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Effect of UV/H₂O₂ Oxidation on Fouling in Textile Wastewater Nanofiltration

Abstract

The aim of the work was to investigate the effect of UV/H₂O₂ chemical oxidation on fouling in the process of nanofiltration. Investigations were carried out for model textile wastewater from the dyeing of cellulose fibers with direct reactive dyes which contained anionic, non-ionic and cationic surfactants. The effect of preliminary UV/H₂O₂ oxidation of the wastewater on nanofiltration parameters was also investigated. It was found that the preliminary UV/H₂O₂ oxidation reduced fouling and thus increased the nanofiltration efficiency of wastewater containing cationic and non-ionic surfactants, which are derivatives of polysiloxanes.

Key words: textile wastewater, nanofiltration, advanced oxidation processes, water reuse.

The wastewater composition has a remarkable effect on the rate of nanofiltration. In the textile industry a number of chemical compounds are used which can significantly disturb the process of filtration by blocking up the membranes, or damage them permanently. The compounds which may affect filtration rates include surfactants. Particularly cationic surfactants which are synthesised on the basis of polysiloxanes or fatty acid condensation products can have a negative effect on the membrane operation. It happens that cationic and non-ionic surfactants have a similar chemical structure. Anionic surfactants are based mainly on alkylaryl sulfonates with a branched alkyl chain and straight-chain alkylaryl alkylates.

Currently the textile industry uses a number of substances which give the final products their special properties. Obtaining these properties involves the use of certain chemical compounds, including enzymes and polymers, which contribute to the specific modification of a textile product. These compounds remaining in the wastewater may induce fouling or damage the membrane permanently. Fouling refers to the accumulation of substances (suspended particles, colloids, soluble high-molecular compounds and salts) on the surface and/or in the pores of the membrane in a way that reduces its permeability. The result of fouling is a decrease in filtration efficiency. The application of the preliminary chemical oxidation of wastewater which contains chemical compounds used in the textile industry can greatly improve the parameters of the membrane filtration of the wastewater.

The aim of the present study was to check if the use of chemical oxidation (UV/H₂O₂) as a preliminary operation could have a favorable effect on the nanofiltration process, i.e. fouling reduction. Investigations were carried out on various components of textile wastewater.

UV/H₂O₂ oxidation is an efficient method for the decolorisation and degradation of textile wastewater which contains water-soluble dyes [7 - 14, 16, 17] and detergents [15, 18]. The high efficiency of this method is a result of the formation of reactive hydroxyl radicals due to the UV irradiation of H₂O₂ particles. The separate action of UV or H₂O₂ alone is generally ineffective, and the degree of colour reduction usually reaches a few percent [10, 12, 13, 16, 17].

Introduction

The textile industry is one of the most water-consuming industries and also requires water of very high quality and specific parameters. Hence, from an economic and environmental point of view, a proper solution is to use an integrated wastewater treatment jointly with technologies that enable the closing of the process water cycle.

One of the most efficient methods of wastewater treatment for its reuse are the membrane techniques. However, these methods require very high operating costs, especially in the case of wastewater which strongly fouls the membranes. In order to reduce these costs, in some cases it is recommended to apply a preliminary stage of wastewater pretreatment using such methods as coagulation, ozonation, advanced oxidation, or ultrafiltration [1 - 6].

Methods

Wastewater oxidation by H₂O₂/UV

As a method of wastewater pretreatment preceding membrane filtration, UV/H₂O₂ oxidation was used. The reaction was carried out in a tube reactor (1) 3500 ml in volume, shown schematically in *Figure 1* (see page 100).

The wastewater was mixed due to liquid circulation forced by the peristaltic pump (3) in a closed system. The reactor was a quartz tube (2) with two UV lamps (monochromatic – $\lambda = 254$ nm) of 22 W total power. Hydrogen peroxide at 30% concentration was added at the beginning of the reaction in doses ranging from 0.0327 to 0.3270 mol/dm³. With the use of syringes A and B, wastewater samples of 5 cm³ were taken every 30 minutes at the inlet and outlet of the reactor. The oxidation process was carried out for 150 minutes.

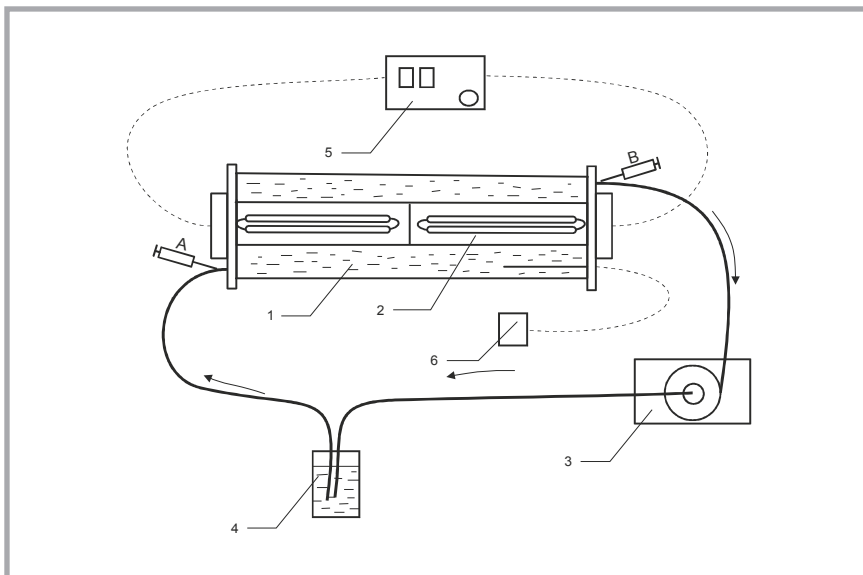


Figure 1. Schematic of the reactor with UV lamp for UV/H₂O₂ treatment of wastewater: 1 – glass reactor, 2 – quartz tube with UV lamp, 3 – peristaltic pump, 4 – tank closing the system, 5 – UV lamp power supply, 6 – temperature sensor with a meter, A, B – syringes to take wastewater samples at the reactor inlet and outlet.

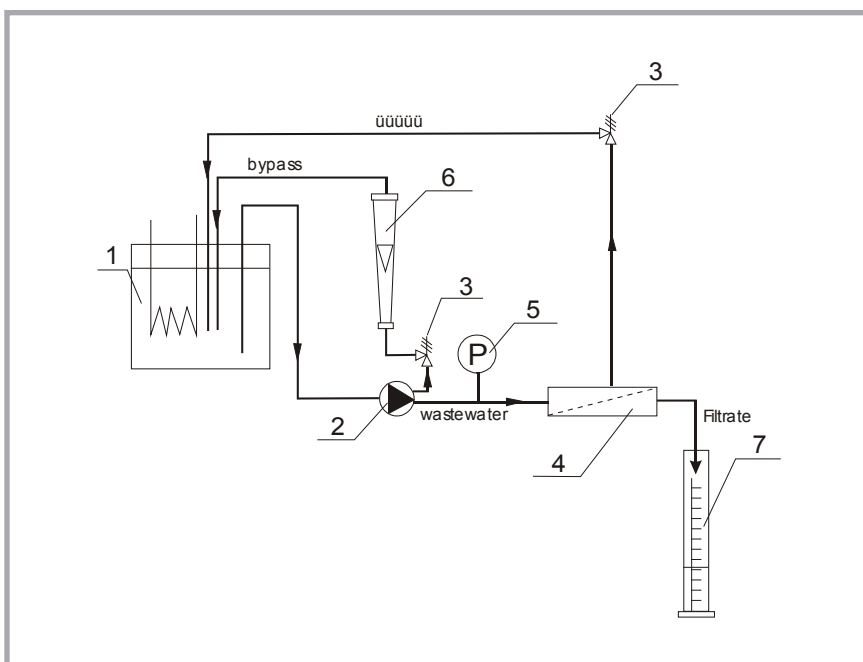


Figure 2. Schematic diagram of nanofiltration system: 1 – thermostat, 2 – pump, 3 – control valves, 4 – pressure chamber with a membrane, 5 – manometer, 6 – rotameter, 7 – measuring cylinder.

Table 1. Detergents used in the experiments.

Code of wastewater	Ionic character of surfactants	Base of chemical structure	Name / Producer
A-S1	Anionic	n-hexadecyl sulfate sodium salt and n-octadecyl sulfate sodium salt	Pretepon G / PZCh, Łódź
A-S2	Anionic	acrylic copolymer	Decol SN / BASF
N-S3	Non-ionic	polysiloxane-based compound	Rucofin GWA New / Rudolf GmbH & Co. KG
N-S4	Non-ionic	fatty acids condensation product	Perrustol VNO / Rudolf GmbH & Co. KG
C-S5	Cationic	fatty acids condensation product	Perrustol IPD 500 / Rudolf GmbH & Co. KG
C-S6	Cationic	polyammonium-modified polysiloxane compound	Rucofin TWO / Rudolf GmbH & Co. KG

Nanofiltration of the wastewater

After oxidation, the wastewater was subjected to nanofiltration on a DK membrane (TF polymer, reaction size 98 MgSO₄, 25 °C, pH range 2 – 11, typical flux/psi 22/100). The filtration was performed by the cross-flow method at a constant flow rate of 2 dm³/min inside the system (controlled by rotameter 6) at a temperature of 40 °C. The experiments were made at a pressure of 1.5 or 0.7 MPa. The nanofiltration system is shown schematically in **Figure 2**.

Tested material

The tested material was model textile wastewater prepared on the basis of many analyses of real textile wastewater generated in the course of the dyeing process. The wastewater contained two types of dyes: reactive dye - 0.1 g/dm³ *Helactin Red DEBN* (BORUTA-ZACHEM), direct dye - 0.04 g/dm³ *Direct Scarlet 4BS* (BORUTA-ZACHEM), NaCl - 7 g/dm³ Na₂CO₃ - 2 g/dm³ and one of the selected surfactants - 0.17 g/dm³. During the experiments, several types of detergents, including anionic, cationic and non-ionic surfactants were tested (**Table 1**).

The efficiency of the wastewater treatment was determined by physicochemical parameters such as the Chemical Oxygen Demand (COD, mineralisation and spectrophotometric determination by the HACH-LANGE method), the Total Organic Carbon (TOC, mineralization and spectrophotometric determination by the HACH-LANGE method) and the colour reduction degree (A/A⁰, spectrophotometric determination at wavelength λ = 525 nm).

Results and discussion

Chemical oxidation of wastewater

UV radiation alone

Figure 3.a shows the dependence of the wastewater decolorisation degree (given as A/A⁰ ratio) on the time of UV irradiation of the wastewater tested, while **Figure 3.b** illustrates the dependence on the time of the reaction with H₂O₂. The following wastewater types were tested: A-S1 (sulfate sodium salt), A-S2 (acrylic copolymer), N-S4 (fatty acid condensation product) and C-S6 (polysiloxane-based compound).

Table 2 gives the reduction degree of wastewater parameters (in %) after UV irradiation for 150 minutes. The UV irradiation alone had only a small effect

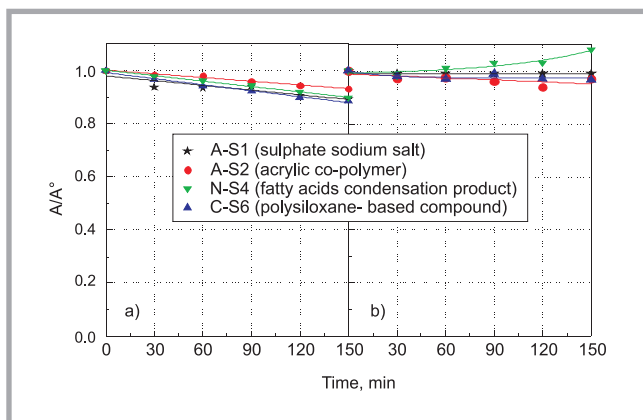


Figure 3. Dependence of A/A° on time: a) UV irradiation of wastewater samples tested, b) reaction with H_2O_2 , where: A – absorbance after irradiation, $\lambda = 525$ nm, A° – absorbance of non-irradiated sample, $\lambda = 525$ nm, dose of $H_2O_2 = 0.1675$ mol/dm³.

on the reduction in wastewater parameters. The degree of COD reduction ranged from 2.5 to 8%, while the degree of decolorisation was from 7 to 11%. No changes in the TOC were found, which confirmed that during UV irradiation no organic matter mineralisation occurred in the wastewater. A tendency can be observed that with an increase in the COD reduction, the degree of colour reduction decreases. The compound containing a polysiloxane chain decomposes the most slowly, which follows directly from the low COD reduction at a relatively high decolorisation degree. The acrylic copolymer-based compound is relatively the most susceptible to UV, which may be confirmed by the highest degree of COD reduction at the lowest degree of colour removal from the wastewater.

Treatment with H_2O_2 alone

The types of wastewater selected were treated with hydrogen peroxide for 24 hours. For the first 150 minutes the absorbance was measured every 30 minutes, with the last measurement being taken 24 hours after the beginning of the experiment. The action of hydrogen peroxide alone did not significantly affect wastewater decolorisation either (cf. **Figure 3.b**). Hydrogen peroxide is a weak oxidant, with a redox potential of 1.05 eV. At a dose of $H_2O_2 = 0.1675$ mol/dm³, colour reduction after 150 minutes usually did not exceed 2%. The best results were obtained for wastewater containing acrylic copolymer (A-S2), in which case the maximum COD reduction was 5%. An increase in the H_2O_2 dose to a concentration of 0.3270 mol/dm³ did not cause any significant improvement of the reduction in wastewater parameters. At both H_2O_2 doses of 0.1675 and

0.3270 mol/dm³, the reduction in wastewater parameters after 150 minutes did not exceed a few percent.

After 24 hours the highest COD reduction was 14% for wastewater A-S2 (containing acrylic copolymer), while the highest degree of color reduction was obtained for wastewater C-S6 (containing a polysiloxane-based compound) - **Table 3**.

Wastewater oxidation by means of UV/ H_2O_2

The synergistic action of H_2O_2 and UV caused an almost complete decolorisa-

tion of the wastewater and a reduction in TOC from 15 to 48% and COD from 5 to 43%. The mechanism of UV/ H_2O_2 oxidation is relatively complex. Besides the desirable reactions which result in organic matter decomposition in the wastewater, there are many chain reactions in which hydroxyl OH^\bullet radicals can be recombined to make inefficient products. One of the agents that may influence the unfavourable recombination of OH^\bullet radicals is H_2O_2 [3, 4, 14]. Hence, an important stage of the process is to specify an optimal dose of this agent. **Figure 4** shows the dependence of the constant

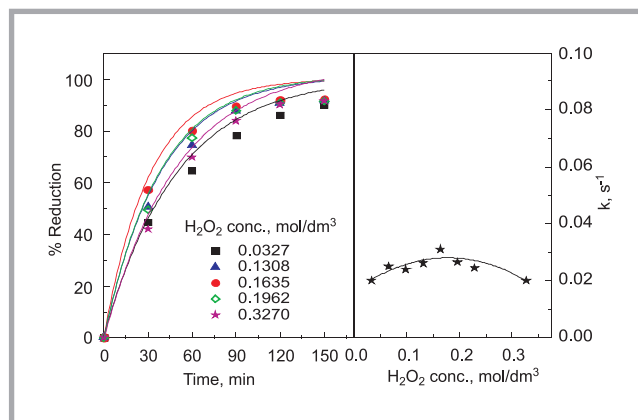


Figure 4. Dependence of the decolorisation rate of wastewater A-S1 by UV/ H_2O_2 on the H_2O_2 dose.

Table 2. Reduction in wastewater parameters after UV irradiation.

Code of wastewater	Reduction in parameters, %		
	COD	TOC	Absorbance ($\lambda = 525$ nm)
A-S1	6.0	0	7.6
A-S2	8.0	0	7.0
N-S4	5.0	0	11.0
C-S6	2.5	0	10.3

Table 3. Reduction in wastewater parameters after 24 hours of H_2O_2 oxidation.

Code of wastewater	Reduction in parameters, %		
	COD	TOC	Absorbance ($\lambda=525$ nm)
A-S1	4.0	0.0	0.1
A-S2	14.0	0.0	9.0
C-S6	1.8	2.4	16.9

Table 4. Reduction in wastewater parameters after H_2O_2 /UV oxidation.

Code of wastewater	Reduction in parameters after 150 min of oxidation by H_2O_2 /UV system, %			Pseudo-first order rate constant k , s ⁻¹
	COD	TOC	Absorbance ($\lambda = 525$ nm)	
A-S1	43	48	98.6	$3.19 \cdot 10^{-2}$
A-S2	42	26	98.5	$2.62 \cdot 10^{-2}$
N-S3	30	22	96.6	$2.86 \cdot 10^{-2}$
N-S4	5	16	95	$2.62 \cdot 10^{-2}$
C-S5	10	15	95	$2.49 \cdot 10^{-2}$
C-S6	24	16	95.5	$2.40 \cdot 10^{-2}$

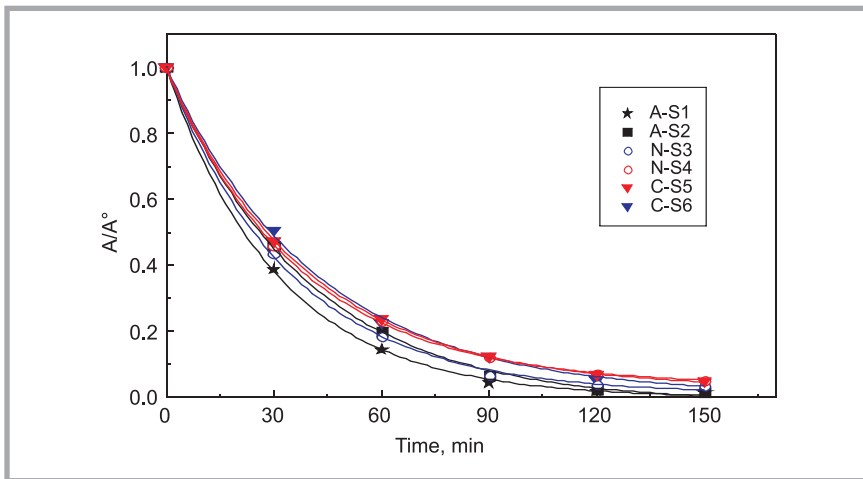


Figure 5. Colour decay in the wastewater containing different surfactants.

Table 5. Reduction in the parameters of wastewater subjected to H_2O_2/UV oxidation and nanofiltration.

Code of wastewater	Reduction in filtrate parameters after nanofiltration, %		
	COD	TOC	Absorbance ($\lambda=525$ nm)
A-S1	80	82.5	99.9
A-S2	84	83	99.9
N-S3	76	64	99.9
N-S4	83	77	99.9
C-S5	80	67	99.9
C-S6	78.5	70	99.9

rate of the pseudo-first order reaction (k) of textile wastewater decolorisation (A-S1) on the hydrogen peroxide dose. Based on the constant (k), the wastewater decolorisation rate was analyzed at an H_2O_2 concentration ranging from 0.0327 to 0.3270 mol/dm³. Hydrogen peroxide was added in a single portion at the beginning of the reaction. The optimal hydrogen peroxide dose was found to be 0.1635 mol/dm³.

After determining the optimal H_2O_2 dose at which the oxidation of wastewater A-S1 was most efficient, a series of investigations were carried out for different types of wastewater using a dose of 0.1635 mol/dm³. Figure 5 shows curves of colour decay for wastewater of different chemical composition (cf. also Table 1). The decolorisation rates of the wastewater tested were practically comparable. However, colour was

most quickly removed from wastewater A-S1, which contained an anionic surfactant, while this occurred most slowly for wastewater containing cationic surfactants C-S5 and C-S6. Table 4 gives the degrees of reduction in the wastewater parameters tested after oxidation. The wastewater decolorisation ranged from 95 to 98%.

As a result of H_2O_2/UV oxidation, the reduction in TOC ranged from 15 to 48% and that of COD from 5 to 43%. The highest TOC and COD reduction was obtained for the wastewater containing anionic surfactants, while the worst results were achieved for wastewater N-S4 and C-S5, which contained fatty acid condensation products of a non-ionic and cationic character.

Nanofiltration of the wastewater

After UV/H_2O_2 oxidation, the wastewater was subjected to nanofiltration on a DK membrane. The experiments were conducted for various types of wastewater, testing the effect of a surfactant on the filtration efficiency.

Table 5 presents the reduction in TOC, COD and color of the wastewater subjected to preliminary chemical oxidation by H_2O_2/UV and nanofiltration. The process of nanofiltration was carried out at a pressure of 1.5 MPa and temperature of 40 °C. The filtrate obtained was colourless, while the COD and TOC reduction ranged from 64 to 83%. Irrespective of the surfactants applied, the filtrate satisfied the requirements for process water

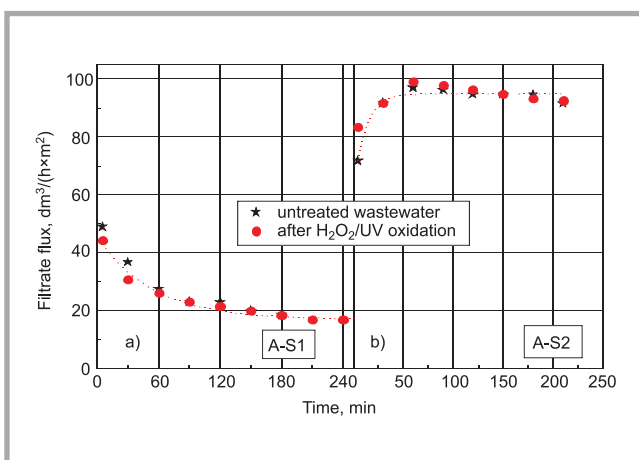


Figure 6. Dependence of filtrate flux on time for wastewater not subjected to pretreatment and after chemical treatment: a) wastewater containing an anionic surfactant based on sulfate sodium salt A-S1, b) wastewater containing anionic acrylic copolymer A-S2, H_2O_2 dose = 0.1635 [mol/dm³], oxidation time 150 min, lamp power 22 W, filtration pressure 1.5 MPa, temperature 40 °C.

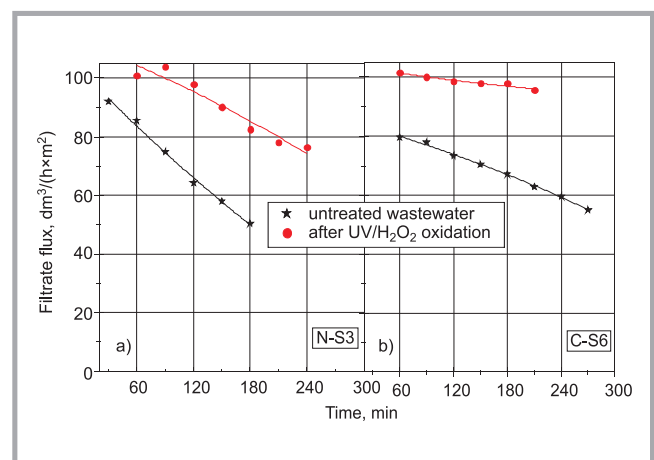


Figure 7. Effect of chemical oxidation on the filtration efficiency of wastewater containing polysiloxane-based compounds: a) wastewater containing a non-ionic surfactant N-S3, b) wastewater containing a cationic surfactant C-S6, nanofiltration pressure 1.5 MPa, temperature 40 °C.

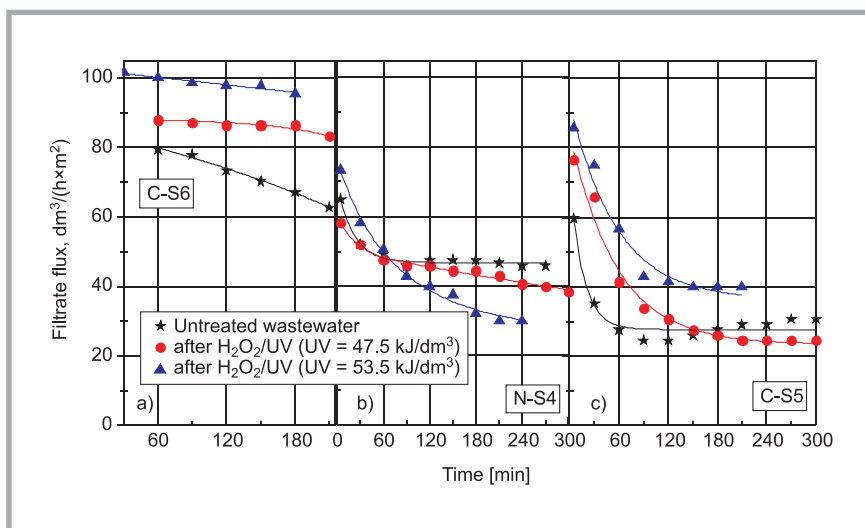


Figure 8. Dependence of filtrate flux on time for untreated wastewater and after chemical treatment by H_2O_2/UV : a) wastewater containing a cationic surfactant based on polysiloxane compounds (C-S6), b) wastewater containing a non-ionic product of fatty acid condensation (N-S4), c) wastewater containing a cationic product of fatty acid condensation (C-S5), H_2O_2 dose = $0.1635, mol/dm^3$.

to be used in technological processes in the textile industry.

The type of surfactant applied had an influence on the process efficiency. The surfactants of similar chemical structure had a comparable effect on the filtration rate.

Wastewater containing anionic surfactants

Figures 6.a & 6.b show the results of experiments on the effect of chemical oxidation on the filtration efficiency of wastewater containing anionic surfactants (A-S1 and A-S2). Preliminary wastewater oxidation had no effect on the improvement of nanofiltration efficiency. For both wastewater A-S1 and A-S2 the rate of filtration was practically the same for non-pretreated and chemically treated wastewater.

Wastewater containing polysiloxane-based compounds

The best results were obtained for wastewater N-S3 and C-S6, containing polysiloxane-based compounds. In the case of both cationic and non-ionic surfactants, a remarkable improvement in the filtration parameters of the wastewater after

chemical pretreatment was achieved (Figure 7.a & 7.b). A significant increase in the filtrate flux and a decrease in fouling, confirmed by the smaller slope of the filtration curve, were observed.

An increase in the UV radiation dose during the chemical treatment of the wastewater caused an increase in the filtrate flow rate in the nanofiltration process. Tests were performed at irradiation doses of 53.5-kJ/dm^3 and 47.5-kJ/dm^3 (Figure 8.a). An increased dose of UV irradiation also caused a fouling reduction. The slope of the curve at UV dose = 53.5-kJ/dm^3 was much lower than for untreated wastewater.

Wastewater containing fatty acid condensation products

In the case of fatty acid condensation products, interpretation of the results of experiments on the effect of chemical oxidation on filtration efficiency appeared to be more complicated. Figures 8.b & 8.c show the dependence of the filtrate flux on the filtration time for wastewater not subjected to treatment and after chemical oxidation.

When analysing the curves which illustrate the dependence of the filtrate flux on time for untreated wastewater, the process can be divided into two stages. At the first one significant fouling can be observed (Figure 8.b & 8.c). In the case of wastewater C-S5, which contains a cationic surfactant, the decrease in the filtrate flux was 60%. In the case of wastewater N-S4, the decrease in the filtration rate was about 15%. After 60 minutes a kind of equilibrium could be observed at which the filtration rate was approximately constant.

It was reported that H_2O_2/UV oxidation could have a negative effect on nanofiltration efficiency (Figure 8.b & 8.c). The oxidation of wastewater N-S4 (with a non-ionic surfactant) causes the decomposition of organic compounds to products which foul the membrane. With an increase in the UV irradiation dose, intensified fouling was observed. At a dose of UV = 53.5-kJ/dm^3 a significant reduction in the filtration efficiency was observed, despite the fact that at the initial stage of the process a slight increase in the filtrate flux occurred. The fouling phenomenon is difficult to interpret because there can be many factors which have an influence on the final result of the process. Fouling may be induced by low-molecular compounds that block membrane pores and decrease their capacity. Additionally, it was reported that high-molecular compounds could also induce strong fouling by pressing and blocking membrane pores and forming cake or gel on the membrane surface [19]. The effect of fouling can be related to micro-coagulation of the wastewater as a result of oxidation [1, 20]. The unfavourable effect of preliminary oxidation can be associated with the process occurring during the oxidation. There are reports in the literature which show that certain bivalent cations (e.g. Ca and Mg) may be combined with carboxylic groups in the presence of some fractions of natural organic compounds, causing a decrease in the particle load and reducing electrostatic repulsion from the membrane surface. This phenomenon may lead to increased fouling [21].

When analysing Figures 7.a, 7.b, 8.b and 8.c, one can find that fouling depended to a larger extent on the chemical structure of the surfactant than on its ionic character.

Table 6. Reduction in wastewater parameters subjected to H_2O_2/UV oxidation and nanofiltration.

Code of wastewater	Reduction in filtrate parameters, %		
	COD	TOC	Absorbance ($\lambda=525\text{ nm}$)
N-S4 untreated	82	77	98
N-S4 after UV/H_2O_2	78	62	100
C-S5 untreated	75	67	98
C-S5 after UV/H_2O_2	73	65	100

Effect of chemical oxidation on nanofiltration efficiency

Table 6 presents the reduction in wastewater parameters after nanofiltration for wastewater containing products of the condensation of fatty acids subjected to oxidation and not oxidised (filtration pressure 0.7 MPa). Preliminary oxidation caused an increase in the colour reduction to 100%. However, a slight decrease in the TOC and COD reduction was reported during the filtration of the wastewater after preliminary oxidation, which may be due to the fact that during oxidation, chemical compounds were decomposed into smaller particles which could pass through the membrane pores. The location of oxidation products in the membrane pores resulted in the growth of the retention coefficient of dye particles; hence the degree of filtrate colour reduction increased.

Conclusions

It was observed that in certain cases the application of chemical oxidation prior to nanofiltration can significantly enhance the efficiency of nanofiltration, particularly when the wastewater contains big amounts of cationic and non-ionic surfactants. However, it was found that in some cases a disadvantageous effect of the secondary fouling of the membrane may occur, which is probably due to the presence of microfloculants. The best results of the application of preliminary oxidation were obtained for the wastewater containing non-ionic and cationic polysiloxane-based compounds. For this wastewater the process of oxidation by H₂O₂/UV greatly improved filtration efficiency and contributed to a decrease in membrane fouling. The application of preliminary oxidation to wastewater containing anionic surfactants did not improve filtration parameters.

The application of wastewater pretreatment with hydrogen peroxide and UV irradiation prior to nanofiltration contributes to the reduction in fouling, increases membrane efficiency and prolongs its durability. This can lead to a substantial cost reduction in the nanofiltration process, in which the cost of membranes is essential.

Acknowledgments

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