# Integration of advanced oxidation process with nanofiltration for dairy effluent treatment

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The paper presents the research results on the possibility of the integration of advanced oxidation process (AOP) involving Fenton reaction with nanofiltration (NF) for dairy effluent treatment. It has been found that Fenton oxidation reduces organic compounds, total phosphorus and total nitrogen. However, NF enables high ions retention derived from both effluent and Fenton oxidation components. As a result, it was possible to obtain water, which, without any harmful effects, could be discharged into environment. This water also fulfilled most of the requirements to be reused in dairy industrial plant.

**Keywords:** Advanced Oxidation Process, Dairy Effluent Treatment, Fenton Reaction, Nanofiltration

## Introduction

Among the food industries, the dairy industry is a leading one in the production of huge amounts of polluted effluents [1]. Dairy effluents are characterized by high levels of pollutants such as soluble organic compounds, fats, proteins, and carbohydrates that contribute to high BOD and COD contents [2]. The parameters of pollutants in dairy effluents vary significantly within 24 hours and highly depend on the type of production, raw materials used, and the process of plant washing [3]. Dairy effluents discharged into water bodies contribute to a significant reduction of dissolved oxygen, which affect the aquatic ecosystem.

Due to the emerged problems with the thorough elimination of pollutants and large amounts of effluents generated in dairies, the effective methods of purification and reduction of pollutants in these effluents have been increasingly sought. The preferential solution for dairy effluents utilization are biological methods. However, there are limitations in maintaining optimal pH of the processes, and high content of organic matters may overload treatment and contribute to the sludge swelling [4]. Dairy effluents also contain volatile fatty acids, which may be removed in the processes of advanced oxidation. According to one study [5], there is a possibility of AOP applied as a post-treatment of membrane filtration, which is not very favourable, since AOP generate secondary pollutants e.g. iron compounds. Other additional treatment methods would generate further operating costs.

In this study, Fenton reaction, as one of the advanced oxidation processes (AOP) was investigated in order to oxidize organic compounds in dairy effluents. This process involves free hydroxyl radicals HO•, which enable effective oxidation of pollutants in effluents [6]. However, secondary pollutants derived from AOP might be completely removed in the process of nanofiltration (NF), which allows the removal of substances (organic compounds, mono- and multivalent ions) up to 99.99%. The integration of chemical oxidation and membrane filtration might provide the possibility of complex removal of organic and inorganic components from dairy effluents.

The aim of this work was to investigate the possibility of using AOP with Fenton reagents as a pre-treatment step for dairy effluent prior to nanofiltration.

## Methods

The material to be tested was a mixture of raw dairy effluents from different production processes (Table 1).

The analytical measurements involved the raw and the dairy effluent pre-treated with AOP (supernatant), and the permeate and retentate after nanofiltration. Physical quality parameters such as total nitrogen (TN), ammonium nitrogen (N-NH4), total phosphorus (TP), chemical oxygen demand (COD), sulphate, total iron and volatile fatty acids (VFAs) were measured in the samples using HACH cuvette tests with UV-VIS DR6000 spectrophotometer. The turbidity (HACH turbidimeter), dry residue (Radwag's moisture), pH (Mettler Toledo) were analysed according to standard methods. The concentrations of ions such as calcium, sodium, potassium, chloride and nitrate were determined with standard curves based on the electric potentials measured with ion selective electrodes (Mettler Toledo).

Table. 1. Composition of the dairy effluent used in the experiments

| Parameter | Value |
|---|---|
| pH | 7.76 |
| Turbidity (FNU) | 1128 |
| Conductivity ($\mu S \cdot cm^{-1}$) | 2030 |
| Dry residue ($mg \cdot dm^{-3}$) | 3800 |
| COD ($mg \cdot dm^{-3}$) | 4750 |
| TN ($mg \cdot dm^{-3}$) | 76.4 |
| N-$NH_4$ ($mg \cdot dm^{-3}$) | 15.5 |
| TP ($mg \cdot dm^{-3}$) | 26.4 |
| Calcium ($mg \cdot dm^{-3}$) | 251 |
| Sulphate ($mg \cdot dm^{-3}$) | 390 |
| Potassium ($mg \cdot dm^{-3}$) | 91 |
| Nitrate ($mg \cdot dm^{-3}$) | 2.4 |
| Chloride ($mg \cdot dm^{-3}$) | 95 |
| Sodium ($mg \cdot dm^{-3}$) | 933 |
| VFAs ($mg \cdot dm^{-3}$) | 424 |

### Fenton Oxidation

Advanced oxidation process (AOP) was carried out in two 5 $dm^3$ standard chemical reactors equipped with magnetic stirrers. Fenton reagents ($FeSO_4 \cdot 7H_2O$ and 30% hydrogen peroxide solution $H_2O_2$ were used to carry out the Fenton oxidation in the following concentrations 1.5g $Fe^{2+} \cdot dm^{-3}$ and 0.75g $H_2O_2 \cdot dm^{-3}$, selected based on the literature data [7]. Prior to reaction, raw effluent was adjusted to 3.5 pH with 1 M HCl. After $FeSO_4$ and $H_2O_2$ had been introduced, the phase of rapid stirring have been carried out for 5 minutes. The slower stirring procedure had been conducted for 15 minutes and pH was adjusted to 7.5 with 0.5 M NaOH to precipitate iron ions. After sedimentation, pre-treated effluent (supernatant) was subjected to nanofiltration (NF). The stages of AOP were presented in Fig. 1.

### Nanofiltration

The nanofiltration was carried out using laboratory scale set-up with detailed description given in the work [8]. The

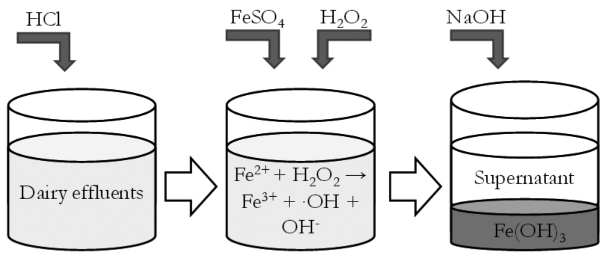


Figure 1. Stages of dairy effluents pre-treatment with Fenton oxidation

Table. 2. Characteristic of nanofiltration membrane used in the experiments

| Surface material | Polyamide |
|---|---|
| $MgSO_4$ retention (%) | 99 |
| NaCl retention (%) | 80-90 |
| Cut-off (Da) | ~150 |
| pH range | 2-11 |
| Maximum temperature (°C) | 45 |

permeate was collected in a separate tank and retentate was recycled to the feed tank. The NF process was performed under transmembrane pressure equal to 14 bar. The retentate flow rate was 0.23 $m^3/h$. During the membrane process, the temperature in the feed tank was constant and equal to 25±1°C.

The commercial nanofiltration flat sheet membrane (designation: TS80) with an active area of 0.0140 $m^2$ provided by TriSep was used in the experiments. The characteristics of nanofiltration membrane to be tested were presented in Table 2.

The efficiencies of the processes of Fenton oxidation and NF of dairy effluent were assessed based on the retention coefficient/percentage reduction of pollutant degradation (R, %):

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

$C_P$ – concentration of the component in purified liquid, mg/$dm^3$; $C_F$ – initial concentration of component in effluent/ retentate, mg/$dm^3$.

The efficiency of the membrane processes of dairy effluent were determined with permeate flux ($J_P$, $dm^3/(m^2h)$ and Volume Reduction Factor (VRF):

$$J_P = \frac{V_P}{A \cdot t} \qquad (2)$$

where: $V_P$ – permeate volume, $dm^3$; A – membrane area, $m^2$; t - time needed to receive a defined volume of permeate, h.

$$VRF = \frac{V_F}{V_R} \qquad (3)$$

where: *VRF* – volume reduction factor [-], $V_F$ – volume of feed [$dm^3$], $V_R$ – volume of retentate after defined permeate receiving time [$dm^3$].

## Results and discussion

### Efficiency of Fenton oxidation in the pre-treatment of dairy effluents

Oxidation with Fenton reagents resulted in the reduction of COD as well as nutrients such as TP and TN. As a result of Fenton reaction the COD was reduced by 76%, and TP and TN were reduced by 98% and 63%, respectively. A slightly lower decrease in ammonium nitrogen content was observed, which was 29%. A great decline of turbidity was also observed, which amounted to 58%. Fenton's reagent was found to be very effective in eliminating bacteria from effluent. Microbiological tests confirmed bacterial absence in the supernatant. This was due to the changes in pH during the process of advanced oxidation, which affected the microbial environment. Preliminary pH reduction of the medium using HCl to 3.5 and the high reactivity of toxic hydroxyl radicals produced during the Fenton reaction caused the death of bacterial microorganisms. The pH adjusted during the Fenton reaction, both with HCl and NaOH solutions, contributed to an increase in chloride and sodium ions in the supernatant. However, $FeSO_4$ contributed to an increase in the concentrations of iron and sulphate ions. The increase in the dry residue was also observed compared to the initial value of raw effluent. It was due to the precipitation of iron hydroxide resulting from the reaction. In order to decrease the concentrations of remaining ions such as $SO_4^{2-}$, $Na^+$ and $Fe^{3+}$, which significantly exceeded limits for the discharge of effluents into water and soil (Table 3), it was necessary to use the NF process that enables effective removal of these ions [9].

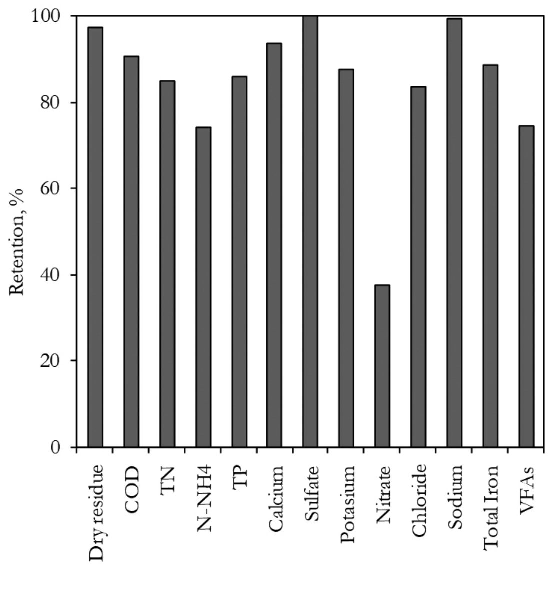


Figure 2. Retention of dairy effluent components in NF of dairy effluents pre-treated with AOP

### The effects of Fenton reaction on the efficiency of nanofiltration

Dairy effluent pre-treated by Fenton reaction was subjected to nanofiltration (Fig. 2). NF membrane retained efficiently multivalent sulphates and ferrous ions. The decrease was also observed in the concentration of chloride ions in 83%, and sodium ions in 99%. High retention of COD, N-$NH_4$, TN and TP and VFAs was also obtained. (Fig. 2).

The selected parameters in the water obtained as a result of NF, were compared to the limits forced by Regulation of the Minister of Environment of 18 November 2014 regarding the discharge of effluents into environment, Warsaw, 16 December 2014*, and to The Drinking Water Directive (DWD) – Council Directive 98/83/EC** (Table 3). All of the parameters tested for discharge into environment were fulfilled signifying the treated water is not harmful to the surface water or soil. Some of the parameters was also met for drinking water quality.

As a result of NF of dairy effluent pre-treated by Fenton's reaction, the permeate flux ($J_P$) decreased by 38% during the twofold reduction in an initial effluent volume (Fig. 3).

The decrease in permeate flux was mainly due to the deposition of the thin layer of precipitated $Fe(OH)_3$ on the NF membrane surface (Fig. 4).

In order to reduce the deposition of the filter cake, it is necessary to select appropriate process parameters that will enable the efficient treatment of effluent in the NF process. Thus, it will be necessary to investigate the effects of process pressure and shear flow on the efficiency of nanofiltration

Table. 3. Physico-chemical properties of the water obtained in the NF of dairy effluent pre-treated with Fenton oxidation

| Parameter | AOP Supernatant | NF Permeate | Limits * | Limits ** |
|---|---|---|---|---|
| pH | 7.41 | 6.76 | 6.5-9.0 | 6.5-9.5 |
| COD ($mg \cdot dm^{-3}$) | 1147 | 110 | 125 | 5 |
| TN ($mg \cdot dm^{-3}$) | 28.2 | 4.3 | 30 | - |
| N-$NH_4$ ($mg \cdot dm^{-3}$) | 11.0 | 2.9 | 10 | 0.5 |
| TP ($mg \cdot dm^{-3}$) | 0.605 | 0.083 | 2 | - |
| Sulphate ($mg \cdot dm^{-3}$) | 2030 | 6.8 | 500 | 250 |
| Potassium ($mg \cdot dm^{-3}$) | 91.0 | 11.4 | 80 | - |
| Chloride ($mg \cdot dm^{-3}$) | 837 | 140 | 1000 | 250 |
| Sodium ($mg \cdot dm^{-3}$) | 8511 | 70.8 | 800 | 200 |
| Total Iron ($mg \cdot dm^{-3}$) | 15.0 | 1.8 | 10 | - |

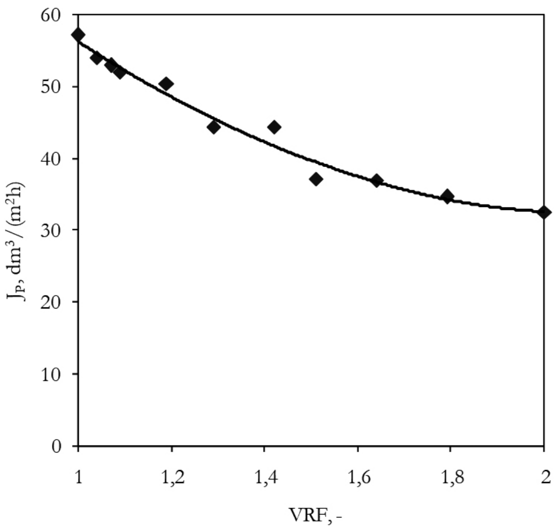


Figure 3. Permeate flux (JP) vs. Volume Reduction Factor (VRF) of nanofiltration of dairy effluents pretreated by Fenton reaction

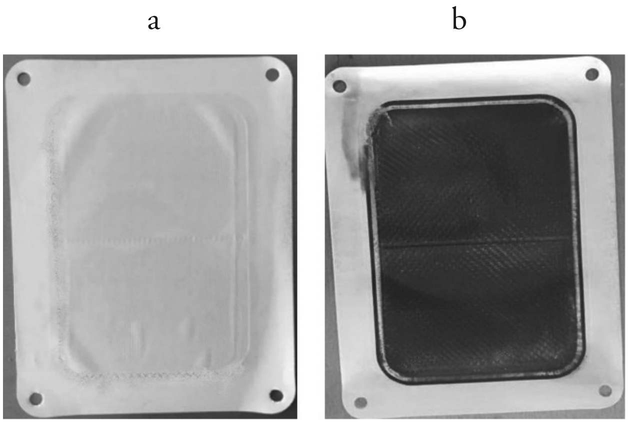


Figure 4. Membrane surface before (a) and after (b) nanofiltration of pre-treated dairy effluents by advanced oxidation using Fenton reagents

of pre-treated dairy effluents by advanced oxidation process. The selection of back flush frequencies and the development of the NF membrane cleaning procedure should be also taken into consideration.

## Conclusion

Based on the results, it was found that the integration of two treatment methods such as Fenton reaction and NF is efficient for dairy effluents treatment. The obtained water might be discharged into environment successfully. Some of parameters also met the law regulations for drinking water. However, during the NF process, a decrease in the effluent treatment efficiency was observed, due to the deposition of the filter cake on the surface of the membrane. Therefore, it is necessary to carry out research that allows the selection of process parameters that will improve the efficiency of nanofiltration of pre-treated dairy effluents in the AOP.

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