and membranes used, for the filtration of aqueous solutions with various chemical composition were performed (Table 5). The tests also included the membrane used to filter the mixture obtained by the oxidation of salicylic acid with UV/H₂O₂. For the TS80 membrane, the tests included measurement of the contact angle and free surface energy for the pure membrane and the membrane used for the filtration of salicylic acid (Table 6).

Table 6. Average values of contact angle for three standard liquids and free surface energy of pure TS80 membrane and membrane after salicylic acid filtration.

No.	Sample	Contact Angle Θ , deg.			Free Surface Energy FSE, mJ/m ²		
		Θ_W	Θ_F	Θ_{DIM}	γ^{LW}	γ^{AB}	γ
1	Pure TS80 membrane	53.4	52.5	32.9	43.5	7.5	48.3
2.	TS80 membrane after salicylic acid filtration	59.7	48.1	30.0	44.2	0.3	44.5

wetting liquids: Water (W), formamide (F), diiodomethane (DIM).

The pure HL membrane is a relatively hydrophilic membrane, and the determined contact angle for this membrane is 59.0°. Adsorption of salicylic acid molecules on the membrane surface resulted in an increase in the contact angle to 75.9°. The increase of the contact angle indicates a decrease in the hydrophilic properties of the membrane surface. A similar effect was obtained for the TS80 membrane,

although the increase in the contact angle was not so significant. The contact angle increased from 53.4° (for pure membrane) to 59.7°. At the same time, a slight decrease in free surface energy was observed. In the case of the HL membrane, the free surface energy decreased from 43.3 mJ/m² to 42.5 mJ/m². In the case of the TS80 membrane, the value of FSE decreased from 48.3 mJ/m² to 44.5 mJ/m².

The polar, that is, acid-base component γ_S^{AB} of FSE for the pure TS80 membrane was over six times higher than for the pure HL membrane. It should be remembered that the individual components of FSE depend on interactions at the liquid-solid interface. The polar component depends on the appearing interactions which have mainly chemical nature, that is, hydrogen, acceptor-donor, acid-base, and inductive bonds [46]. The dispersion component, on the other hand, depends on the dispersion of a given liquid and is closely related to the adsorption of liquid on the solid surface [47]. Considering the above, it can be assumed that the TS80 membrane was covered with a layer rich in polar groups. It was observed that after filtration of salicylic acid, the HL membrane showed a much higher value of the acid-base component than the value for the pure HL membrane, while in the case of the TS80 membrane, the effect was reversed. Further research is necessary in order to thoroughly explain this phenomenon. The use of the van Oss-Good model for HL membrane has shown that the values of the base component γ_S^- varied from 4.32 to 6.43 [48]. The highest value was obtained for HL membranes after filtration of oxidized salicylic acid. The lowest values were obtained for the membrane after SA (4.32) and the SA + 2,3-DHBA mixture (4.33) filtration. The value of the acid component γ_S^+ ranged from −0.87 to 1.33. The lowest values were obtained for the membrane after SA (−0.87) and the SA + 2,3-DHBA mixture (−0.27) filtration, while the highest values were obtained for the clean membrane (1.25) and after filtration of the SA + Catechol mixture (1.33).

In the case of the HL membrane, which was used to filter the oxidized salicylic acid solution, a significant decrease in the contact angle was reported (to 48.6°). At the same time, a considerable decrease in the value of free surface energy to 37.0 mJ/m² was observed. The acid-base component γ_S^{AB} of FSE was zero mJ/m². The dispersion (non-polar) component γ^{LW} has also been reduced. This may indicate damage to the top layer of the membrane due to too long exposure to hydrogen peroxide. This sample, before the measurements, was kept in the refrigerator at 4 °C for several days. Additional studies have shown that a relatively short exposure to hydrogen peroxide during nanofiltration (2–3 h) did not significantly affect the membrane properties and its surface morphology. This seems to be confirmed by the measurements of contact angle and FSE for the HL membrane used for filtration of water with the addition of hydrogen peroxide (0.324 mL/L), which were made immediately after the filtration process. All parameters remained without major changes, apart from the acid-base component γ_S^{AB} of free surface energy, which increased to 4.1 mJ/m².

After filtration of the mixture of salicylic acid and 2,3-DHBA, the HL membrane showed a markedly increased hydrophobicity (contact angle 66.4°) compared to the hydrophobicity of the pure membrane, but lower than the membrane used for the filtration of pure salicylic acid. The acid-base component γ_S^{AB} of free surface energy also slightly increased. On the other hand, the addition of catechol to the salicylic acid solution caused a slight decrease in the contact angle (55.1°) of the HL membrane during filtration. A decrease in the polar component of FSE to 0.3 mJ/m² was also observed. The determined values of contact angles correlated well with solubility (S) of the tested compounds. With increasing solubility of the filtered compound ($S_{SA} < S_{2,3-DHBA} < S_{CAT}$), the contact angle of the membrane in use was decreasing.

4. Summary

Experiments with the removal of salicylic acid by means of UV/H₂O₂ and nanofiltration have been carried out. From the point of view of oxidation products, two basic conclusions were drawn: i) 2,3-dihydroxybenzoic acid, whose structure practically did not differ from the salicylic acid molecule except for the attached −OH group in the ortho position, showed similar retention coefficients as salicylic acid; ii) catechol, whose molecules were deprived of −COOH substituent but enriched with an additional −OH group, showed very little ability of being retained on the membrane.

2,3-dihydroxybenzoic acid has a negative impact on retention degree of SA during nanofiltration. Catechol, another oxidation product of SA, improves SA retention. Probably in an alkaline environment, catechol improves SA retention because its presence contributes to the increase in hydrophilicity of the membrane, thereby increasing the driving force of electrostatic repulsion.

The example of catechol showed that the use of integrated methods of removing hazardous compounds from wastewater, in which advanced oxidation and nanofiltration processes are applied, may contribute to the emission of secondary pollutants in the form of oxidation products, whose chemical structure and low molecular weight contribute to low efficiency of the separation on a membrane. Although catechol belongs to biodegradable products, it has been shown, in this example, that there is a potential risk of emission of toxic oxidation products which constitute a serious environmental hazard. Therefore, it is necessary to carry out research in this area and analyze threats resulting from the integration of advanced oxidation methods and membrane filtration for wastewater purification and water treatment.

Author Contributions: R.Ż. - making a research plan, performing nanofiltration experiments and UV/H₂O₂ oxidation, interpretation and description of results, preparation of publications, preparation of the article after the review. R.M. - development of an analytical method for the determination of test compounds and measurement of samples by HPLC-MS. I.K. - SEM microscopic image and determination of contact angle and free surface energy (FSE). M.K. - Contribution to the preparation of the publication. M.G. - participation in the preparation of the publication, participation in the preparation of the article after the review. S.L. - contribution to the preparation of the publication.

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