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# Application of Fenton Reaction and Nanofiltration for the Recovery of Process Water

**DOI:** 10.5604/01.3001.0012.7516

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**Abstract**
*In this study, the Fenton process and nanofiltration were used to purify wastewater from dyeing with reactive dyes. Ferrous sulfate doses ranging from 100 to 1000 mg/dm³ and hydrogen peroxide doses ranging from 2.5 to 10 cm³/dm³ were applied. It was found that in the whole range of ferrous sulfate doses, the degree of decolorisation was very high, reaching 97-99%. Consequently the wastewater from the Fenton process was practically completely decolorised. In the case of COD, with increasing doses of ferrous sulfate, the reduction rate initially increased from 25 to 38% and then decreased to 28%. An increase in the hydrogen peroxide dose resulted in an rise in COD reduction to about 50%. It was found that application of the Fenton reaction before the nanofiltration process improved filtration parameters. A clear reduction in the fouling effect of the membrane in the integrated wastewater treatment process was reported as compared to nanofiltration alone.*

**Key words:** *membrane filtration, Fenton process, textile wastewater.*

## Introduction

The textile industry is one of the most water-consuming industries. Despite the fact that the modern textile industry is characterised by lower water consumption, the problem of wastewater production is still an urgent issue.

One of the most effective methods of wastewater treatment is membrane filtration (nanofiltration, reverse osmosis) [1-8]. Membrane techniques are based on the separation processes of substances which form colloidal solutions or colloidal systems, where the difference in physical and chemical properties of the separated substances, such as the particle size difference, partial vapour pressure, chemical affinity, electrical charge and other chemical properties, is used.

Methods for reducing the concentration of pollutants in textile wastewater include oxidation/precipitation in the Fenton process. This is one of the easiest and most economical methods. It consists in a non-selective and highly efficient oxidation of organic compounds by means of hydroxyl radicals produced in the chain process of the decomposition of hydrogen peroxide with the participation of divalent iron salts. The process is a radical reaction during which significant amounts of hydroxyl radicals HO• are generated. Due to the very high oxidation potential of hydroxyl radicals, they are able to decompose organic compounds in the wastewater that are difficult to oxidise and biodegrade. The efficiency of Fenton's reagent depends, among other things, on the pH of the solution and the ratio of reactants involved in the reaction. It was found that an optimum pH of the solution ranged from 2 to 5, while the amount of reactants depended largely on the type of compound and the desired degree of its oxidation. The main advantages of the method are high efficiency of the oxidation reaction, cheap and easily accessible substrates, and easy handling. Constant interest in the Fenton process as a method for the treatment of sewage as well as textile wastewater is evidenced by publications on this subject which are still appearing in large numbers in scientific and technical journals [9-18].

In the Fenton process, the oxidised organic fraction is precipitated as a result of the correction of pH above 10, which unfortunately is related to the necessity of sludge management. On the other hand, there is no danger that oxidation products can block membrane pores because they are precipitated. Banerjee [19] investigated various combinations of Fenton-nanofiltration processes in which oxidation was applied before or after the nanofiltration process. The authors stated that purification was more efficient when the Fenton process was carried out prior to nanofiltration. It required a shorter oxidation time to achieve a dye concentration of less than 1 mg/dm³.

## Materials and methods

In the study, model wastewater from textile dyeing processes with reactive and direct dyes was investigated. The wastewater consisted of two types of dyes: reactive dye [0.1 g/dm³] (*Helactin Red DEBN*, BORUTA-ZACHEM, Poland) and direct dye [0.04 g/dm³] (*Direct Scarlet 4BS*, BORUTA-ZACHEM, Poland]; $Na_2CO_3$ [2 g/dm³], one of the surfactants selected [0.17 g/dm³], and $CH_3COOH$. Two surfactants were used in the experiments: polyammonium-modified polysiloxane-based cationic surfactant (Rucofin TWO/Rudolf GmbH& Co. KG, Germany), and anionic n-hexadecyl and n-octadecyl sodium sulfate salts (Pretepon G/PZCh, Poland).

### Fenton process

The textile wastewater was adjusted to a pH of 3.5 with 5 N sulfuric acid. Next solid ferrous sulfate was added to the wastewater and the solution was stirred until it was completely dissolved. Then 32% hydrogen peroxide solution was added dropwise to the wastewater. After $H_2O_2$ was added, the wastewater was stirred vigorously for 2 minutes and then slowly for another 10 minutes. The solution was allowed to stand for 2, 4 or 24 hours. Subsequently the wastewater was neutralised with 10% NaOH to a pH of about 11. After 2, 4 or 24 hours the purified wastewater was decanted and filtered. In the wastewater samples treated. the values of COD (chemical oxygen demand) and colour were determined.

### Nanofiltration

After pretreatment the wastewater was subjected to nanofiltration on a selected membrane. A DK membrane (GE Os-

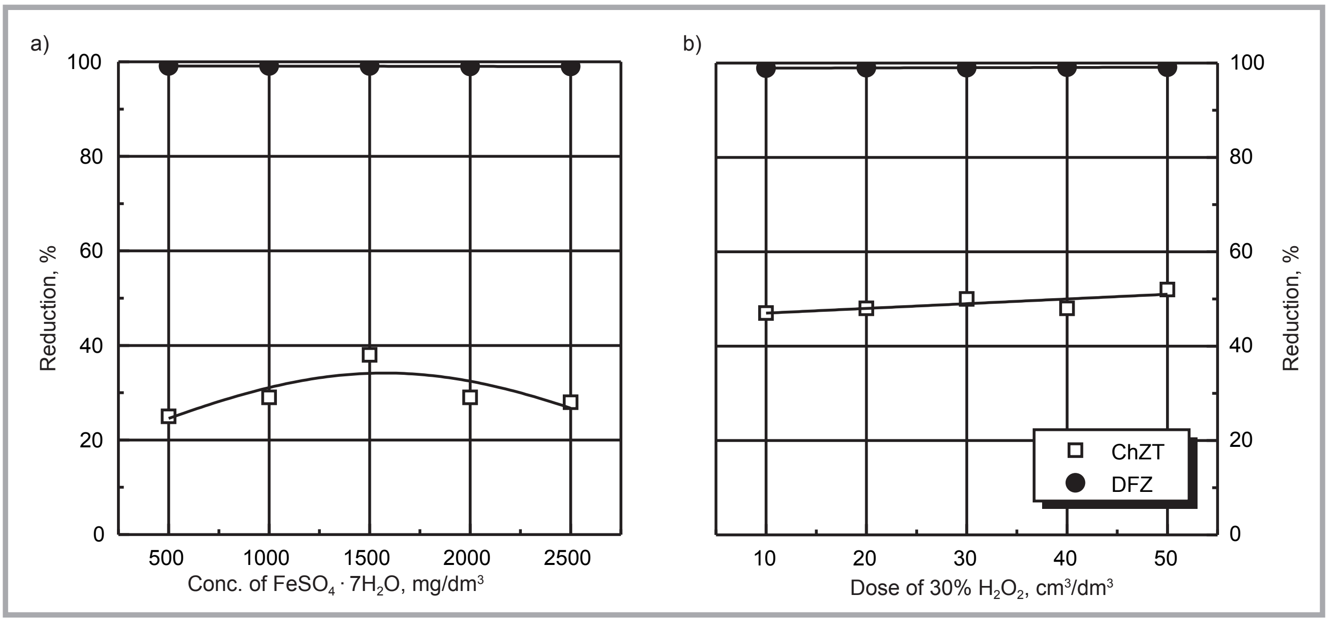


***Figure 1.*** *Changes in degrees of colour reduction and COD in wastewater from dyeing with reactive and direct dyes in dependence on: a) ferrous sulfate dose (dose of $H_2O_2$ = 30 cm³/dm³) and b) hydrogen peroxide dose (ferrous sulfate dose = 1500 mg dm³).*

monics) was used for the tests. Its parameters are given in ***Table 1***. Filtration was carried out by the cross-flow method at a constant flow rate of 2 dm³/min in the system (controlled by rotameter) at 40 °C. The tests were performed at a pressure of 1.5 MPa.

The efficiency of the treatment processes was assessed on the basis of the process rate as well as parameters of the purified wastewater:
– chemical oxygen demand COD; mg $O_2$/dm³;
– total organic carbon TOC; mg C/dm³];
– absorbance (λ = 525 nm).

The chemical oxygen demand and total organic carbon were analysed using HACH LANGE cuvette tests. Cuvette tests were conducted at 100 °C or 148 °C in an LT 200 HACH LANGE oven. The measurement of COD and TOC was based on the change in colour of the heated samples using a DR 2800 HACH LANGE spectrometer. In the case of wastewater samples that may contain residual hydrogen peroxide, which can affect COD and TOC measurements, trace amounts of catalase were added to the samples. The catalase enabled rapid $H_2O_2$ decomposition and had little effect on the COD and TOC parameters.

The spectral absorption coefficient was measured using a Medson UV-VIS JASCO V-630 spectrophotometer.

Conductivity and pH measurements of the wastewater were made using a Mettler Toledo S47-K SevenMulti pH/conductivity meter. The pH measurements were made using an InLab®RoutinePro electrode, while an InLab®731 electrode was used to measure the conductivity of the electrolyte.

## Results

### Wastewater treatment using the Fenton process

Preliminary studies on the optimisation of wastewater from the dyeing of cellulose fibres with reactive and direct dyes by the Fenton process were performed on model wastewater containing an anionic surfactant. Studies on the model wastewater guarantee a known, constant composition of wastewater, which is essential for optimisation studies.

The study began with determination of the effect of the ferrous sulfate dose on treatment efficiency. The doses of ferrous sulfate used in the study ranged from 500 to 2500 mg/dm³ at a constant dose of hydrogen peroxide of 30 cm³/dm³. The changes in the reduction of colour (as measured by the absorbance at λ = 525 nm) and COD obtained are shown in ***Figure 1.a***. Next the impact of hydrogen peroxide on the efficiency of the Fenton process was determined. The doses of hydrogen peroxide ranged from 10 to 50 cm³/dm³ at a constant ferrous sulfate dose equal to 1500 mg/dm³. ***Figure 1.b*** shows changes in the degrees of colour reduction (measured by the absorbance at λ = 525 nm) and COD.

***Table 1.*** *Parameters of the DK nanofiltration membrane.*

| Membrane type | Polymer | Rejection, % ($MgSO_4$) | pH range | Typical flux/psi | Producer |
|---|---|---|---|---|---|
| DK | TF (polisulphone) | 98 | 2-11 | 22/100 | GE Osmonics |

***Table 2.*** *Degrees of COD reduction in the model wastewater after the Fenton process in dependence on the dose of $FeSO_4 \cdot 7H_2O$ and volume of $H_2O_2$ added.*

| No. | $FeSO_4 \cdot 7H_2O$ dose, mg/dm³ | Volume of $H_2O_2$, cm³/dm³ | | | |
|---|---|---|---|---|---|
| | | 2.5 | 5.0 | 7.5 | 10.0 |
| | 1 | 2 | 3 | 4 | 5 |
| 1 | 100 | 54 | 41.3 | 31.7 | 53.2 |
| 2 | 250 | 55.5 | 53 | 39.6 | 59.0 |
| 3 | 500 | 58 | 52 | 38.5 | 59.2 |
| 4 | 750 | 55.5 | 52.4 | 36.8 | 61.2 |
| 5 | 1000 | 57 | 50 | 39.1 | 61.2 |

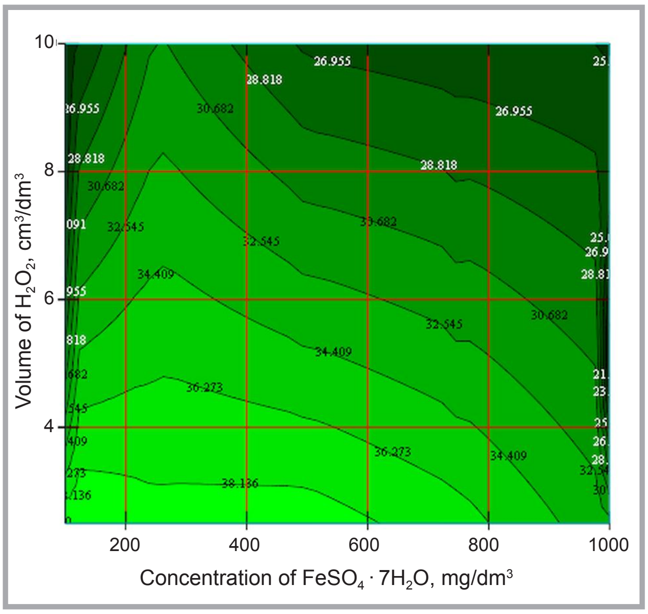


***Figure 2.** Contour plot of the dependence of COD reduction during oxidation on the concentration of $FeSO_4 \cdot 7H_2O$ and $H_2O_2$.*

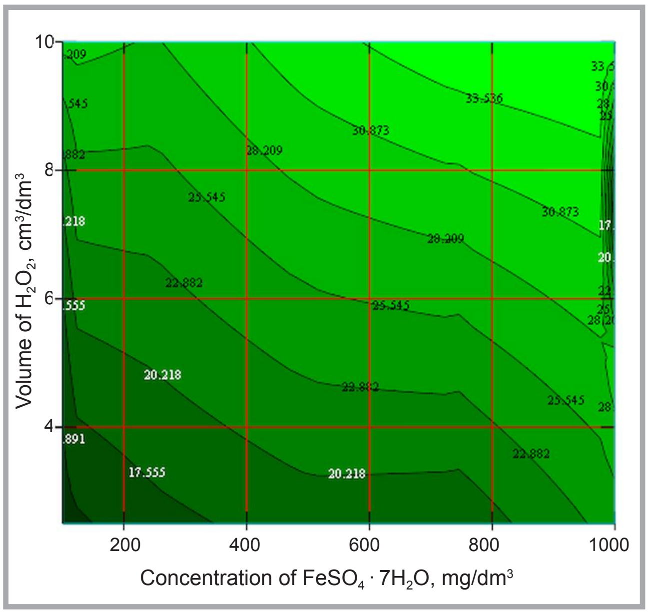


***Figure 3.** Contour plot of the dependence of COD reduction during coagulation on the concentration of $FeSO_4 \cdot 7H_2O$ and $H_2O_2$.*

It was found that in the whole range of ferrous sulfate doses, the degree of decolorisation was very high, reaching 97-99%. As a consequence, the wastewater from the Fenton process was practically completely decolorised. In the case of COD, with increasing doses of ferrous sulfate, the reduction rate initially increased from 25 to 38% and then decreased to 28%. By increasing the dose of hydrogen peroxide, COD reduction rose to about 50%.

In the next series of experiments, tests were conducted on the Fenton process using lower doses of ferrous sulfate and hydrogen peroxide. Doses of ferrous sulfate ranged from 100 to 1000 $mg/dm^3$ and hydrogen peroxide from 2.5 to 10 $cm^3/dm^3$. ***Table 2*** shows the degree of COD reduction in dependence on the doses of reactants applied.

The highest COD reduction, amounting to 54-58% and 53-61%, in dependence on the ferrous sulfate dose, was obtained at the lowest (2.5 $cm^3/dm^3$) and highest (10 $cm^3/dm^3$) dose of hydrogen peroxide, respectively.

Taking into account the technological and economic benefits of minimising the dosage of reactants, it was assumed that the optimal doses were $FeSO_4 \cdot 7H_2O$ – 500 $mg/dm^3$ and $H_2O_2$ – 2.5 $cm^3/dm^3$.

Besides oxidation, coagulation also occurs in the Fenton process. Alkalisation of the wastewater after oxidation leads to the precipitation of sludge which adsorbs organic compounds that have not oxidised and products of their decomposition which have not mineralised. Simultaneously iron salts used in the oxidation are removed from the wastewater. As a consequence, data on the share of individual processes (oxidation, coagulation) in the total COD reduction levels have technological importance for the total reduction of pollutants expressed by COD.

Therefore further studies were conducted to determine the contribution of oxidation and coagulation processes to wastewater treatment. The total COD reduction in wastewater after oxidation and coagulation as well as the COD reduction achieved exclusively in oxidation processes and only in coagulation processes were determined in the study. For this purpose, the value of COD was determined in:
- the initial wastewater;
- wastewater after oxidation and alkalisation processes, including the sludge formed;
- wastewater after oxidation and alkalisation after sludge removal.

The calculated difference between the COD of the initial wastewater and that of the wastewater after the oxidation and alkalization processes containing sludge corresponds to the COD of that part of pollutants that have been oxidised. The calculated difference between the COD of the wastewater after the oxidation and alkalization processes containing sludge and that of the wastewater after oxidation and alkalisation after removal of the sludge corresponds to the COD of that part of pollutants which, as a result of the coagulation process, have passed to the sludge. Based on the COD determined in this way, the degree of pollutant reduction for the oxidation and coagulation steps can be calculated.

Studies on the oxidation step were conducted for the Fenton process at $FeSO_4 \cdot 7H_2O$ doses ranging from 100 to 1000 $mg/dm^3$ and hydrogen peroxide doses ranging from 2.5 to 10 $cm^3/dm^3$. ***Figure 2*** shows a contour plot illustrating the dependence of the COD reduction stages during the oxidation step on the concentration of $FeSO_4 \cdot 7H_2O$ and the volume of $H_2O_2$ added. It was found that the oxidation process was most efficient for low doses of $FeSO_4 \cdot 7H_2O$ in the range of 100 to 500 $mg/dm^3$ with the volume of $H_2O_2$ being 2.5 $cm^3/dm^3$ (light green field in ***Figure 2***). The highest COD reduction achieved in the oxidation step was 38%. With an increase in the $FeSO_4 \cdot 7H_2O$ dose and volume of $H_2O_2$ added, a gradual decrease in COD reduction was observed (dark green field in ***Figure 2***).

For the same wastewater with the same treatment parameters, research was conducted on the coagulation step. ***Figure 3***

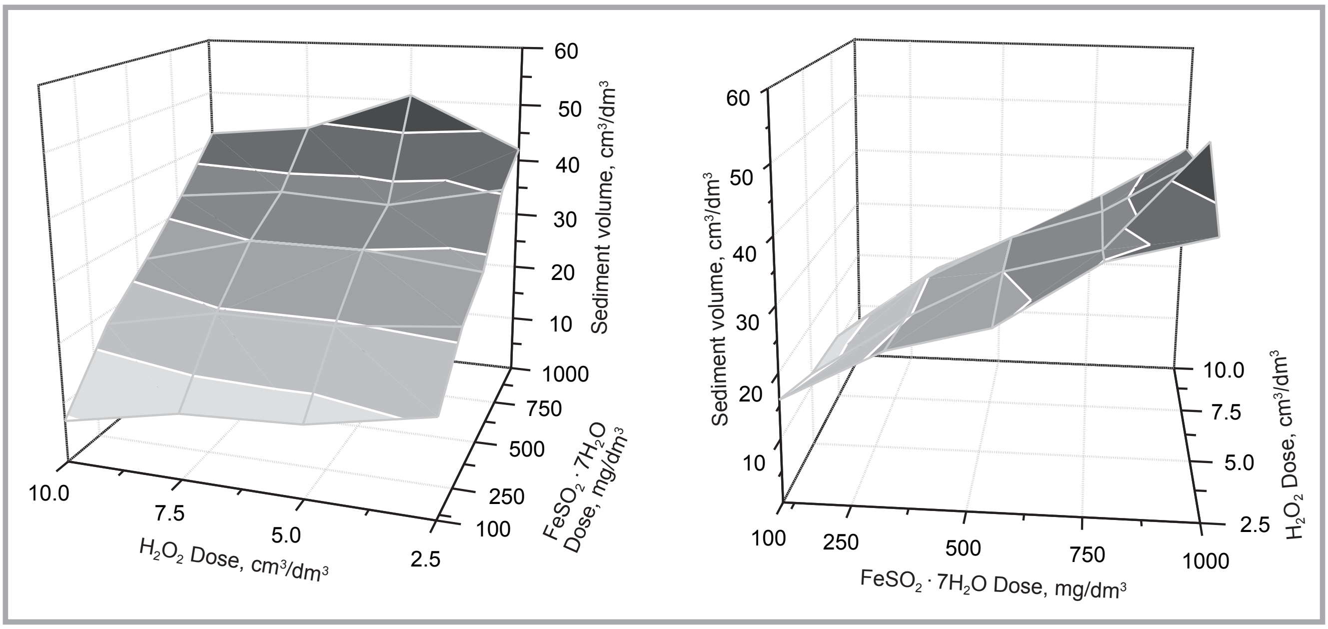


***Figure 4.*** *Dependence of the volume of sludge formed during the Fenton reaction on the concentration of $FeSO_4 \cdot 7H_2O$ and volume of $H_2O_2$.*

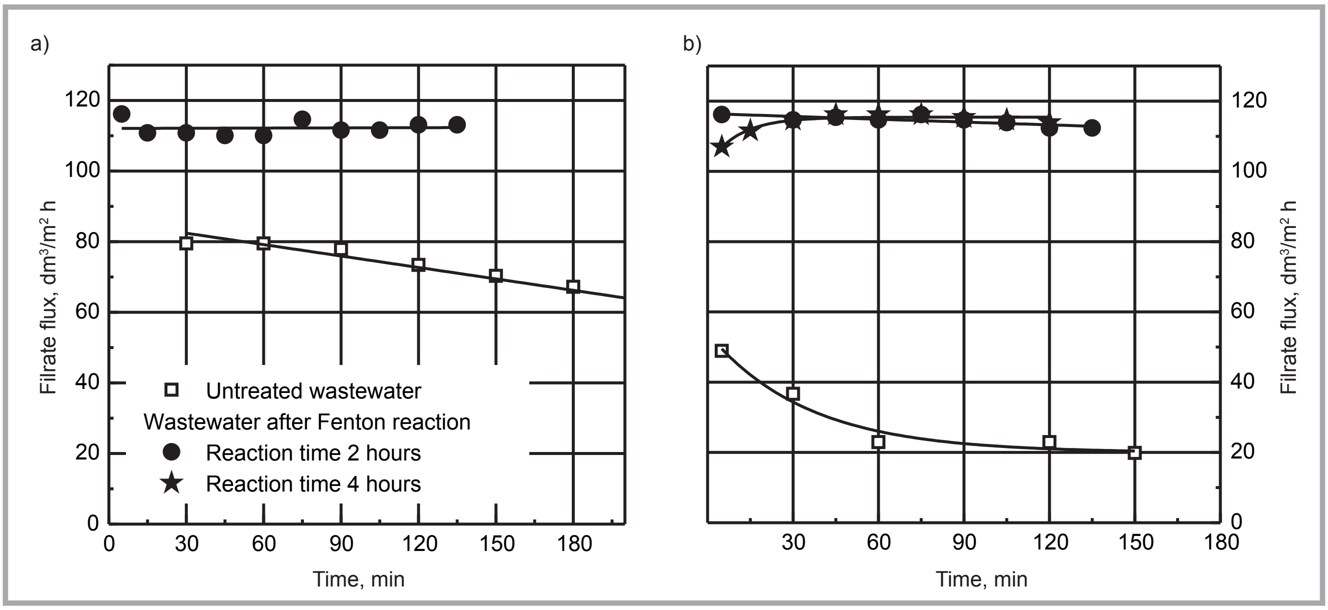


***Figure 5.*** *Dependence of filtrate flow rate on nanofiltration time for model wastewater containing anionic surfactant (graph A) and cationic surfactant (graph B) after Fenton process ($FeSO_4 \cdot 7H_2O$ dose 500 mg/dm³, amount of $H_2O_2$ 2.5 cm³/dm³); oxidation time 2 and 4 hours; DK membrane, pressure 15 bar.*

shows a contour plot illustrating the dependence of COD reduction during the coagulation step on the concentration of $FeSO_4 \cdot 7H_2O$ and volume of $H_2O_2$ added. In the case of coagulation, the efficiency of COD reduction increased as the concentration of the reactants increased. The highest COD reduction, amounting to 61%, was achieved at a dose of $FeSO_4$ $7H_2O \cdot$ equal to 1000 mg/dm³ and $H_2O_2$ volume of 10 cm³/dm³.

By analysing the relationships shown in ***Figures 2*** and ***3***, it can be concluded that the products of oxidation of organic pollutants are difficult to remove in coagulation processes. In the case of low doses of $H_2O_2$ and $FeSO_4 \cdot 7H_2O$, oxidation processes are primarily responsible for the removal of pollutants, while at higher doses of reactants they account for coagulation processes.

In the case of coagulation, the amount and characteristics of the resulting sludge are a very important factor to consider when designing a wastewater treatment plant. ***Figure 4*** shows the dependence of the volume of sludge formed at the coagulation step on the dose of $FeSO_4 \cdot 7H_2O$ and volume of $H_2O_2$ added. It was found that the concentration of iron salt was the main factor influencing the amount of sludge produced. The volume of $H_2O_2$ added is of minor importance, although a decreasing tendency of sludge volume can be observed with an increase in the volume of $H_2O_2$ at a low dose of $FeSO_4 \cdot 7H_2O$.

**Effect of the Fenton reaction as a preliminary step on the nanofiltration process**

***Figure 5*** shows the dependence of the filtrate flow rate on time for model

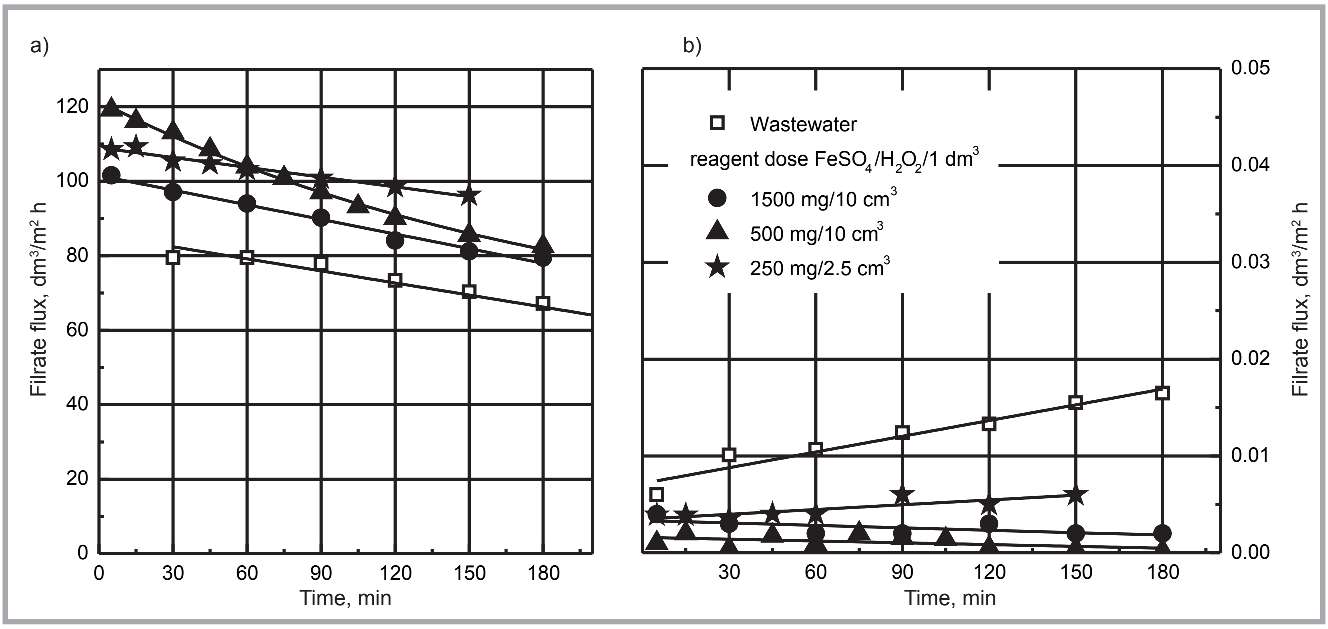


***Figure 6.*** *Dependence of filtrate flow rate on nanofiltration time for wastewater after Fenton treatment at different doses of reactants.*

wastewater containing anionic surfactant (SPC) (***Figure 5.a***) and cationic SPC (***Figure 5.b***). For the wastewater tested, a significant increase in the filtrate flow rate and a nearly complete reduction in fouling was observed. Curves representing the dependence of the filtrate flow rate on time have a practically horizontal course, which proves that the membrane is not fouled. Based on ***Figure 5***, it can be concluded that in the case of the Fenton process, the structure and ionic nature of compounds present in the wastewater are not significant. This is due to the fact that oxidised compounds and oxidation products are precipitated after alkalisation of the wastewater. This is an important advantage of this method. In the case of oxidation with UV/$H_2O_2$, the oxidation products remain in the wastewater and can affect the membrane filtration parameters [20].

***Figure 6*** shows the dependence of the filtrate flow rate on time for the wastewater subjected to pretreatment with Fenton's reagent at different doses of reactants. Tests were performed for $FeSO_4 \cdot 7H_2O$ doses from 250 to 1500 mg/dm$^3$. Two doses of $H_2O_2$ were used: 2.5 and 10 cm$^3$/dm$^3$ (corresponding to molar concentrations of 0.0817 and 0.3270 mol/dm$^3$, respectively). Oxidation with Fenton's reagent and sedimentation after the addition of NaOH was carried out for 24 hours. Prior to nanofiltration the wastewater was passed through a non-woven filter K. The nanofiltration process was carried out on a DK membrane at a pressure of 15 bar. Regardless of the amount of reagent dose used, the efficiency of the nanofiltration process was improved (***Figure 6.a***) and the filtrate absorbance reduced (***Figure 6.b***). The process was fastest at the lowest doses of $FeSO_4 \cdot 7H_2O$ and $H_2O_2$. At a dose of $FeSO_4 \cdot 7H_2O$ equal to 500 mg/dm$^3$ and an amount of $H_2O_2$ equal to 10 cm$^3$, a significant increase in the filtrate flow was achieved in the first step, but it gradually decreased due to the secondary fouling of the membrane.

***Table 3.*** *Reduction in COD, TOC and colour of wastewater after pretreatment with Fenton's reagent and nanofiltration at various doses of reactants; DK membrane, pressure 15 bar.*

| Doses of reactants per 1 dm$^3$ of wastewater | Reduction in parameters during nanofiltration, % | | |
|---|---|---|---|
| | COD | TOC | Absorbance (λ = 525 nm) |
| Untreated wastewater | 87.3 | 82.4 | 99.5 |
| Dose of $FeSO_4 \cdot 7H_2O$ 1500 mg<br>Dose of $H_2O_2$ 10 cm$^3$ | 79.7 | 72.48 | 99.9 |
| Dose of $FeSO_4 \cdot 7H_2O$ 500 mg<br>Dose of $H_2O_2$ 10 cm$^3$ | 78.7 | 70.0 | 99.9 |
| Dose of $FeSO_4 \cdot 7H_2O$ 250 mg<br>Dose of $H_2O_2$ 2.5 cm$^3$ | 66.7 | 62.9 | 99.9 |

***Table 3*** shows the COD, TOC and colour reduction degrees after complex Fenton treatment and nanofiltration. Regardless of the dosage of reactants, the wastewater showed lower absorbance and higher COD and TOC degrees than that without pretreatment. A decrease in COD and TOC reduction with a simultaneous increase in colour reduction may indicate that the products of pollutant oxidation pass through the membrane to the filtrates. The lowest COD and TOC reduction was achieved at the lowest doses of $FeSO_4 \cdot 7H_2O$ and $H_2O_2$. It was observed that oxidation products of low molecular weight were not precipitated. This may be the reason for deterioration of the parameters of the filtrates obtained after nanofiltration preceded by pretreatment with the Fenton method.

## Conclusions

The Fenton process proved to be an effective method of reducing colour and COD. The doses of ferrous sulfate applied in the range of 100 to 1000 mg/dm$^3$ and hydrogen peroxide doses in the range from 2.5 to 10 cm$^3$/dm$^3$ led to a colour reduction of 97-99%. In consequence, the wastewater after the Fenton process was practically completely discoloured. In the case of COD, with increasing doses of ferrous sulfate, the reduction rate initially increased from 25 to 38% and then decreased to 28%. By increasing the dose of hydrogen peroxide, the COD reduction was increased to about 50%. It was found that the application of the Fenton process prior to nanofiltration improved the filtration parameters. There was a clear reduction in the fouling effect of the membrane in the integrated wastewater treatment process as compared to nanofiltration alone.

## Acknowledgements

*The study was financed by the Polish National Centre for Research and Development, Project no. N R14 0038 06.*

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***Received 05.12.2017 Reviewed 06.12.2018***