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Integration of photocatalysis with membrane processes for purification of water contaminated with organic dyes

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ABSTRACT

The aim of the presented work was the investigation on the possibility of application of the hybrid photocatalysis/membrane processes systems for removal of azo dyes (Acid Red 18, Direct Green 99 and Acid Yellow 36) from water. The photocatalytic reactions were conducted in the flow reactor with immobilized photocatalyst bed and in the suspended system integrated with ultrafiltration. A commercially available titanium dioxide (Aeroxide® P25, Evonik (former Degussa), Germany) was used as a photocatalyst. The solution after the photocatalytic reaction was applied as a feed in nanofiltration or membrane distillation. The changes of various parameters, including concentration of dyes, pH and conductivity of the solution, TOC and TDS content were analyzed during the processes. It was found that the solutions containing the model azo dyes could be successfully decolorized during the photocatalytic processes applied in the studies. The application of ultrafiltration process results in separation of photocatalyst from the treated solutions whereas during nanofiltration and membrane distillation high retention of degradation products was obtained.

1. Introduction

Organic pollutants are present in the water environment usually as a result of their occurrence in industrial effluents. The treatment of such wastewater is based on various mechanical, biological, physical and chemical processes. The increasing volume of wastewater containing nonbiodegradable pollutants discharged into the environment demands the development of new powerful, clean and safe decontamination technologies. Photocatalysis represents a promising alternative technology for degradation of organic pollutants in water [1–14]. Photocatalysis is one of the advanced oxidation processes (AOPs). Although there are different reaction systems used in AOPs, all of them are characterized by the production of hydroxyl radicals, which are able to oxidize and mineralize almost any organic molecule, yielding CO_2 and inorganic ions [15–22].

The common material used in the photocatalytic processes is titanium dioxide. TiO_2 can be applied in the form of powder suspended in slurry or it can be immobilized on various supports. Photocatalytic reactors with suspended catalyst give much better contact between the photocatalyst and dissolved impurities comparing to reactors with immobilized catalyst. However, in this case the step of separation of the catalyst is necessary, which increases the overall costs of the process. Although TiO_2 shows high photocatalytic activity, the problem of separation of its particles emerges in the practical applications.

A very promising method for solving problems concerning separation of photocatalyst as well as products and by-products of photodecomposition from the reaction mixture is application of hybrid systems based on membrane processes and photocatalysis [23–33]. Hybrid photocatalysis – membrane processes are conducted in the installations often called “photocatalytic membrane reactors” (PMRs). In the PMRs, similarly as in case of classical photoreactors, the catalyst might be immobilized on/in a membrane (photocatalytic membranes) or suspended in the reaction mixture. Fixation of the photocatalyst often results in a loss of photoactivity [34]. Therefore, numerous investigations have been recently focused on PMRs with a catalyst in suspension. In case of these reactors the membrane might act as a barrier for the molecules which are degraded and products and by-products of their decomposition. However, this role strongly depends on the separation characteristics of the membrane used and the membrane process applied. The products and by-products of photodecomposition of organics are, in general, low molecular weight compounds. Therefore, in case of pressure driven membrane processes, NF and RO only might be considered as processes able to separate these substances. In case of membrane techniques in which the mechanism of separation is other than the sieve one, other properties of reactants, for example volatility, should be taken into consideration.

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However, the main purpose of coupling of photocatalysis in suspension with membrane techniques is separation and recovery of photocatalyst particles. The pressure driven membrane processes such as MF, UF and NF were found to be very effective in retention of TiO_2 particles. Choo et al. [33] investigated the effectiveness of separation of TiO_2 P25 with application of PSU MF membrane having a nominal pore size of 0.1 μm. The authors reported that rejection of photocatalyst particles from the treated water was very effective. Turbidity of permeate was <0.1 NTU although the sizes of TiO_2 grains in water were in the range of 0.04–10 μm, meaning that some portion of the catalyst particles exhibited diameters smaller than the pores of the membrane. These small TiO_2 particles had a chance to pass the membrane; however, the concentration of TiO_2 measured in permeate was nearly negligible (<0.5 ppb). So high effectiveness of TiO_2 separation by MF membrane was attributed to the formation of a dense cake layer on the membrane surface (so called "dynamic membrane"), which improved the rejection of smaller particles [33].

Similarly, Meng et al. [35] observed no catalyst drainage in the effluent during treatment of polluted river water in a PMR utilizing MF membrane having pore size of 0.4 μm. The catalyst had a mean particle size of 1.35 μm, but the distribution of the catalyst size allowed those of smaller sizes to penetrate the pores of the membrane used. The authors explained high effectiveness of TiO_2 separation by the change of the catalyst properties after dosing into the reactor. When staying in the reactor the fine particles aggregated to form larger agglomerates, which were rejected by the membrane [35].

Sopajaree et al. [36] reported that UF was very effective in separation of TiO_2 from the treated solution. The initial turbidity of the feed was 5200 NTU (corresponding to TiO_2 dose of 1 g/dm^3), whereas the turbidity of permeate was in the range of 0.22–0.45 NTU [36]. Similar results were obtained in our earlier investigations on the hybrid photocatalysis – UF system [27,37]. The turbidity of permeate ranged from 0.07 to 0.08 NTU, for TiO_2 concentrations in the feed solutions of 0.1–0.5 g/dm^3, respectively.

The membrane technology combined with photocatalysis seems to be suitable for waste water treatment showing many advantages, like: control of a residence time in the reactor; realization of a continuous process with simultaneous products and catalyst separation from the reaction environment and possibility of further reuse of catalyst recovered from the reaction mixture.

The aim of the presented work was the investigation on the possibility of application of the hybrid photocatalysis/membrane processes systems for removal of azo dyes from water. The changes of various parameters, including concentration of dyes, pH and conductivity of the solution, TOC and TDS content were analyzed during the process.

2. Materials and methods

A commercially available titanium dioxide (Aeroxide® P25, Evonik (former Degussa), Germany) was used as a photocatalyst. According to the manufacturer, the specific surface area of the catalyst is ca. 50 m^2/g and the average primary particle size is 21 nm.

Acid Red 18 (AR18), Direct Green 99 (DG99) and Acid Yellow 36 (AY36), produced by the Chemical Factory "Boruta-Kolor" (Poland), were used as model azo dyes. Selected dyes are characterized by various chemical structure, light fastness and molecular weight (Table 1). The structural formulas of dyes are presented in Fig. 1.

The process of purification of water contaminated with azo dyes was conducted in the following hybrid configurations combining photocatalysis with membrane processes: (i) photocatalysis with immobilized catalyst bed/nanofiltration (NF), (ii) photocatalysis in suspension/ultrafiltration (UF)/membrane distillation (MD).

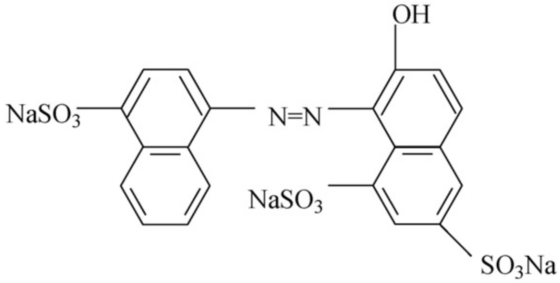
The experiments of the photocatalytic decomposition of dyes with application of the immobilized catalyst bed were conducted in the apparatus presented in Fig. 2. The initial concentration of dyes was equal to 10 mg/dm^3. The volume of the treated solution was 4.5 dm^3. The detailed characteristic of the reactor, the procedure of photocatalyst fixation and illumination conditions were described by Mozia et al. [28]. The main component of the system was the flow reactor with immobilized catalyst bed (1). The reactor was built of quartz tubes partly covered with TiO_2 particles. The total area covered with catalyst, determined for one tube (number of tubes = 7), amounted to 6030 mm^2. The amount of TiO_2 coated per m^2 of the covered area was ca. 1.45 g/m^2. The solution circulated in the reactor with the help of peristaltic pump (4) with the flow rate of 14.6 dm^3/h. The reaction solution was illuminated with a Philips Cleo mercury lamp emitting UV-A light (λ_{max} = 355 nm). The UV lamp (2) was placed above the feed tank (3). The intensity of irradiation was equal to 141.92 W/m^2. The photocatalytic experiments were conducted until complete discoloration of the solution was achieved. The concentration of dyes in the solution was determined by UV–vis spectroscopy. The absorbance was measured at the maximum absorption wavelength (λ_{max} = 508 nm for AR18, λ_{max} = 628 nm for DG99 and λ_{max} = 414 nm for AY36) using Jasco V-530 spectrometer in a 5 cm quartz cells. The samples of the reaction solution were taken for analysis every hour during the first 5 h of the experiment and then every 5 h until the solution was decolorized. Total organic carbon (TOC) concentration was measured using the "multi N/C 2000" analyzer (Analytik Jena, Germany). Total dissolved solids (TDS) content, conductivity and pH of the solution were monitored using Ultrameter^{TM} 6P (MYRON L COMPANY USA). The colorless solutions were also analyzed in respect of inorganic ions (sulfate, nitrate, nitrite and ammonium) using UV–vis spectroscopy. Sulfates were determined using turbidimetric method with barium chloride [38], nitrogen-nitrate was determined using sodium salicylate method [39], nitrogen-nitrite according to the Griess method [40,41] and nitrogen-ammonia according to the Nessler method [42]. The reaction solution after discoloration was then employed as a feed in the nanofiltration process.

The NF process was carried out in a laboratory installation with a module equipped with the flat-sheet thin film composite membrane Desal DK5 (126 cm^2). The cut-off of this membrane is 150 and the mean pore diameter is about 2 nm. The scheme of NF system is presented elsewhere [29]. The process was operated in a cross-flow mode. The transmembrane pressure was 0.5 MPa and the feed flow rate amounted to 800 dm^3/h. In the feed, permeate and retentate the TOC concentration, TDS content, conductivity and pH values were measured. The colorless solutions were also analyzed in respect of inorganic ions (sulfate, nitrate, nitrite and ammonium).

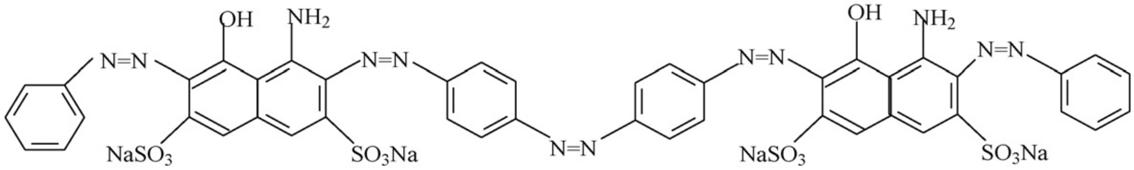
The photocatalytic reaction in the suspended system was conducted in the photocatalytic membrane reactor utilizing ultra-

Table 1
Characteristics of dyes applied in the studies.

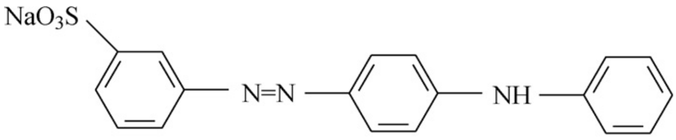
Dye	Molecular weight [g/mol]	Light fastness [Blue Wool Scale]
Acid Red 18, monoazo acid dye, $C_{20}H_{11}N_2Na_3O_{10}S_3$	604.5	4
Direct Green 99, polyazo direct dye, $C_{44}H_{28}N_{12}Na_4O_{14}S_4$	1168.0	3
Acid Yellow 36, monoazo acid dye, $C_{18}H_{14}N_3NaO_3S$	375.4	7



Acid Red 18



Direct Green 99



Acid Yellow 36

Fig. 1. The structural formulas of dyes.

filtration where the catalyst particles were retained in the feed solution by means of the membrane. The experiments of photocatalytic degradation of dyes were conducted with the initial concentration of dyes equal to 10 mg/dm^3 and the photocatalyst loadings of 0.1, 0.3 and 0.5 g/dm^3. The volume of the treated solution was 4.5 dm^3. The permeate was recirculated to the feed tank until a complete discoloration was achieved. The detailed characteristic of the apparatus applied in the photocatalysis/UF experiments can be found in Mozia et al. [27]. The main component of the system was the membrane module with a flat-sheet polysulfone membrane (15.2 cm^2). UF experiments were carried out at a pressure of 0.3 MPa with the feed flow rate of about 90 dm^3/h. The reaction solution containing suspended photocatalyst was illuminated in the feed tank using the same light source as in the system with immobilized catalyst bed. After discoloration of the solution, the permeate was collected (3 dm^3) and was then applied as a feed in the MD process. The procedure of the collection and analysis of the samples during the process was the same as described above for the immobilized system. The effectiveness of TiO_2 separation by the UF membrane was determined on the basis of turbidity removal. Turbidity was measured using HACH 2100N IS turbidimeter.

A schematic diagram of the apparatus for the MD process was presented by Mozia et al. [26]. MD process was conducted in a laboratory-scale installation equipped with a capillary module composed of nine polypropylene Accurel PP S6/2 membranes (Membrana GmbH, Wuppertal, Germany). The inlet temperatures of the feed and distillate were maintained at 343 and 293 K, respectively. The volatile compounds present in warm feed were transferred through the pores of the MD membrane and then condensed/dissolved directly in cold distillate (ultrapure water) whereas the non-volatile compounds were retained on the feed side. The procedure of the analysis of the samples during the process was the same as described above for the photocatalysis/NF system.

3. Results and discussion

Blank tests conducted in the dark revealed no discoloration of the dyes solutions. The direct photolysis was also negligible. The

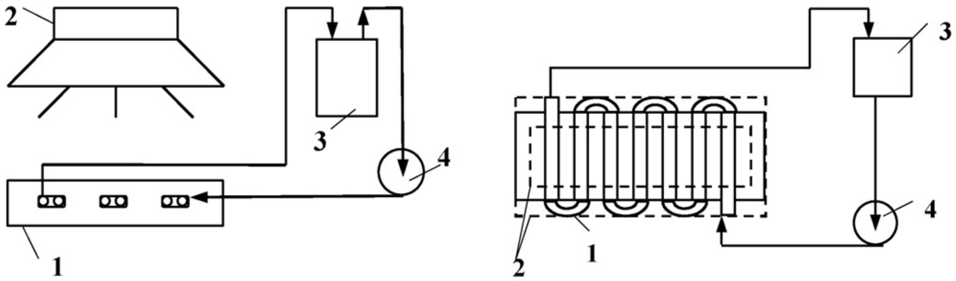


Fig. 2. Schematic diagram of the reaction system with immobilized catalyst bed: left – side view; right – top view.

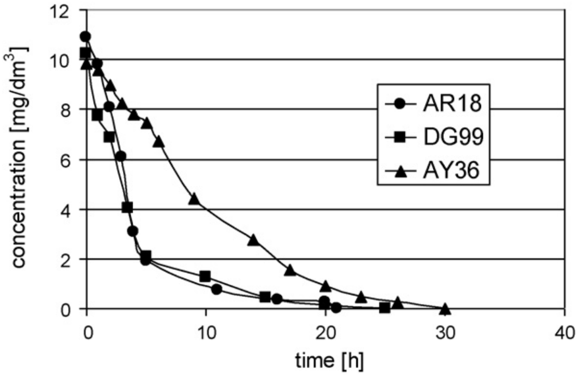


Fig. 3. The changes of dyes concentration during the photocatalytic process conducted in the immobilized system.

reactions of photocatalytic decomposition of dyes were conducted until the solution was colorless.

3.1. Photocatalysis with immobilized catalyst bed/nanofiltration

Fig. 3 presents the changes in dyes concentration during the photocatalytic process. The concentration of dyes decreased with time of the photocatalytic reaction. After 5 h of the process, the highest decomposition (82.5%) was observed for AR18 solution. A similar decomposition degree (79.6%) was obtained for DG99 solution, while for AY36 solution the degree of decomposition was only 24%.

The AY36 discoloration required the longest time of the irradiation – it took 30 h to obtain the complete color removal. For AR18 and DG99 the solutions were colorless after 21 and 25 h, respectively. Although the light fastness is the lowest for DG99, the highest rate of discoloration was observed for AR18. Acid Red 18 is a monoazodye so it is more easily degradable than DG99 which has five azo bonds in the structure. From the other hand, AY36 which is a monoazodye, likewise AR18, showed the lowest rate of discoloration. However, AY36 has the highest light fastness equal to 7 (in the 8-grade scale) and this factor can explain the longest time required for discoloration of AY36 solution.

The removal of color does not indicate the complete removal of organics from the treated solutions. Decomposition of dyes can lead to formation of organic molecules which do not give the color but the organic matter is still present in the solution. TOC analysis revealed the presence of organic carbon in the solution even after the complete discoloration of the solutions. For AR18, analysis showed 60.3% of TOC reduction after 21 h of the process. For AY36 and DG99 TOC removal amounted to 75.5% (after 30 h of irradiation) and 78.1% (after 25 h), respectively. The time required for discoloration of AR18 solution was the shortest from all the cases investigated so these results suggest that with the elongation of the reaction time also the products of dye decomposition undergo the photocatalytic oxidation resulting in TOC content decrease. Although the time of fading of the dye solutions was different for the three model compounds, the obtained results showed that the differences between TOC concentration at the end of the process were not significant. The TOC concentration determined after discoloration of the solutions amounted to 1.46, 1.28 and 1.14 mg/dm^3 for AR18, AY36 and DG99, respectively.

The rate of dyes decomposition is also reflected by TDS content and conductivity of the solution. The TDS parameter indicates all dissolved species present in the solution, i.e. inorganic ions and all kinds of organic compounds.

It was observed, for all studied cases, that both TDS and conductivity values tended to slightly decrease during the first few hours of the process and after that they increased. This observation can be explained by the adsorption of dyes and degradation products onto the photocatalyst surface. P25 photocatalyst is characterized by a high specific surface area which favors the strong adsorption of the species present in the solution. After desorption, the presence of these compounds in the solution results in the TDS and conductivity increase.

Table 2
Changes of parameters monitored during the NF conducted with the solutions obtained after the photocatalytic process (flow reactor with immobilized photocatalyst bed).

Dye		Cond. [μS/cm]	TDS [ppm]	pH	TOC [mg/dm^3]
AR18	NF feed	32.09	20.49	5.61	1.46
	NF permeate	11.28	9.89	6.19	1.21
DG99	NF feed	35.90	22.43	5.49	1.14
	NF permeate	15.98	10.66	5.57	0.49
AY36	NF feed	34.78	22.23	7.3	1.28
	NF permeate	18.17	7.88	7.41	0.67

The pH value of the solution during the process also gives information about the course of the photocatalytic reaction. The obtained results show that the pH value decreased with the time of the process indicating acidification of the solution. This pH drop resulted from oxidation of organics to CO_2 or formation of H_2SO_4 from sulfate groups of the dyes. Moreover, the formation of carboxylic acids also took place during the process.

The solution after the photocatalytic process was then applied as a feed in the NF process. Table 2 shows the results obtained during the NF of the solution after discoloration. After the NF process, the values of TDS and conductivity of the solutions decreased considerably. Concurrently, the values of these parameters increased in the concentrate. The increase of pH in the permeate after the nanofiltration was observed. This indicates retention of species giving the acidic reaction of the solution. The analysis of inorganic ions (sulfate, nitrate, nitrite and ammonium) showed, for all studied cases, that over 95% of sulfate ions and about 80% of total inorganic nitrogen (the sum of nitrate, nitrite and ammonium nitrogen) was retained during NF.

Application of NF did not result in a complete retention of organic matter from the treated solution. The TOC concentration determined at the end of the process amounted to 1.21, 0.67 and 0.49 mg/dm^3 for AR18, AY36 and DG99, respectively. Although the removal of TOC was not complete, the obtained permeate meets the legal regulations in respect of TOC concentration in water.

3.2. Photocatalysis in suspension/ultrafiltration/membrane distillation

Fig. 4 presents changes of AR18 concentration during the photocatalytic reaction conducted in the hybrid photocatalysis – UF

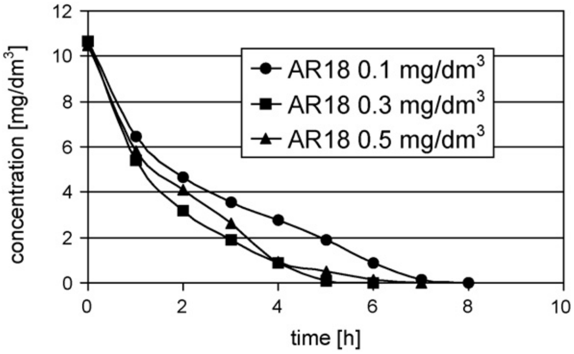


Fig. 4. The changes of dyes concentration during the photocatalytic process conducted in the suspended system.

Table 3
Changes of parameters monitored during the MD conducted with the solutions obtained after the photocatalysis/UF process (catalyst dosage – 0.3 g/dm^3).

Dye		Cond. [μS/cm]	TDS [ppm]	pH	TOC [mg/dm^3]
AR18	MD feed	42.21	28.93	5.85	1.40
	MD distillate	2.05	1.81	6.70	0
DG99	MD feed	35.21	26.97	5.09	2.51
	MD distillate	4.59	3.65	6.61	0.15
AY36	MD feed	27.84	21.29	5.29	1.86
	MD distillate	3.36	2.11	6.49	0.15

system. The concentration of dyes decreased with time of irradiation. For AR18 solution with the photocatalyst concentration equal to 0.3 g/dm^3 the solution was colorless after 6 h of irradiation, whereas for the smaller (0.1 g/dm^3) and higher (0.5 g/dm^3) catalyst loadings the time of discoloration was longer. It took 7 h to obtain the colorless solution for TiO_2 concentration equal to 0.5 g/dm^3 and 8 h for the concentration of 0.1 g/dm^3. For the other two dyes, the time of discoloration was also the shortest for the photocatalyst loading equal to 0.3 g/dm^3.

TOC analysis revealed the presence of organic carbon in the solution even after the complete discoloration of the solutions. For AR18, analysis showed 73% of TOC reduction after 6 h of the process. For AY36 and DG99 TOC removal amounted to 67% (after 10 h of irradiation) and 48% (after 8 h), respectively. The TOC concentration determined at the end of the process amounted to 1.4, 1.86 and 2.51 mg/dm^3 for AR18, AY36 and DG99, respectively.

The aim of the application of ultrafiltration together with the photocatalytic process was to separate the TiO_2 particles from the treated solution. The obtained results indicated that UF membrane successfully retained the photocatalyst particles in the feed solution and the permeate was free of photocatalyst. The turbidity of permeate was <0.1 NTU, whereas the turbidity of feed solution ranged from 370 to 1680 NTU, for TiO_2 loadings of 0.1–0.5 g/dm^3.

During the UF process a decrease of the permeate flux was observed. This fact was associated with the formation of a cake layer built of TiO_2 particles onto the membrane surface. The observed fouling of the membrane was reversible, since the initial permeate flux was recovered after application of the back-washing with distilled water. The process of back-washing was conducted for 2 min with the water flow rate equal to 150 cm^3/h.

Since the photocatalysis/ultrafiltration system did not give a complete removal of organic matter from the reaction mixture, the permeate after the photocatalysis/UF process was used as a feed in the MD. The MD was conducted for 5 h. The distillate flux amounted to 336 m^3/m^2 d and no decrease of the flux was observed during the process. Table 3 presents the values of parameters analysed during the MD process (TOC, TDS, conductivity and pH) for feed and distillate. The presented results refer to the feed being the photocatalysis/UF permeate obtained during the process conducted with the optimal catalyst loading of 0.3 g/dm^3. For all the other studied cases the tendency of changes of the parameters was similar. As can be seen from Table 3, the values of the analysed parameters in distillate considerably decreased compared to the feed. The most important is the fact that TOC value in distillate is very low, that is to say that MD process successfully separates the organic species presented in the feed. The best results in respect of TOC reduction were obtained for AR18 – 100%. For DG99 and AY36 these values amounted to 94% and 91.9%, respectively.

Fig. 5 presents the comparison of the investigated hybrid processes. It can be seen that MD process gives product with better quality in respect of TOC, TDS and conductivity values than NF. The retention of inorganic ions is comparable for the both systems. Since the compositions of feed solutions applied in both, NF and MD, were similar (Tables 2 and 3) it could be assumed that the main factor affecting the product (permeate) quality was different mechanism of mass transfer in the membrane processes applied. In case of NF the separation is based on a sieving mechanism (porous membranes) or on a solution-diffusion mechanism (nonporous membranes, e.g. TFC Desal DK5). Moreover, when ions are involved Donnan exclusion is often the main mechanism of retention [43]. In MD the driving force of the mass transfer through the membrane pores is a vapour pressure difference on both sides of a membrane, which depends on the temperature and the solutions composition in the layers adjacent to the membrane. The MD membrane is permeable for volatile compounds and water vapour only. Low concentration of TOC and TDS in MD distillate as well as its low conductivity suggest that the amount of volatile compounds in the feed solution was not high. As a result, the quality of MD distillate was much higher than that of the NF permeate.

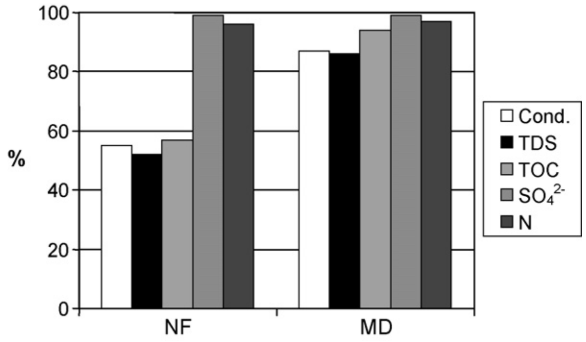


Fig. 5. Comparison of the applied processes.

4. Conclusions

1. The application of hybrid photocatalysis/nanofiltration system did not succeed in total removal of organic matter from the treated solutions; however, the obtained permeate exhibited a very good quality in respect of TOC, TDS, conductivity and inorganic ions values.
2. The time of discoloration was much shorter in the suspended system than in case of the fixed photocatalyst bed.
3. Application of ultrafiltration together with photocatalytic process resulted in a complete separation of photocatalyst from the treated solution.
4. The removal of organic matter from the treated solution was much higher in the MD process comparing to NF process.

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