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KINETIC STUDIES OF DECOLOURISATION OF CONCENTRATES FROM NANOFILTRATION TREATMENT OF REAL TEXTILE EFFLUENTS IN ANAEROBIC/AEROBIC SEQUENCING BATCH REACTORS

The aim of the research was to investigate the degradation of real textile wastewater concentrate obtained in the nanofiltration processes. An anaerobic/aerobic sequencing batch reactor system working in a 24-h cycle was applied. The anaerobic phase aimed at the reduction of Reactive Red 120 molecules was followed by the aerobic oxidation of aromatic amine (orthanilic acid) released from azo dye. Two different successive decolourisation periods were observed in the anaerobic bioreactor for two tested concentrates of textile wastewater. A first-order reaction model was used to describe the decolourisation process. Furthermore, the relation between COD reduction and the concentrate decolourisation was observed. The aromatic amine was completely degraded in the aerobic stage only in the case of two-fold-concentrated textile wastewater.

1. INTRODUCTION

Textile industry demands huge quantities of water and wide spectrum of chemicals (QIN et al. 2007). Typically, production of 1 kg of coloured fabric requires 70–400 dm^3 of high-quality fresh water (ALLEGRE et al. 2006). Environmentally sustainable development in textile industry due to closing of water cycle and reduction of the produced wastewater toxicity is highly recommended (ELDEFRAWY and SHAALAN 2007; ŻYŁŁA et al. 2006). QIN et al. (2007) concluded that the nanofiltration allowed 70% water to recover from effluents. ŻYŁŁA et al. (2006) investigated the nanofiltration of real post-dyeing wastewater and its reuse in a dyeing process, which confirmed that the purified

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filtrate could be applied as process water. However, high concentration of dyes and other chemicals in the remaining concentrate (retentate) creates a serious problem. The different chemical, physical methods such as incineration or the direct cathodic reduction can be applied to remove dyes from wastewater. However, the methods mentioned above might be characterized by high energy consumption (BECHTOLD and TURCANU, 2004). The biological methods are generally considered as environmental friendly. Furthermore, they can lead to a complete mineralization of organic pollutants at a relatively low cost (PANDEY et al. 2007; ROBINSON et al. 2001). Azo dyes represent the largest class of colourants and are most commonly used in the textile industry. The colour of those dyes is connected with the presence of one or more azo bonds (-N=N-) that link together different aromatic groups into one molecule (ISIK and SPONZA, 2007). The azo dyes present more than 60–70% of the 800 thousand tons annual worldwide dyes production and approximately 15% of the used dyes is released to wastewater (MOUTAOUAKKIL et al. 2003). Dangerous are not only negative aesthetic aspects, a decrease of water transparency and low gas solubility connected with the presence of dyes, but also the potential toxicity and carcinogenic effect of their decomposition, i.e. aromatic amines (ISIK and SPONZA, 2007). Such an uncontrolled reduction of azo dyes can occur in the anaerobic water zone or in human intestines. It is known that the conventional aerobic processes used in the municipal wastewater treatment plants are insufficient for dye degradation. However, azo bonds can be biodegraded under anaerobic conditions in the presence of external electron donors e.g.: glucose (ISIK and SPONZA, 2007), acetic acid (VAN DER ZEE et al. 2003), ethanol (TAN et al. 2005) or starch (LOURENÇO et al. 2006). The total biodegradation of azo dyes generally requires a combination of two stages, an anaerobic reduction of the azo bond and an aerobic degradation of the formed aromatic amines (ISIK and SPONZA 2007, LOURENÇO et al. 2006). The literature overview showed that the decolourisation of azo dyes was thoroughly investigated (DOS SANTOS et al. 2007, KIM et al. 2008, DAFALE et al. 2008, ONG et al. 2008) but there is limited knowledge of the nanofiltration concentrate treatment and its decolourisation kinetics. YOO (2002) concluded that azo dye biological reduction kinetics depended on the concentration of the dye and reducing equivalents. Investigations of Brilliant Violet 5R and Remasol Black B decolourisation kinetics conducted by LOURENÇO et al. (2006) led to a conclusion that also structural complexity is important. In many research works monoazo dye decolourisation has been reported as the first-order kinetics with respect to dye concentration (VAN DER ZEE et al. 2003), whereas also the zero-order reaction was considered. Furthermore, the kinetics was altered during the anaerobic period which could suggest a different mechanism of dye reduction contributing to the dye molecule degradation. The three main mechanisms can be distinguished in the anaerobic azo dye reduction: direct enzymatic, indirect enzymatic with redox mediators and strictly chemical one (PANDEY et al. 2007). Studies of the reduction kinetics of nanofiltration concentrates and the oxidation of aromatic amines are crucial to investigate the sequential anaerobic/aerobic system behaviour. Additionally, a compari-

son of the kinetic constants enables an observation of the inhibition effects on the bacterial metabolism and the decolourisation rate caused by the different dyes concentration and process condition (VAN DER ZEE et al. 2003). In the case of nanofiltration concentrates such an approach allows to check dependency between the nanofiltration concentration degree and the decolourisation process.

In this paper the kinetic studies of two different post-filtration concentrates are presented. Experiments were carried out in the sequential anaerobic and anaerobic two-reactor system. The kinetic studies were preceded by one-month acclimatization of microorganisms to the concentrate and additional carbon source.

2. MATERIALS AND METHODS

2.1. TESTED MATERIAL

2.1.1. NANOFILTRATION CONCENTRATE

Textile wastewater was obtained after dyeing (followed by washing and rinsing) of a knitted cotton fabric with reactive dye Reactive Red 120 (figure 1) in a Pyrotec S laboratory dyeing machine (Roaches, UK), according to procedures recommended for this dye. The produced wastewater was subjected to nanofiltration in which different concentration degrees (factors) were obtained: two-fold (50% of the total volume was collected as a permeate) and ten-fold-concentrated (90% of the total volume was collected as a permeate). The nanofiltration concentrates of textile wastewater were characterised by high pH value above 10 (a strongly alkaline solution). Furthermore, the nanofiltration concentrates were heavily loaded by electrolytes (conductivity from 16 mS·cm^{-1} for concentration factor 2 up to 31 mS·cm^{-1} for concentration factor 10) as a result of the dyeing procedure.

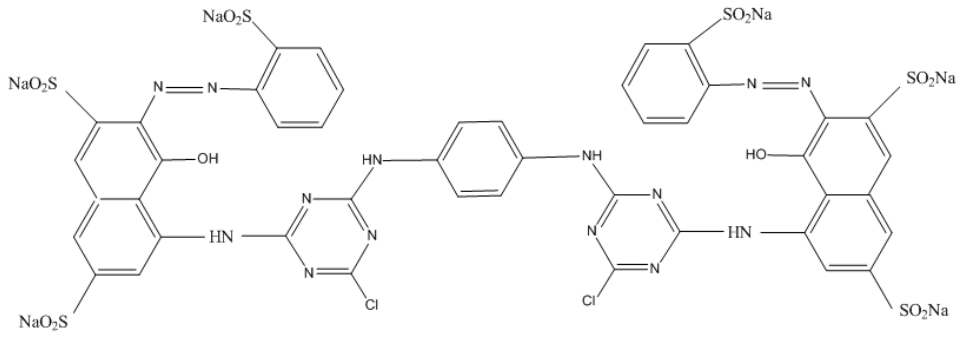

Fig. 1. Structure of Reactive Red 120

The experimental set-up for nanofiltration was described previously by ŻYŁŁA et al. (2006). The process of nanofiltration was carried out under the pressure equal to 1.5 MPa and the temperature 31–46 °C, with DL membrane, previously selected for the textile wastewater treatment. The flow rate was constant – ca. 2 dm^3/min.

Reactive Red 120 (RR 120) was synthesized in the Institute of Polymer & Dye Technology, Technical University of Łódź, Poland. RR 120 was chosen as a dye used in the industry whose degradation led to the formation of aromatic amines – orthanilic acid.

2.1.2. ADDITIONAL CARBON SOURCE

The concentrated synthetic wastewater solution of the following composition (g· dm^{-3}): glucose (20), acetic acid (5), casein peptone (1.56), dry broth (1.05), NH_4Cl (0.20), NaCl (0.07), $CaCl_2 \cdot 6H_20$ (0.075 g), $MgSO_4 \cdot 7H_2O$ (0.02), KH_2PO_4 (0.20), K_2HPO_4 (0.50), was used in all experiments.

Sulphuric or hydrochloric acid at pure grade was used as a neutralizing agent.

2.2. INOCULA FOR THE BIOREACTORS

A surplus activated sludge and fermented sludge taken from the methane fermentation stage of the Municipal Wastewater Treatment Plant (WWTP) in Łódź (Poland) were used as inocula for the bioreactors.

The aerobic reactor was inoculated with 400 cm^3 of the surplus activated sludge, while the anaerobic one was inoculated with 200 cm^3 of the fermented sludge.

2.3. EXPERIMENTAL SET-UP

The biodegradation of the post-filtration concentrate was conducted in the sequential anaerobic-aerobic two-sludge system consisting of two reactors and a transition tank (shown in Figure 2). The first (working volume 0.4 dm^3) was operating under anaerobic conditions at constant temperature 25 ºC controlled by an thermostat. The second one (working volume 0.8 dm^3) was operating under aerobic conditions at ambient temperature (around 25 °C – not controlled). Peristaltic pumps (Vertex, type PPO1) and digital timers (Metron, type PCg.O3) enabled filling and drawing of both reactors and the transition tank. The aerobic bioreactor was aerated by an air pump. The gas flow rate was controlled by a rotameter. A gas distributor was placed on the bottom of the reactor (aeration rate – 0.8 vvm). Both reactors were mixed by propeller stirrers (IKA, Eurostar Digital type, mixing speed in the anaerobic reactor was 60 rpm, while in the aerobic one 150 rpm).

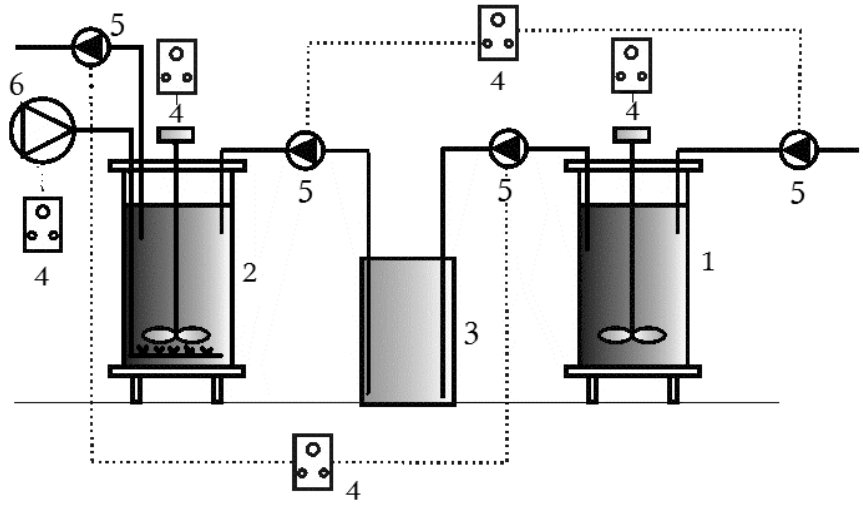

Fig. 2. Schematic diagram of the experimental set-up: 1 – anaerobic bioreactor, 2 – aerobic bioreactor, 3 – transition tank, 4 – digital timers, 5 – peristaltic pumps, 6 – air pump with rotameter

2.4. EXPERIMENTAL PROCEDURE

Both bioreactors were working in 24-h cycles (sedimentation 60 min, drawing 20 min (10 $cm^3 \cdot min^{-1}$), filling 20 min (10 $cm^3 \cdot min^{-1}$), reaction 22 h 20 min). Hydraulic retention time was two days for the anaerobic bioreactor and four days for the aerobic one. SRT was longer than 21 days – sludge was not drawn from the bioreactors.

During the first week of the operation, synthetic wastewater was treated in both reactors – in order to adapt microorganisms to new conditions. Concentration of the synthetic wastewater solution in the feed was 10% (feed volume 200 cm^3).

Next, an adaptation of sludge to concentrate started. The feed volume was 200 cm^3, at a very beginning of the acclimatization process it contained only 30% of the two-fold-concentrated post-filtrated liquid, 10% of the synthetic wastewater solution and water. Every five days the ratio of the concentrate was increased until it achieved 90% of the total feed volume. The progress of the acclimatization was controlled by taking samples of the influent and effluents. The acclimatization procedure was repeated in the case of ten-fold-concentrated wastewater. A week before the kinetic experiments, the tested wastewater composition was constant. It was assumed that the whole system was operating in the steady-state conditions. During the presented experiments, samples from both bioreactors were drawn simultaneously. In the anaerobic bioreactor a new portion of the tested concentrate was treated, while the anaerobic effluent from a previous day was subjected to the aerobic treatment.

2.5. ANALYTICAL METHODS

The following parameters were determined for the wastewater in the bioreactor: redox potential using SenTix ORP electrode connected to a Multi Lab 2 apparatus, pH (WTW pH-meter), dry matter content in the suspension and organic dry matter content.

Samples collected from the bioreactors in regular time intervals were centrifuged at 13,000 rpm for 10 min and the supernatant was used for further analysis: conductivity (WTW pH-meter), COD (standard dichromate method, Hach-Lange), spectrophotometric analysis and HPLC analysis.

2.5.1. SPECTROPHOTOMETRIC ANALYSIS

The absorbance of cell-free bioreactors' supernatant was read out at 512 nm (λ_{max} of Reactive Red 120) using a Spectrolab UV-VIS spectrophotometer. When necessary, the samples were diluted with distilled water to obtain absorbance lower than one. The decolourisation percentage was calculated according to the following equation:

$$Decolourization(\%) = \frac{F - O}{F} \cdot 100$$

where: F – the first measured absorbance in the bioreactor after the filling phase (before sample drawing the whole reaction mixture was intermixed – ideal mixing was assumed); O – absorbance at the end of the process (before the settling phase).

The samples were also scanned in the range of 400–800 nm to observe shifting of peaks due to dye transformations after the biological treatment. The mass-concentration of dye in the feed was calculated based on the calibration curve.

2.5.2. HIGH PRESSURE LIQUID CHROMATOGRAPHY (HPLC)

HPLC analyses were performed using the Waters 600 HPLC unit equipped with a UV detector at λ = 240 nm and Waters NovaPak C18 column (150 mm 4.6 mm). The mobile phase consisted of phosphorus acid/water solutions (0.01% H_3PO_4). The eluent flow rate was 1 cm^3 min^{-1} and the sample injection volume was 0.05 cm^3. The samples used for HPLC analyses were prepared by centrifugation as described above and then filtered through 0.45 μm nylon syringe filters.

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

3. RESULTS AND DISCUSSION

3.1. DECOLOURISATION

The decolourisation of two post-nanofiltration liquids characterised by a different concentration degree was measured as a decrease of the visible light absorbance (figure 3) at maximum absorbance for RR120. The obtained decolourisation degrees were high – 93% in the case of concentration factor 2 and 90% for concentration factor 10 of post-nanofiltration liquid. An increasing amount of additional chemicals used during the dyeing process in the concentrated wastewater had no or very small influence on the decolourisation process. The paper of DAFALE et al. (2008) confirmed that adaptation of the microbial community towards the toxic or recalcitrant compounds improved the rate of the decolourisation process.

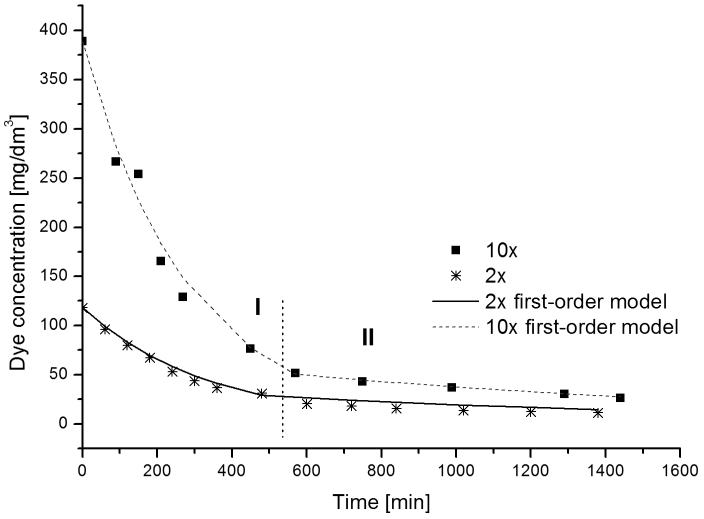

Fig. 3. Decolourisation of the nanofiltration concentrates with two concentration factors in the anaerobic bioreactor. I, II – the first and the second period of decolourisation, respectively

Additionally, samples were scanned in the range 400–800 nm (visible light absorbance) to check if there were no shifts between colours (figure 4). There were no maximum peak shifts but the textile wastewater concentrates had a yellow background colour which was removed in a very small degree during the decolourisation process. This colour was also observed in the dye solution and was not connected with the use of additional chemicals in the dyeing process. The lack of changes in the peaks may suggest that both azo bonds in the dye molecule were degraded simultaneously.

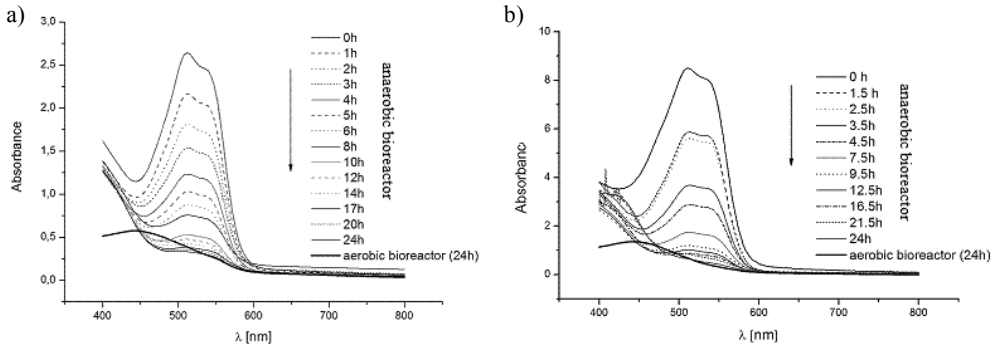

Fig. 4. Visible absorption spectrum: a) two-fold and b) ten-fold-concentrated textile wastewater

The colour reduction was not affected by the rapid change of redox potential between the anaerobic and aerobic reactor (figure 4). The visible absorption spectrum of the effluent from the aerobic reactor did not have the peak at 512 nm either.

3.2. TEST OF THE FIRST-ORDER REACTION MODEL FOR DECOLOURISATION

In order to check if the first-order reaction model could be applied to the nanofiltration concentrate decolourisation, the values of $\ln(C/C_0)$ were plotted versus time. The reaction proceeded without a visible lag phase. However, on the basis of curves in Figure 3 and their kinetic analysis, two different periods may be distinguished. In both tested nanofiltration concentrates the decolourisation phases may be described by the first-order reaction kinetics. The calculated values of the kinetic constants were much higher in the first period of decolourisation (two-fold-concentrated wastewater – 1st period 0.18 h^{-1}, 2nd one – 0.045 h^{-1} and for ten- fold-concentrated wastewater – 0.21 h^{-1} and 0.042 h^{-1}, respectively). The course of the decolourisation process approximates the first-order kinetics with respect to the dye concentration (changes of the kinetic constants for different nanofiltration concentrates). A comparison of the experimental results with those calculated from the first-order reaction model is illustrated in Figure 3.

3.3. AROMATIC AMINE DEGRADATION

The highly electrophilic azo bond can be cleaved under reductive conditions (ISIK and SPONZA 2007). The Reactive Red 120 molecule has two azo bonds (figure 1). As a result of the azo bonds cleavage in the molecule two molecules of the orthanilic acid can be released. Such a mechanism was observed during the experiment. Figure 5 shows changes of the orthanilic acid concentration, its accumulation in the anaerobic

bioreactor (a) and degradation in the aerobic one (b). In the case of two-fold-concentrated post-nanofiltration liquid the aromatic amine was completely degraded, while in the case of the ten-fold-concentrated one there was a small amount of the orthanilic acid left in the bioreactor. Surprisingly, there was no correlation between the aromatic amine production and the decolourisation periods. Probably, the aromatic amine may absorb on the bacterial cell but such behaviour has not yet been confirmed during any experiments conducted by the authors.

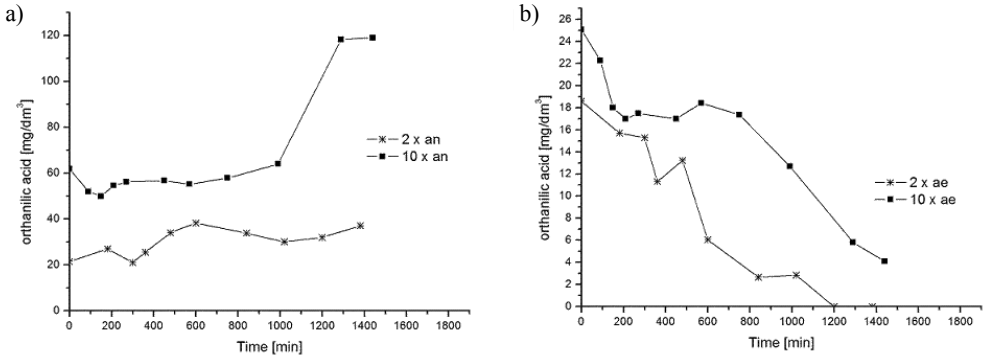

Fig. 5. The orthanilic acid concentration: a) anaerobic bioreactor and b) aerobic bioreactor

3.4. COD REDUCTION

COD reduction in both cases was high: there was 91.8% reduction for two-fold-concentrated wastewater and 89% for ten- fold-concentrated one. However, the effluent after sequential treating of the ten-fold-concentrated nanofiltration concentrate was above the legally approved level – 125 mg COD·dm^{-3}. The COD reduction is shown in Figure 6.

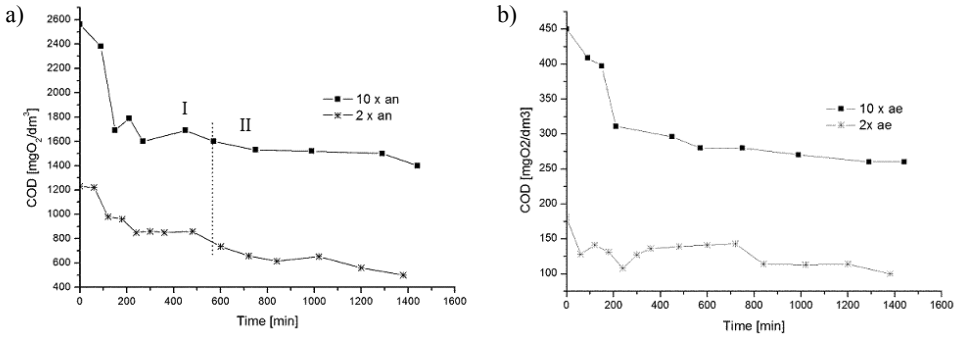

Fig. 6. COD reduction: a) anaerobic bioreactor and b) aerobic bioreactor;
I, II – the first and the second period of decolourisation, respectively

Similarly to the decolourisation the highest COD removal (figure 6) occurred in the first period of decolourisation. That can lead to the conclusion that the dye molecule reduction may be strictly connected with the carbon source degradation and production of reductive equivalents. The performance of two different decolourisation periods may be caused rather by easily biodegradable COD depletion than other parameters. A similar behaviour of the decolourisation process was reported by LOURENÇO et al. (2006). However, in the above mentioned paper, such performance was related to the reduction of the first and then the second azo bond in the case of diazo dyes or the mass transfer limitations. VAN DER ZEE et al. (2003) suggest that the degradation of azo dye proceeds according to two different mechanisms (direct electron transfer from the cell to the dye molecule or via sulphide reduction) and it can be a reason why two phases of decolourisation occur.

4. CONCLUSIONS

The two- and ten-fold-concentrated wastewater was the object of these studies. The anaerobic biological reductin of azo dyes was successfully applied to the decolourisation of the nanofiltration concentrates. Colour removal was high – around 90% in both cases. The anaerobic phase was followed by aerobic oxidation aimed at the destruction of the aromatic amine released from the azo dye breakdown. However, total degradation of the aromatic amine was achieved in the case of two-fold-concentrated wastewater. In both tested nanofiltration concentrates the decolourisation phases may be described by the first-order reaction kinetics and divided into two periods characterised by different dye removal rate constants. On the basis of the observation of COD and colour reduction curves, one may notice that dye molecule reduction is connected with the carbon source degradation. However, there is no correlation between the aromatic amine production and the decolourisation periods. In general, the presented results indicate that the anaerobic/aerobic sequencing batch reactor system can be applied to the nanofiltration concentrate treatment and contribute to the reduction of textile wastewater production and its toxicity. However, the whole process requires a further careful investigation – specially the aromatic amine oxidation and its degradation products.

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