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# INTEGRATION OF NANOFILTRATION AND BIOLOGICAL PROCESSES FOR TEXTILE WASTEWATER TREATMENT

The implementation of the biological anaerobic–aerobic system in separated reactors to the nanofiltration concentrate treatment was presented. The concentrate was obtained during the nanofiltration of the textile wastewater containing azo dye Reactive Red 120. The experiments were conducted on the wastewater concentrated from 2 to 10 times. The concentration factors had no significant influence either on the decolourization of the azo dye in the anaerobic reactor or on the orthanilic acid degradation in the aerobic one. However, the higher the concentration factor was achieved, the more products of the dye decolourization were formed and the higher COD values in the outflow of the system were observed.

## 1. INTRODUCTION

Textile industry is known for using large quantities of water and a large spectrum of chemicals, both organic and inorganic ones [10]. Furthermore, high-quality water is a crucial factor in many processes such as cleaning, rinsing, dyeing and washing [3]. Since the closing of water cycle is highly recommended, environmentally sustainable development in textile industry should be stimulated [2]. This can be done by the application of membrane processes, especially by nanofiltration and reverse osmosis, which enable the process water reuse, thus reducing freshwater consumption [3]. QIN et al. [10] concluded that nanofiltration allowed us to recover 70% of water from effluents whose quality could meet requirements of the dyeing process. However, the remaining concentrate poses a serious problem due to high concentration of dye and other chemicals. Different chemical, physical and biological methods can be applied to remove dyes from wastewater, but there is a limited knowledge about the dye con-

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centrate treatment. The biological methods are generally considered as environmentally friendly. Furthermore, they can lead to a complete mineralization of organic pollutants at relatively low costs [9]. It is known that the conventional aerobic processes used in the municipal wastewater treatment plants are insufficient for the dye degradation, especially in the case of the azo dyes, which represent the largest colorant class and are most commonly used in textile industry [4]. However, the azo bonds can be biodegraded under anaerobic conditions in the presence of the external electron donors [6]. The anaerobic azo reduction can be carried out by three main mechanisms: direct enzymatic, indirect enzymatic with redox mediators and strictly chemical [9], which lead to the formation of aromatic amines. The latter cannot be degraded further under anaerobic conditions [6], [7]. Nevertheless, aromatic amines can be degraded under aerobic conditions [8]. Total biodegradation of the azo dyes generally requires a combination of two stages: the anaerobic reduction of azo bond and the aerobic degradation of the aromatic amines formed.

Anoxic biological degradation of azo dyes was applied by ŻYŁŁA et al. [11] to utilize the nanofiltration concentrate. A successful anaerobic treatment application in the colour removal from NF concentrate was reported by GOMES et al. [5], who used the upflow anaerobic sludge blanket bioreactor.

The goal of this paper was to present the implementation of the anaerobic–aerobic system in the separated reactors (two-sludge system) in the nanofiltration concentrate treatment, focusing on the finding of the optimal concentration factor. The experiment was focused not only on the decolourization of the concentrate, but also on the aromatic amine degradation and COD reduction.

## 2. MATERIALS AND METHODS

The material tested was real textile wastewater. This wastewater was obtained from dyeing (followed by washing and rinsing) a knitted cotton fabric with a reactive dye C.I. Reactive Red 120 (RR 120, Color Index) in the Pyrotec S laboratory dyeing machine (Roaches, UK), according to the procedures recommended for this dye. The textile wastewater was then subjected to nanofiltration and, consequently, the concentrate was obtained.

The experimental set-up for nanofiltration was described previously by ŻYŁŁA et al. [11]. The experiments with the post-filtration concentrate biodegradation were conducted in the sequential anaerobic–aerobic two-sludge system. The system consisted of two reactors and a transition tank. One reaction (working volume of 0.4 $dm^3$) was operating under anaerobic conditions, whereas the other one (working volume of 0.8 $dm^3$) was operating under aerobic conditions. Both reactors were working at the ambient air temperature (20–25 °C). The peristaltic pumps (Vertex, PPO1 type) and the digital timers (Metron, PCg.O3 type) enabled filling and drawing both re-

actors and the transition tank. The bioreactor was aerated by an air pump through a rotameter. A gas distributor was placed on the bottom of the reactor (aeration rate of 0.8 vvm). The suspensions in both reactors were stirred by a propeller (IKA, Eurostar Digital type; mixing speed: anaerobic reactor, 100 rpm; aerobic reactor, 170 rpm).

Nanofiltration was carried out with DL OSMONICS membrane under the pressure of 1.5 MPa and at the temperature of 31–46 °C. The flow rate was constant – ca. 2 $dm^3$/min. The concentrate stream flowed back to the feed vessel, while the permeate stream was collected separately. The process was conducted until the necessary concentration factors were obtained. The concentration factors were changed in the range of 2–10.

The aerobic reactor was inoculated with 400 $cm^3$ of the surplus activated sludge (SAS), while the anaerobic one was inoculated with 200 $cm^3$ of the fermented sludge (FS) taken from the methane fermentation tank of the municipal wastewater treatment plant (WWTP) in Łódź (Poland). At the beginning, the bioreactor system was working in a 24 hour cycle: 60 min of sedimentation, 20 min of drawing (10 $cm^3 \cdot min^{-1}$), 20 min of filling (10 $cm^3 \cdot min^{-1}$), 22 h 20 min of reaction (aerobic reactor – aeration and mixing; anaerobic reactor – only mixing). For the concentration factors above 2, the cycle length was changed to 72 or 96 hours, depending on the colour of the effluent.

During the first week of operation, synthetic wastewater of the following composition ($g \cdot dm^{-3}$): casein peptone (1.56), dry broth (1.05), $NH_4Cl$ (0.20), NaCl (0.07), $CaCl_2 \cdot 6H_20$ (0.075), $MgSO_4 \cdot 7H_2O$ (0.02), $KH_2PO_4$ (0.20), $K_2HPO_4$ (0.50) was treated in the system in order to adapt microorganisms to new conditions. Synthetic wastewater solution was diluted ten times and supplemented with 1 $cm^3$ of acetic acid and 2 g of glucose per liter. Thereafter, an adaptation of sludge to concentrates started. Every two or three days, 20% v/v more of concentrate (concentration factor 2) was added until 90% v/v of the concentrate in the feed was achieved. Afterwards, other concentrates were used. All influents were supplemented with 10% of synthetic wastewater, glucose, acetic acid and different amounts of sulphuric acid. The progress of acclimatization was controlled by taking samples of influents and effluents.

The samples collected from bioreactors were centrifuged at 13,000 rpm for 10 min and supernatant was used for further analyses: electrolytic conductivity (WTW pH-meter), COD (standard dichromate method, Hach), spectrophotometric analysis and HPLC analysis.

The absorbance of cell-free bioreactors' supernatant was read out at 512 nm ($\lambda_{max}$ of Reactive Red 120) using Spectrolab UV-VIS spectrophotometer in order to calculate the decolourization degree. The samples were also scanned in the range of 400–800 nm to observe the shifting of peaks due to the transformations after biological treatment.

HPLC analyses were performed using Waters 600 HPLC unit equipped with UV detector at $\lambda$ = 240 nm, Waters NovaPak C18 column (150 mm × 4.6 mm). The mobile phase consisted of phosphorus acid/water solutions (0.1% $H_3PO_4$). The eluent flow rate was 1 $cm^3$/min and the sample injection volume was 50 $\mu dm^3$. The samples used for HPLC analyses were prepared by centrifugation (as described above) and then filtered through 0.45 μl nylon syringe filters.

The orthanilic acid of technical purity degree was used as amine standard.

## 3. RESULTS AND DISCUSSION

Biomass has specific demands for carbon and energy sources, microelement availability and environmental conditions (pH, temperature, toxins). The textile wastewater usually does not contain high amounts of biodegradable carbon compounds. It was established in former experiments that $BOD_5$/COD ratio for the two times concentrated wastewater was below 0.1. Moreover, the decolourization of azo dye requires an external electron donor in the form of co-substrate [6]. Hence, the usage of external carbon source was necessary in the experiments conducted – both for biomass growth and azo dye decolourization. Acetic acid, glucose and concentrated solution of synthetic domestic wastewater were used during the whole experiment. Textile wastewater does not contain all microelements which are necessary for biomass growth. In order to ensure non-limited (by this factor) biomass growth, a concentrated solution of synthetic domestic wastewater was used. Additionally, the textile wastewater can be characterised as a strongly alkaline solution of pH above 10. Although sulphuric acid was used as a neutralising agent, the average pH in the anaerobic reactor approached 7, while in the aerobic one it reached 9. As biomass is able to adapt itself to new environmental conditions to some extent, no adverse effect of the high pH value (about 9) was observed. Furthermore, nanofiltration concentrates were heavily loaded with electrolytes (conductivity from 16 $mS \cdot cm^{-1}$ for concentration factor 2 up to 31 $mS \cdot cm^{-1}$ for concentration factor 10) as a result of the dyeing procedure (demanding high concentrations of sodium chloride) and the concentration in the nanofiltration unit. However, due to the adaptation process, the inhibition of microorganism activity was not observed until the end of the experiment. DAFALE et al. [1] confirmed that the adaptation of the microbial community to the toxic or recalcitrant compounds improves the rate of the decolourization process. It is also possible that a halo-tolerant bacterial community has developed during the experiment.

The effective colour reduction was observed in the anaerobic reactor. The colour reduction values varied between 93 and 97% during the whole experiment (figure 1). The reduction degree was significantly higher than that reported by ŻYŁŁA et al. [11]. There was no clear dependence of the concentration factor on colour reduction (fig-

ure 1). The smallest colour reduction was observed for concentration factors 2, 6 and 10, while the greatest one was noticed for concentration factors 3, 5 and 8. There were some differences between the colour reduction calculated for the whole system (between inlet and outlet of the aerobic reactor) and that calculated for the anaerobic system only (figure 1) – connected with dilution or concentration in the aerobic reactor (especially at the end of the experiment).

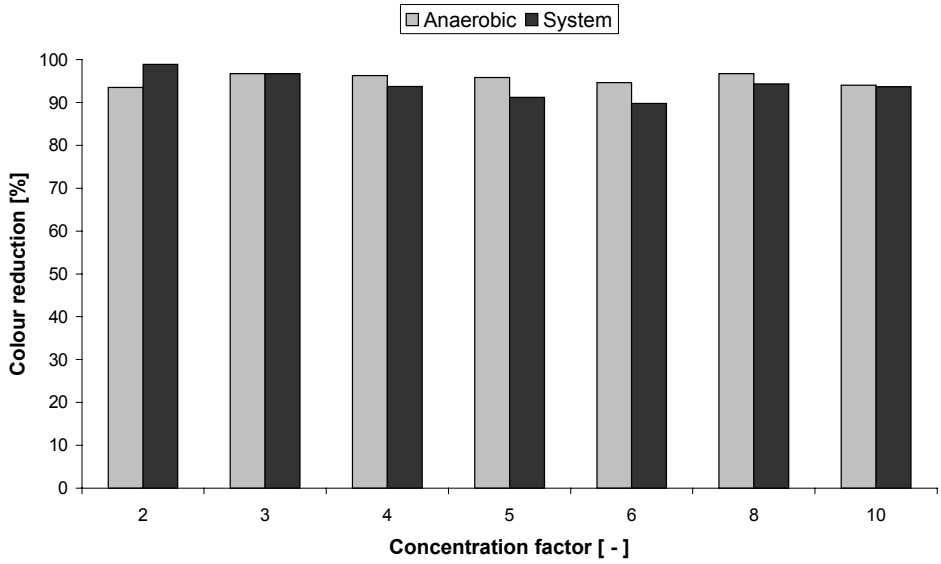


Fig. 1. Colour removal in anaerobic reactor and in whole anaerobic/aerobic system

The highly electrophilic azo bond can be cleaved under reductive conditions [6]. The Reactive Red 120 molecule has two azo bonds. As a result of azo bonds cleavage in Reactive Red 120 molecule, two molecules of orthanilic acid were released. The chromatogram of anaerobic reactor outflow showed the appearance of three peaks, one of which corresponds to orthanilic acid (figure 2). Orthanilic acid and one of the components occurring as a peak after about 1 min 45' (retention time) were further biodegraded under aerobic conditions, while the third component represented as a peak after about 1 min 30' (retention time) seemed to be recalcitrant to biodegradation – the chromatogram of the aerobic reactor effluent showed this peak untouched (figure 2). The orthanilic acid reduction exceeded 98% for all concentration factors (figure 3). Surprisingly, by the concentration factor 10, the peak of orthanilic acid has split into two peaks (figure 2) – most probably, a very similar product to orthanilic acid was formed. However, in the effluent from the aerobic reactor, only one peak was observed (figure 2).

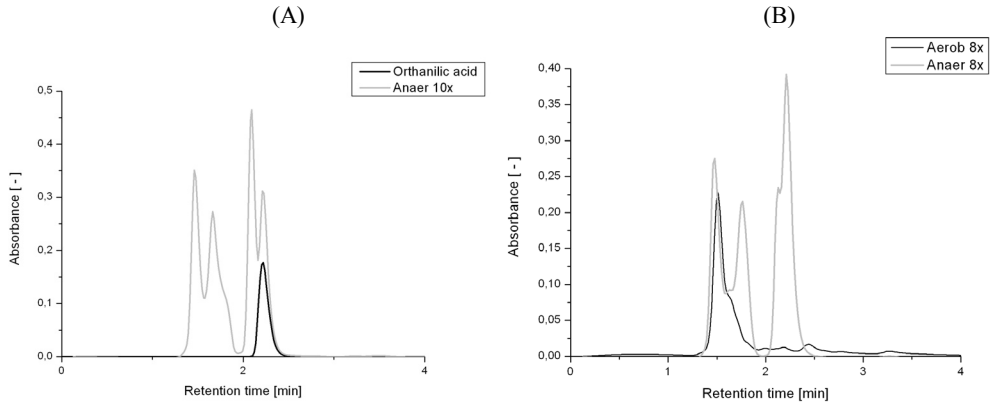


Fig. 2. Chromatograms for orthanilic acid and filtered samples taken from bioreactors' outflows: (A) orthanilic acid and anaerobic outflow for concentration factor 10, (B) outflows from anaerobic and aerobic reactors for concentration factor 8

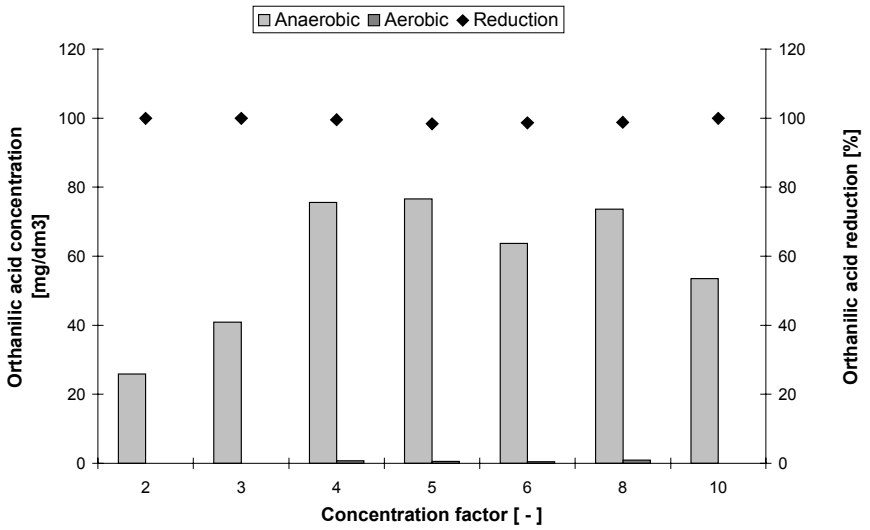


Fig. 3. Orthanilic acid concentration in anaerobic and aerobic reactors and removal in aerobic reactor

It was revealed that COD reduction was most sensitive to the concentration changes. COD reduction calculated between the influent to and the effluent from the bioreactors' system decreased from 97% for concentration factor 2 to 84% for concentration factor 10 (figure 4). Much lower COD reductions were visible if the difference between concentrated COD loads and effluents was taken into account, reaching 82% for the concentration factor 2 and 55% for the concentration factor 10 (figure 4). However, the lowest COD reduction (49%) was observed for the concentration fac-

tor 6. Additionally, only the effluent after a sequential treating of the two times concentrated nanofiltration wastewater was below the level forced by legislation for the discharges into surface water – 125 mg COD·dm$^{-3}$.

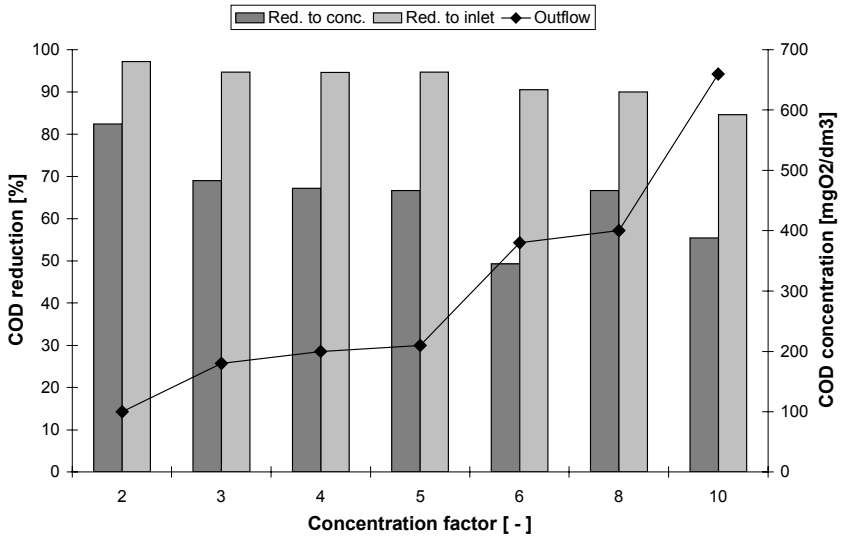


Fig. 4. COD reduction and concentration in system outflow

## 4. CONCLUSIONS

The two-sludge anaerobic–aerobic system was successfully implemented in the degradation of the nanofiltration concentrate. The efficiency of the colour removal in the anaerobic bioreactor was high as it exceeded 93%. Aromatic amine (orthanilic acid) produced as a result of the azo bond cleavage was biodegraded further in the aerobic reactor. The orthanilic acid reduction exceeded 98%. Such good results were obtained irrespective of the concentration factor (in the range of 2–10). The system used was not so efficient in COD reduction and sensitive to the concentration factors. The effluents obtained for the concentration factors above 2 were characterised by the COD values above the level forced by legislation for the discharges into surface water. However, these effluents might be treated in conventional wastewater treatment plants as they do not contain dye particles with azo bonds.

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## INTEGRACJA PROCESÓW MEMBRANOWYCH I BIOLOGICZNYCH W OCZYSZCZANIU ŚCIEKÓW WŁÓKIENNICZYCH

Przedstawiono zastosowanie metod biologicznych do unieszkodliwiania koncentratu powstającego po nanofiltracji ścieków pobarwiarskich zawierających barwnik azowy Reactive Red 120. Celem badań było ustalenie optymalnego stopnia zatężenia koncentratu. Wykorzystano dwustopniowy układ beztlenowo-tlenowy pracujący metodą osadu czynnego w systemie SBR. Biodegradacji poddano koncentraty o stopniach zatężenia od 2 do 10 razy. Uzyskiwano ponad 93% redukcję barwy oraz ponad 98% redukcję stężenia kwasu ortanilinowego. Zaobserwowano nieznaczny wpływ stopnia zatężenia na redukcję barwy, widoczny natomiast jest wzrost stężenia ChZT w odpływie z układu bioreaktorów. W trakcie biodegradacji koncentratu 10-krotnie zatężonego powstawał dodatkowy produkt o czasie elucji zbliżonym do czasu elucji kwasu ortanilinowego.