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THE EFFECT OF PRODUCTS OF ADHESIVE WASTEWATER OXIDATION WITH FENTON'S REAGENT ON BIOLOGICAL TREATMENT IN SBR

The advanced oxidation process with Fenton's reagent can be used in industrial wastewater treatment, especially for the degradation of not easily biodegradable contaminations. Chemical oxidation of industrial wastewater or other substances as a pre-treatment before biological purification is the most effective method of wastewater treatment. However the Fenton process requires low pH of wastewater and final neutralization with a big amount of iron-containing precipitate. This paper presents laboratory experiments dealing with the treatment of adhesive wastewater in a sequencing batch reactor following the Fenton process without final neutralization.

1. INTRODUCTION

Advanced oxidation processes (AOPs) are applied for purification of industrial wastewater, especially to facilitate the degradation of not easily biodegradable contaminations. It is possible due to the high redox potential (2.8 V) of hydroxyl radicals OH^\bullet generated in the process, as shown in this simplified equation:



which oxidise nearly all contaminants. One of the AOP methods is Fenton's reaction, applied for chemical degradation of hardly biodegradable or non-biodegradable substances in wastewater to simple forms, which are further biodegraded.

Fe(II) ions catalysing the process, and hydroxyl radicals initiate a series of chain reactions whose products may include peroxide radicals (O_2^\bullet), hydro peroxide radicals (HO_2^\bullet), or hydro peroxide ions (HO_2^-) [1–3]. AOPs are widely applied for the purifi-

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cation of chemical wastewater, wastewater from production of urea adhesive, pesticide- and pigments', matches'-laundry wastewater, textile wastewater, dye wastewater, pulp mill wastewater, etc. [1,4]. It has been shown in numerous studies that chemical oxidation of industrial wastewater or other substances as a pretreatment before biological purification is the most effective method of wastewater treatment [1, 5]. Application of chemical oxidation of contaminants as a pretreatment process makes possible to shield the biological part of a wastewater treatment plant by reducing the load of hardly degradable contaminations and to improve the effectiveness of the biochemical processes. Such a system ensures reduction of non-biodegradable organic matter by as much as 95–98%, with initial values of COD of hundreds or even thousands milligrams per litre. Such results have been achieved in studies of purification of textile wastewater and wastewater from electronic and pharmaceutical industries [6–9].

Despite numerous advantages such as high effectiveness of organic contaminant decomposition, easy process management, availability and low price of the reagents, application of the Fenton process meets a number of limitations: generation of OH[•] requires low pH of wastewater (usually 2–4), and large amounts of iron-containing sludge are produced during the final wastewater neutralization.

In the paper, a part of results of adhesive wastewater treatment have been presented, being was examined in an integrated system of physicochemical and biological processes. The objective of the present study was to investigate the possibility of treatment of adhesive wastewater after the Fenton process without neutralization together with municipal sewage in a biological sequencing batch reactor (SBR). Laboratory initial tests have been performed in order to determine the effect of low pH, high redox potential ORP, the presence of iron ions and products of chemical oxidation on the process of biological treatment of wastewater. Adhesive wastewater was transferred to a SBR immediately after the Fenton process, and their effect on activated sludge condition, the course of biological processes and the effectiveness of purification were analysed.

2. EXPERIMENTAL PROCEDURES

The experiment was conducted at an experimental stand (Fig. 1) consisting of two SBRs with the working capacity of 3.0 dm³. Activated sludge, taken from a municipal sewage treatment plant, was cultured in both reactors for 3 weeks; it was adapted for work in an SBR system and only for synthetic wastewater. The sludge age was maintained at 15 days (excess sludge was removed once a day) and the decantation factor (volume exchange ratio) – at 33%. The reactors worked in 12-hour cycles in accordance with the diagram of the process phases shown in Fig. 2, with an additional deni-

trification phase with filling. The operation of the reactors and the equipment which made up the system were controlled automatically.

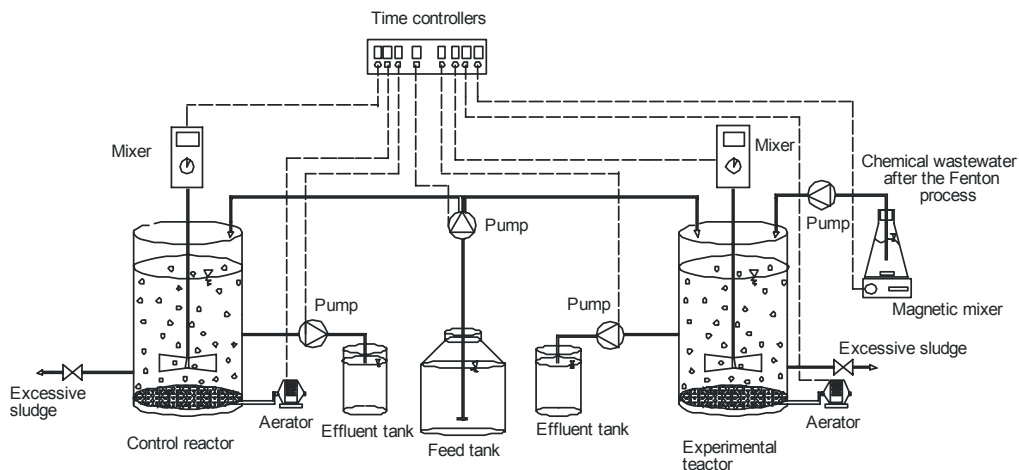


Fig. 1. Scheme of the experimental laboratory-scale SBR system

Time [h]	1	2	3	4–10	11	12
Feeding	sw aw				sw	
Mixing						
Aeration						
Settling						
Decantation						

Fig. 2. Operating time of the 12-hour SBR cycle: sw – synthetic wastewater, aw – adhesive wastewater after the Fenton process

The reactors were fed with synthetic wastewater prepared from tap water with addition of minerals and organic substances: peptone tryptone (225 mg/dm^3), ordinary broth with glucose (153 mg/dm^3), NH_4Cl (20 mg/dm^3), NaCl (7.0 mg/dm^3), $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ (7.5 mg/dm^3), $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (2.0 mg/dm^3), KH_2PO_4 (16 mg/dm^3), K_2HPO_4 (40 mg/dm^3). The wastewater parameters were close to those of real municipal wastewater (Table 1).

Wastewater produced in a window and door production plant, which is a by-product of washing and rinsing of adhesive systems, was used in the experiment. Residues of dispersive adhesive and a hardening agent were the main components of the wastewater. These are substances which contain mainly polyvinyl acetate and vinyl copolymer (50%), aluminium chloride (20%) and aluminium nitrate (20%) [10]. The wastewater was oxidised once a day in the Fenton process ($\text{Fe}:\text{H}_2\text{O}_2 = 1:5$, $\text{FeSO}_4 = 500 \text{ mg/dm}^3$, $t = 2 \text{ h}$, $\text{pH} = 2.5$). Wastewater after the Fenton process had low pH and high redox potential. Since iron(II) sulphate was used as a catalyst, high concen-

tration of iron caused reddish colour to the wastewater and affected the amount of mineral suspension (Table 2).

Table 1

Physicochemical characteristic of synthetic wastewater applied for the research

Parameter	Min–Max	Average
pH,	6.8–7.4	7.2
Conductivity, mS/cm	0.842–1.110	0.930
BOD ₅ , mg O ₂ /dm ³	280–300	282
COD, mg O ₂ /dm ³	356–400	358
TOC (non-filtered samples), mg C/dm ³	130–152	150
Orthophosphates, mg P/dm ³	7.00–13.02	10.00
Ammonia nitrogen, mg N/dm ³	19.00–33.61	26.56
Total nitrogen, mg N/dm ³	34.04–51.81	45.30

Table 2

Characteristic of adhesive wastewater before and after Fenton process without neutralization (Fe: H₂O₂ = 1:5, FeSO₄ = 500 mg/dm³, *t* = 2 h, pH = 2.5)

Parameter	Adhesive wastewater	Adhesive wastewater after Fenton process	
	Min–Max	Min–max	Average
pH	3.7–6.2	2.3–2.6	2.4
Conductivity, mS/cm	1.01–1.40	2.78–4.02	3.25
ORP, mV	140–245	420–523	477
Suspended solids, g/dm ³	4.48–8.67	3.10–8.72	5.06
Mineral suspended solids, g/dm ³	0.32–0.52	1.18–1.85	1.42
TOC (non-filtered samples), mg C/dm ³	3 147–9 906	2 322–5 125	3414
Nitrate nitrogen, mg N-NO ₃ /dm ³	23.10–250.0	8.50–27.22	17.70
Total nitrogen, mg N/dm ³	70.49–272.0	19.57–60.00	35.85

The SBR-1 was a control reactor in the system, whereas the other one additionally received chemical wastewater after the Fenton process (SBR-2). Wastewater was dosed only once per reactor work cycle, at the end of the first reactor filling with synthetic wastewater. The amount of adhesive wastewater transferred to the SBR-2 was gradually increasing within the TOC – load range from 235 to 2050 mg C/d (Fig. 3). The research was conducted without adaptation of the activated sludge to the increased TOC load, on account of the periodicity production of the adhesive wastewater and of the big variation in their quality.

Physicochemical analyses of the dosed and purified wastewater (pH, conductivity, turbidity, redox potential – ORP, DO, TOC, BOD₅, N-NO₃, N-NH₄, P-PO₄), activated

sludge (SVI, OUR) and changes of selected parameters were performed for the full SBR work cycle (pH, DO, ORP, TOC, N-NO₃, N-NH₄, P-PO₄).

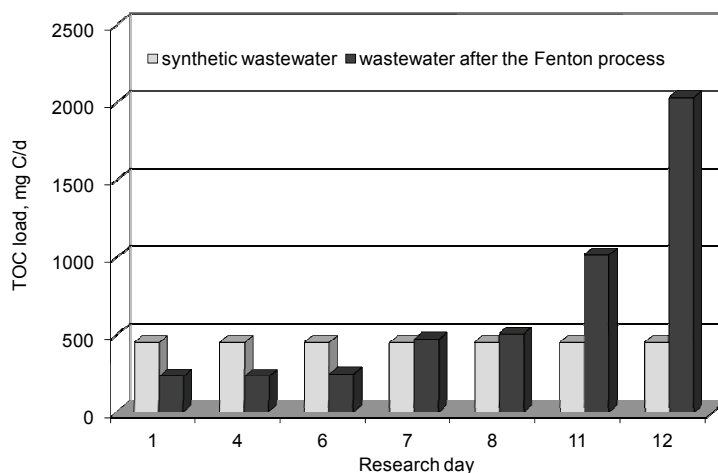


Fig. 3. TOC load of the reactor SBR-2 with synthetic wastewater and adhesive wastewater after the Fenton process without neutralization

3. DISCUSSION OF RESULTS

Due to the quality of the adhesive wastewater after chemical oxidation (a high concentration of organic and mineral suspensions), the activated sludge in the SBR-2 was loaded with an additional amount of contaminants (Fig. 4a). Sludge analysis revealed an increase in the content of the mineral (from 0.82 to 1.20 g/dm³ in the SBR-2, while mean value in the control reactor was 0.75 g/dm³ – Fig. 4b) and organic (adhesive dispersion) fractions (Fig. 4c). The difference in the organic fraction between the reactors was from 0.3 to 1.0 g/dm³ in 15th day of research. The additional load of the sludge during the experiment improved the settling properties of the precipitate in the SBR-2 (effect of iron ions in sludge from Fenton's reagent), decreasing the value of the SVI to 64–47 cm³/g – Fig. 4d (SVI_{SBR-1} = 86–70 cm³/g).

The parameter, providing important information about the metabolic activity of microorganisms in activated sludge, recently applied as a factor indicating the possible hydrodynamic stress, cell damage and cell death is the oxygen uptake rate (OUR) [11]. The examination of the sludge condition showed a small decrease of the oxygen uptake rate by microorganisms in the sludge from SBR-2. The value of OUR changed from 37 to 22 mg O₂/(g·h) in the last day of the experiment. The value of this parameter was higher in the control reactor (45–55 mg O₂/(g·h)). A decrease in the value of OUR in the SBR-2 may be due to the influence of the adhesive wastewater after the Fenton process on microorganisms of the activated sludge.

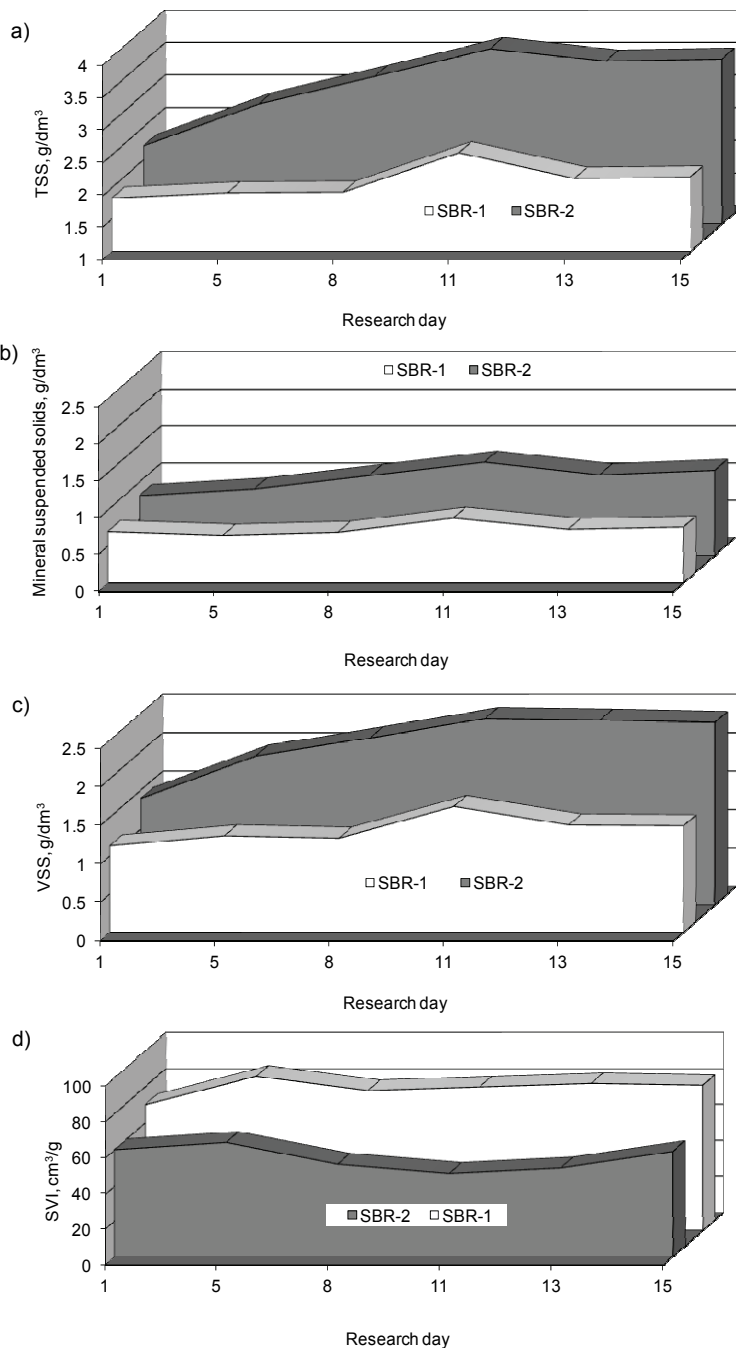


Fig. 4. Statement of activated sludge analysis from SBR-1 and SBR-2 (for details, see the text)

Microscopic analyses showed changes in the sludge characteristic. The sludge became darker, the floccules – more compact and dispersion particles were observed among the sludge floccules. A slight negative influence of adhesive wastewater could be determined by low activity of the part of rotifers from the SBR-2, which were present in big quantities in both reactors. Numerous rotifers present in the activated sludge indicated good conditions of wastewater treatment. These bioindicators are sensitive to toxic substances and observed change of their conditions in SBR-2 could be caused by influence of wastewater fed into the reactor. The parameters of adhesive wastewater were extremely specific and difficult for microorganisms. Wastewater after the Fenton process without final neutralization had low pH and high value of ORP, residues of oxidant, Fe ions from the catalyst and unknown products generated during chemical oxidation.

3.1. ANALYSIS OF THE SBR WORK CYCLE

SBRs worked in terms of pH, ORP, conductivity and oxygen concentration was monitored continuously. Exemplary changes of the analysed parameters (values of parameters were similar over the entire experimental period) are shown in Fig. 5.

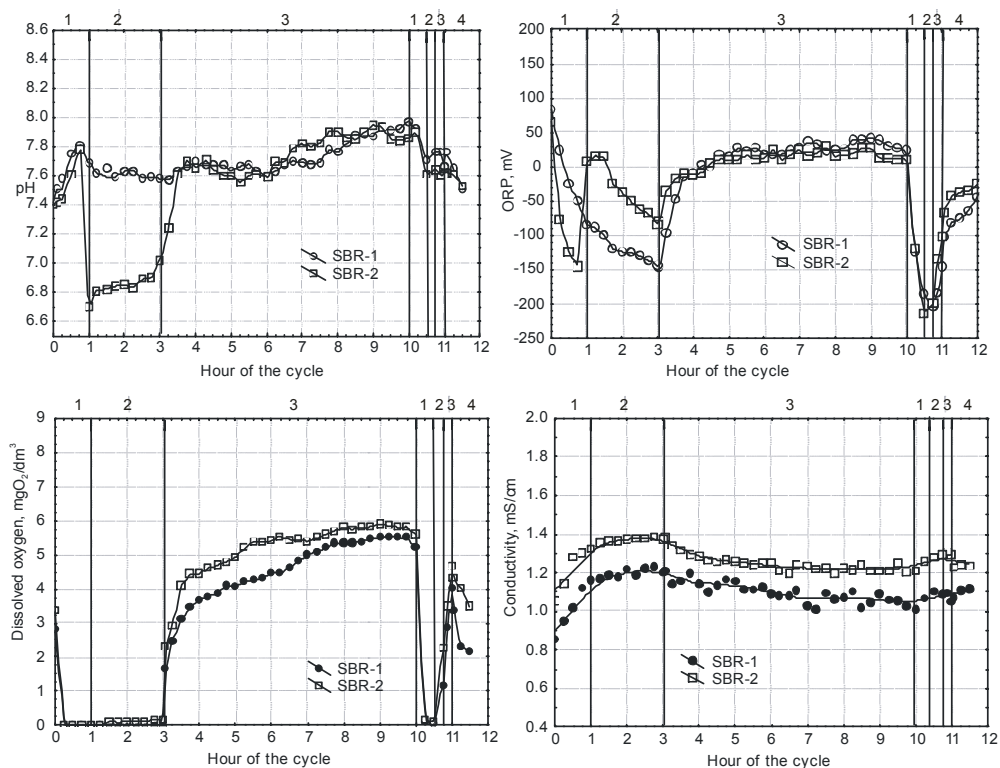


Fig. 5. Basic results of monitoring of selected parameters in reactors during various operation phases of a 12-hour cycle (14th research day): 1 – feeding, 2 – mixing, 3 – aeration, 4 – settling

Wastewater after the Fenton fed into process at the end of the filling phase changed pH and redox potential in the SBR-2. Acidic wastewater (pH 2–3) and a high redox potential of 400–500 mV decreased pH of wastewater in the reactor, from 7.8 to 6.7. During the aeration phase the value of this parameter increased to the level similar to that in SBR-1. Whereas the redox potential in the SBR-2 decreased to –150 mV during the synthetic wastewater filling phase but it increased after the Fenton process feeding (to 20 mV). During the next hour, its value was similar to that in the control reactor. pH and ORP change had a transient character.

The effect of wastewater after the Fenton process was neutralised by the buffer properties of the activated sludge. A higher value of specific conductivity in the SBR-2 was also recorded. During the aeration phase, the value of this parameter slightly decreased in both reactors.

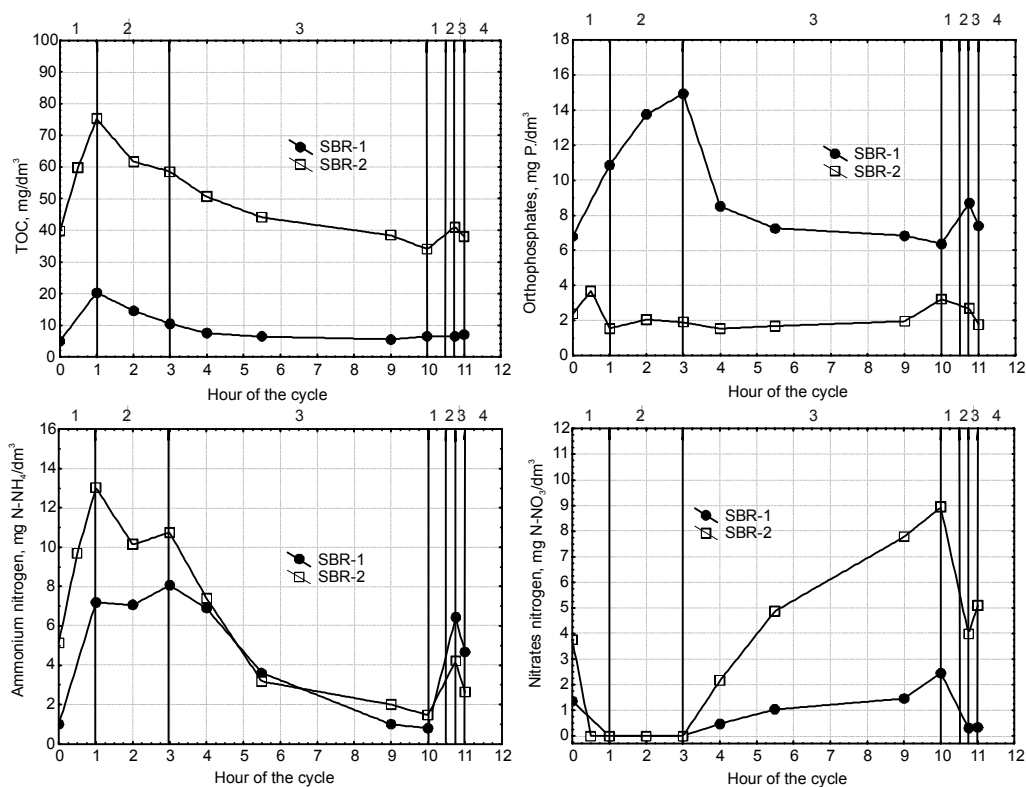


Fig. 6. Concentration of selected parameters in reactors during various operation phases of a 12-hour cycle (15th research day, filtered sample): 1 – feeding, 2 – mixing, 3 – aeration, 4 – settling

Other parameters such as TOC, PO_4^{3-} , NH_4^+ and NO_3^- ions also changed during the process (Fig. 6). Chemical analyses conducted in the 15th research day (the last

day of tests in which the most dynamic changes were observed) showed that TOC changes were the highest. Its increasing concentration in the SBR-2 indicated that only part of organic carbon was used by microorganisms of activated sludge despite a long aeration phase. The initial concentration in the SBR-2 was 8 times higher than in the control reactor (5 mg/dm^3) and increased (from 40 to 75 mg/dm^3) after post-Fenton wastewater was fed into the reactor. The TOC concentration decreased only below the initial level during the mixing and aeration phases.

Addition of post-Fenton adhesive wastewater with high iron concentrations (Fenton process residue) caused phosphorus precipitation from the wastewater in SBR-2 [12]. A biological dephosphatation proceeded residually – a slight increase during the filling phase with synthetic wastewater, but only until the post-Fenton adhesive wastewater was fed into the reactor (influence of a high redox potential and iron-rich suspension).

Changes typical of the biological dephosphatation process were observed in the control reactor: release in anaerobic conditions (from 6.5 to 15.1 mg P/dm^3) and consumption in aerobic conditions (from 15.1 to 6.1 mg P/dm^3).

The nitrification process in SBR-2 was very effective despite a higher reactor load with organic carbon. The level of ammonium nitrogen oxidation was similar to that observed in the control reactor despite a higher initial concentration, whereas nitrate(V) concentrations were much higher. The adhesive wastewater after the Fenton process fed into reactor contained nitrates which were effectively reduced (more organic carbon from added wastewater) during the filling and mixing phases. Dynamic increase of nitrate concentration during aeration in the SBR-2 indicated high process intensity.

3.2. EFFECTIVENESS OF WASTEWATER TREATMENT IN THE SBR

Dosing of wastewater after chemical oxidation affected progressive changes of quality of treated wastewater (Figs. 7, 8). The greatest changes were observed for TOC, which was determined before and after filtering. An increase of wastewater turbidity, observed from the beginning of the wastewater addition, directly caused increase of TOC concentration, which increased from 8 to 47 mg/dm^3 in the filtered samples and from 13 to 117 mg/dm^3 in non-filtered ones during the research period. The turbidity was caused by dispersion of polyvinyl acetate, which was not completely adsorbed and degraded by the activated sludge, despite the earlier process of chemical oxidation. Observations of operation of reactors showed intensive foaming in the SBR-2, which additionally increased the turbidity of the wastewater (from 28 to 237 NTU in the 15th research day). A large decrease of orthophosphate concentration from 9 to 1 mg/dm^3 was observed throughout the experiment period which was caused by precipitation with post-Fenton iron; the concentration in the control reactor was 7–10 mg/dm^3 at the same time.

Nitrogen removal from wastewater was very effective in SBR-2, where lower concentration of ammonium nitrogen was recorded ($<1 \text{ mg/dm}^3$). Initially, an increase of nitrate concentration was observed, indicating favourable conditions for nitrification. Dramatic changes took place after 10th day of the experiment when the amount and concentration of the fed adhesive wastewater increased to value $1017 \text{ mg C per reactor}$ during one cycle.

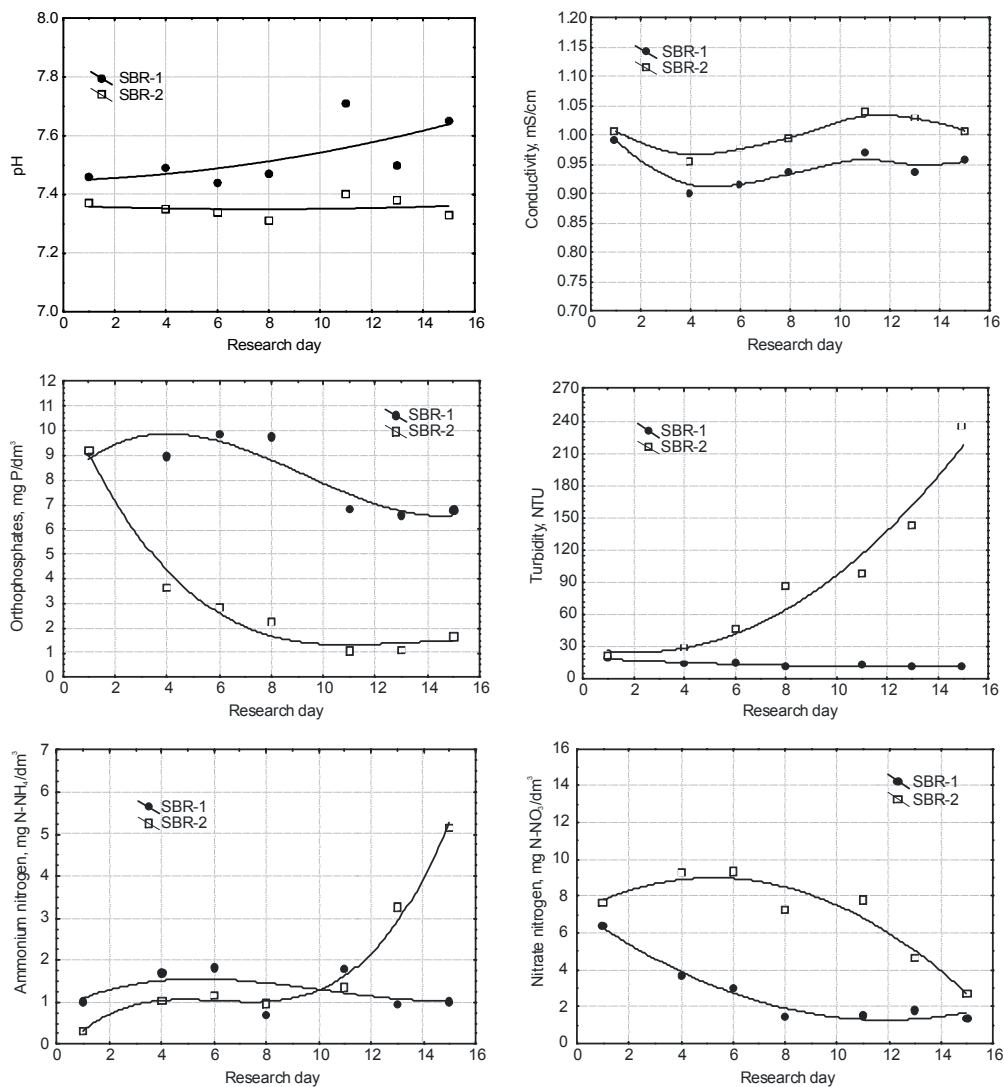


Fig. 7. Results of sewage treatment in SBR-1 (control reactor) and SBR-2 (with dosage of adhesive wastewater after Fenton process without neutralization): time dependences of pH, conductivity, orthophosphate content, turbidity, ammonium and nitrate nitrogen content

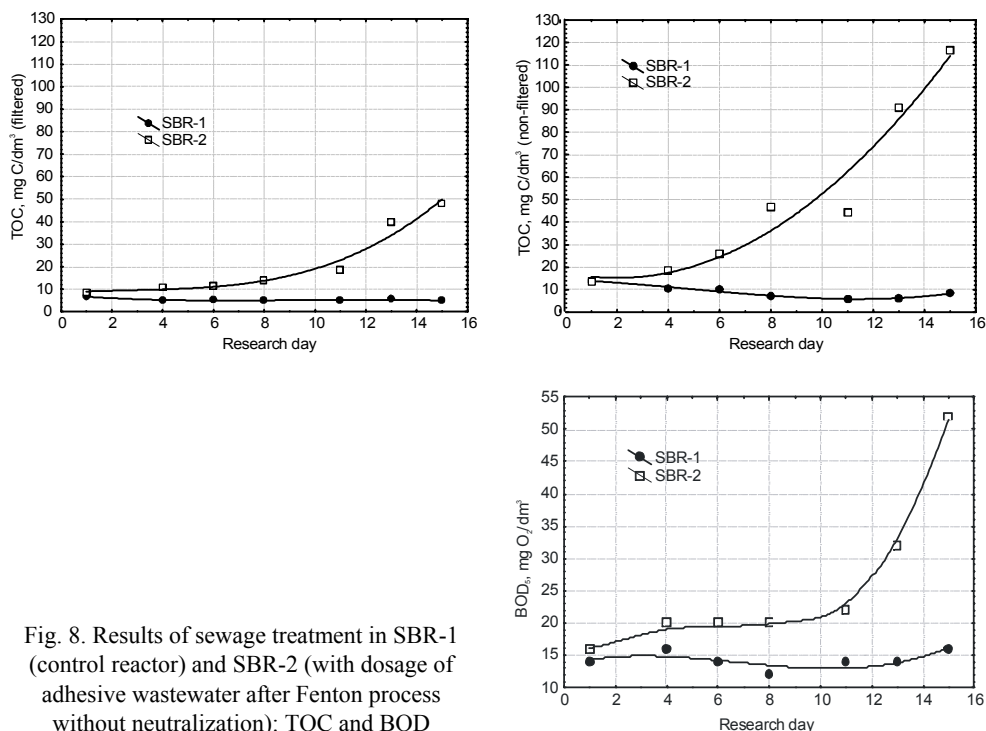


Fig. 8. Results of sewage treatment in SBR-1 (control reactor) and SBR-2 (with dosage of adhesive wastewater after Fenton process without neutralization): TOC and BOD

From this moment an increase of some parameters of treated wastewater from SBR-2 was observed; TOC (from 45 to 115 mg C/dm³ compared to <10 mg C/dm³ in the control reactor), BOD₅ (16 mg O₂/dm³ in the SBR-1 and 52 mg O₂/dm³ in SBR-2 in the 15th research day) and specific conductivity. The degree of removal of total nitrogen was close to that in the control reactor. A rapid increase of concentrations of ammonium nitrogen and decrease of nitrate(V) was observed. All indicated parameters (only concentration of orthophosphates was lower) showed a perturbation of wastewater treatment and exceeding acceptable adhesive wastewater amount in SBR-2.

4. CONCLUSIONS

- Adhesive wastewater after the Fenton process without neutralization did not very negatively affect the activity of the activated sludge in the SBR in the TOC – load range from 235 to 2050 mg C/d and without sludge adaptation.
- Addition of post-Fenton wastewater caused a transient decrease of pH in the SBR from 7.6 to 6.8 only during the feeding phase of the SBR-cycle.
- A high redox potential in adhesive wastewater (400–500 mV) inhibited releases PO₄³⁻ ions from phosphorus accumulating organisms (PAOs) during anoxic and an-

aerobic phases. Orthophosphate removal took place mainly by precipitation with iron from the Fenton's reagent.

- An increase of TOC-load caused increase of the turbidity from 28 to 237 NTU (dispersion of polyvinyl acetate) and intensive foaming in the SBR.

- Removing of organic matter from adhesive wastewater was not complete despite applying chemical oxidation by Fenton reagent.

- Oxidated wastewater did not disturb nitrification or denitrification processes, showing a higher intensity than in the control reactor, up to the TOC load of 1017 mg C/d. A higher load of TOC caused a rapid increase of the content of ammonium nitrogen and decrease of nitrate(V).

- Chemical processes accompanying application of adhesive wastewater after the Fenton process to removal of organic matter requires further explanation.

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REFERENCES

- [1] BARBUSIŃSKI K., *Toxicity of industrial wastewater treated by Fenton's reagent*, Pol. J. Environ. Stud., 2005, 14 (1), 11.
- [2] CHAMARRO E., MARCO A., ESPLUGAS S., *Use of Fenton reagent to improve organic chemical biodegradability*, Water Res., 2001, 35 (4), 1047.
- [3] AL-ANANZEH N.M., *Oxidation processes: experimental study and theoretical investigations*, Dissertation, Worcester Polytechnic Institute, 2004.
- [4] BIANCO B., DE MICHELIS I., VEGLIŃ F., *Fenton treatment of complex industrial wastewater: Optimization of process conditions by surface response method*, J. Hazard. Mater., 2011, 186 (2–3), 1733.
- [5] FONGSATITKUL P., ELEFSINIOTIS P., YAMASMIT A., YAMASMIT N., *Use of sequencing batch reactors and Fenton's reagent to treat a wastewater from a textile industry*, Biochem. Eng. J., 2004, 21 (3), 213.
- [6] TEKIN H., BILKAY O., ATABERK S.S., BALTA T.H., CERIBASI I.H., SANIN F.D., DILEK F.B., YETIS U., *Use of Fenton oxidation to improve the biodegradability of a pharmaceutical wastewater*, J. Hazard. Mater., 2006, 136 (2), 258.
- [7] LIN S.H., PENG C.F., *A continuous Fenton's process for treatment of textile wastewater*, Environ. Technol., 1995, 16 (7), 693.
- [8] LIN S.H., JIANG C.D., *Fenton oxidation and sequencing batch reactor (SBR) treatments of high-strength semiconductor wastewater*, Desalin., 2003, 154 (2), 107.
- [9] LIN S.H., JIANG C.D., *Combined physical, chemical and biological treatment of wastewater containing organics from semiconductor plant*, J. Hazard. Mater., 2003, 97 (1–3), 159.
- [10] PIASKOWSKI K., ŚWIDERSKA-DĄBROWSKA R., *Use of Fenton's process and sequencing batch reactors to treat a wastewater from a wooden windows manufacture*, Annual Set The Environ. Prot., 2010, 12, 503.
- [11] GARCIA-OCHOA F., GOMEZ E., SANTOS V. E., MERCHUK J.C., *Oxygen uptake rate in microbial processes: an overview*, Biochem. Eng. J., 2010, 49 (3), 289.
- [12] Piaskowski K., *Generation and management of wastewater from ground water treatment*, Arch. Environ. Prot., 2009, 35 (3), 35.