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KINETICS OF DAIRY WASTEWATER TREATMENT IN THE SBR SYSTEM

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Abstract: There are two kinds of wastewater that may originate at a dairy plant: post-production and non-production waste. Dairy wastewater treatment is a process consisting of several stages. In the pre-treatment stage, fat and sand is removed from wastewater. The second stage treatment consists mainly in aerobic treatment with activated sludge, advanced oxidation methods and an anaerobic treatment. In recent years, more and more plants have been treating their wastewater in SBR type reactors, because they are flexible at work and enable the user to change conditions to suit the variable quality of raw wastewater. The research on the kinetics of the wastewater treatment process in an SBR reactor has been conducted. The removal of several factors such as nitrogen compounds, TOC, phosphorus and the kinetics of oxygen concentration and redox potential have been analyzed. The experiment was carried out in two 12 dm^3 volume SBR reactors in a lab-scale. The SBR reactors were operated with a cycle time of 12 hours with three hours of filling, seven hours of aeration, an hour of sedimentation, half an hour of decantation and half an hour of technical break. In presented research average parameters of raw wastewater were: TOC 329 mg C/dm^3, ammonium nitrogen 11.15 mg N_{NH4}/dm^3, and total phosphorus 15.42 mg P/dm^3.

INTRODUCTION

There are two kinds of wastewater that may originate at a dairy plant: post-production and non-production waste. Post-production waste is mainly produced during floor and equipment washing, but it also includes milk leakage and loss, as well as brine and casein washing wastewater. Post-production waste contains remnants of milk and dairy products, manufactured at the site, as well as washing agents. In some dairy plants whey is also channeled off into the drain, thereby increasing the impurity load considerably [3]. Non-production, i.e. sanitary, post-cold-storage and rainstorm wastewater may account for a large portion of wastewater, but it contains low concentrations of organic matter. It is produced when washing vehicles, in boiler rooms or in cooling systems (unless water circulates in a closed system).

Dairy wastewater treatment is a process consisting of several stages. In the pre-treatment stage, fat and sand are removed from wastewater. The wastewater is subsequently averaged out. Colloidal impurities are removed by floatation, coagulation and precipitation with calcium at pH > 10 [2]. The amount of wastewater and impurity load may be reduced by recovering milk – separating the first fraction of slops that contain it in considerable quantities – and selling it as fodder [12]. Recovering brine, which is used in hard cheese production, may be regarded as the first step of wastewater treatment [10]. Application of microfiltration in brine purification ensures the almost total removal of microorganisms; it does not significantly alter the chemical composition of brine, it removes all physical contaminations and does not bring about a large loss of salt (0.5–1.0%). After the microfiltration process brine may be returned to the process. The second stage treatment consists mainly in aerobic treatment with activated sludge, which includes rotating biological contractors, trickling filters, classical method of activated bed, the SBR system [2] and other modifications of aerobic methods. Interest has also been growing in advanced oxidation methods, which mainly employ the use of ozone, dihydrogen dioxide, photolysis and radiolysis. Researchers [11] have attempted to determine whether it is possible to apply the methods of advanced oxidation in dairy wastewater treatment. The method chosen for the study involved the use of Fenton's reagent, in which dihydrogen dioxide is activated by iron(II). In its modified version, a magnetic field is applied as the factor generating hydroxyl radicals. The analysis of different samples of synthetic wastewater has shown that a better effect of treatment is achieved for the wastewater containing powdered milk. The COD level in those samples was reduced by 79%, whereas the COD level for the synthetic wastewater prepared from dried and powdered whey was reduced by 52%. Additional magnetic field wastewater treatment made it possible to reduce the amounts of reagents with no negative effect on the result of purification.

Secondary treatment is also an anaerobic process involving a flow-through anaerobic reactor with sludge bed and mixed fermentation [9, 16]. Secondary treatment may also include agricultural use and membrane methods [14], as well as dairy wastewater treatment in hydrobotanic systems [15]. Generally, agricultural industrial waste, including dairy waste, is treated effectively in hydrophytic treatment plants. With high variability of the impurity load, waste pre-treatment should be considered, e.g. in lagoons [6]. Such a system could also be applied in a less favorable (cool) climate [6, 13]. Many dairy plants in Poland channel their post-production waste to municipal wastewater treatment plants. Such wastewater contains proteins supporting the purification of waste that is poor in organic matter. Dairy waste can also be a source of volatile fatty acids (VFA), which can be used as an external source of carbon. Research conducted so far [8] has shown that application of an anaerobic process results in increasing the amount of VFA in wastewater, regardless of the amount of sludge in reactors. Raw wastewater itself does not contain large amounts of such substances: from ca. 50 mg/dm^3 in raw milk wastewater to 800 mg/dm^3 in whey, which is a by-product of cottage cheese manufacture. VFA production is considerably affected by acidification of wastewater [4], which increases with the added impurity load, easily undergoing acidic fermentation. Some heavy metals have also been found to inhibit the process of acidogenesis [5]. Research conducted to evaluate the effect of zinc and copper, which are the most commonly found in heavy industry wastewater, has revealed that zinc concentrations of ≥ 10 mg/dm^3 inhibit the process of acidogenesis, whereas zinc at concentrations below that level significantly improves the process. Copper has been found to inhibit the process of acidogenesis in the entire range of concentrations under study, from 5 to 400 mg/dm^3.

In recent years, more and more plants have been treating their wastewater in SBR type reactors, as these are flexible and enable the user to change conditions to suit the variable quality of raw wastewater. All the stages of purification in SBR reactors are carried out in one tank. They work alternately under aerobic and anaerobic conditions, which enable the removal of nitrogen and phosphorus. Unfortunately, SBR reactors often work with incorrectly selected process phases, with an excessive impurities load, which makes pre-treatment possible and the treatment proper impossible. Lack of pre-neutralization of wastewater may result in degradation of the activated sludge [1]. Therefore, the study presented in this paper sought to explore the possibility of treatment of dairy wastewater in the SBR system.

MATHERIALS AND METHODS

The experiment was conducted using the set-up as shown in Figure 1. The system consisted of two SBR reactors working in a parallel arrangement. The total capacity of a single reactor was 16 dm^3, whereas the active volume was 12 dm^3. Synthetic wastewater was fed to the system with a 4-channel type ISM 828 peristaltic pump, manufactured by Ismatec Reglo; purified wastewater was decanted through a U-shape decanter with a 2-channel PumpDrive 5001 pump manufactured by Heidolph. Using such a decanter shape meant that wastewater could be channeled off without any improperly settling sludge being carried away with it. The depth of the decanter fixing ensured the amount of decantation of ca. 33% of the reactor's active volume. Wastewater was stirred with HEIDOLPH RZR 2051 agitators at a speed that ensured its proper mixing. Stirring was effected with the

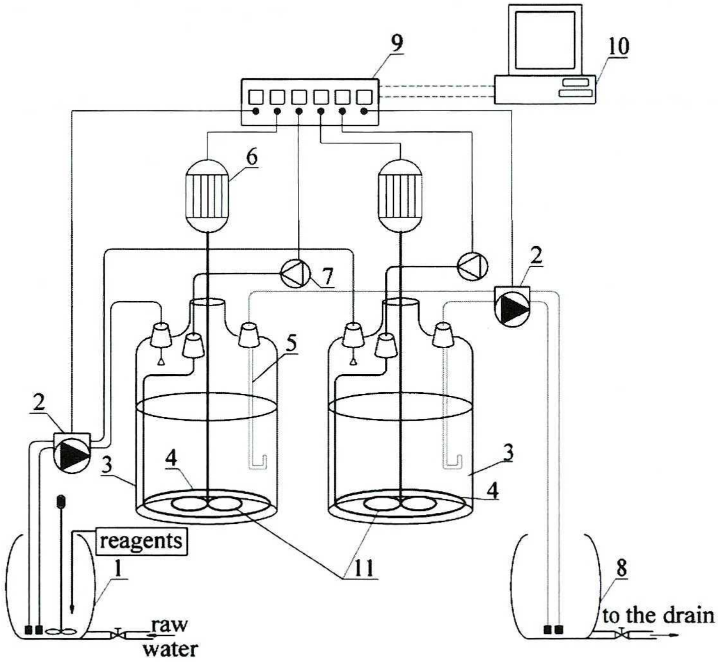

Fig. 1. Diagram of the experimental set-up
1 – raw wastewater tank, 2 – peristaltic pump, 3 – SBR reactor, 4 – aerating curtain, 5 – decanter, 6 – engine, 7 – blower, 8 – purified wastewater tank, 9 – electronic control system, 10 – monitoring computer, 11 – agitator with stirring piece

VISCO JET stirring tips, whose shape ensured the flow without destroying the flocculate structure of the activated sludge. Air was fed into the reactors with HIBLOW AIR PUMP H810, type SPP-15GA blowers through aerating curtains of small air bubbles, the curtains being 90 cm long and situated at the bottom around the container's perimeter. The duration of individual process phases was controlled by a PCm.08 3k digital programmer, manufactured by METRON. Only excessive sludge was removed manually. The values of the basic system indicators were monitored with the computer connected to the experimental set-up; the indicators included oxygen concentration, pH, redox potential, and monitoring was effected by MultiLab® pilot communication software and the appropriate electrodes. The characteristic of synthetic wastewater has been presented in Table 1. The work cycle lasted 12 hours and consisted of the basic process phases – Table 2.

Table 1. Quality characteristics of the basic composition of synthetic dairy wastewater

Indicator		pH	Ammonium nitrogen	Nitrate nitrogen	Total phosphorus	Phosphates	BOD$_5$	TOC
Unit		–	[mg N$_{NH4}$/dm^3]	[mg N$_{NO3}$/dm^3]	[mg P/dm^3]	[mg P$_{PO4}$/dm^3]	[mg O$_2$/dm^3]	[mg C/dm^3]
Sample number	1	7.41	12.6	0.24	16.5	28.8	680	357.6
	2	7.46	8.75	0.31	15.9	27.2	–	348.8
	3	7.25	9.5	0.39	13.3	28.4	680	332.8
	4	7.49	11.6	0.26	14.6	24.4	–	355.9
	5	7.27	9.15	0.48	15.2	24.2	700	353.9
	6	7.25	15.0	0.08	16.7	29.8	–	–
	7	7.12	13.7	0.26	18.3	–	660	353.6
	8	7.26	9.0	0.24	11.1	22.4	640	356.6
	9	7.11	11.6	0.23	15.4	28	–	359.4
	10	7.21	10.5	0.24	13.5	34	720	332.1
	11	7.20	10.8	0.24	15.2	29.6	–	310.4
	12	7.20	11.3	0.22	14.4	29	660	327.4
	13	7.28	11.5	0.21	17.25	28.6	760	294
	14	7.27	10.3	0.21	13.99	33	–	292.2
	15	7.29	11.1	0.18	13.7	27.4	700	–
	16	7.11	11.5	0.28	15.2	27.4	–	300
	17	7.18	11.8	0.3	17	32.6	700	300.3
	18	7.15	11.0	0.42	18.2	33.2	–	303.3
	19	7.21	11.2	0.34	17.6	33.8	680	315.2
Mean		7.25	11.15	0.27	15.42	29.0	689	329.0

Table 2. The process phase system in the SBR system, adopted for treating synthetic dairy wastewater

	1	2	3	4	5	6	7	8	9	10	11	12
Filling up	▨	▨	▨									
Stirring		▨	▨	▨	▨	▨	▨	▨	▨	▨		
Aeration				▨	▨	▨	▨	▨	▨	▨		
Settling											▨	
Decantation												▨
Break												▨

RESULTS AND DISCUSSION

Nitrogen compounds removal

The analysis of the wastewater quality characteristics during different process phases revealed an increase in nitrate(V) nitrogen during the static filling phase – Figure 2. The increase was caused by introducing to the reactor raw wastewater, containing 0.27 mg/dm^3 of silver nitrate(V). The concentration of dissolved oxygen decreased nearly to zero during the dynamic filling phase. The post-nitrification concentration of nitrate(V) nitrogen decreased to the value of 0.52 mg/dm^3 as a result of its reduction by heterotrophic denitrificators. With the beginning of the aeration phase, the concentration of nitrate(V) nitrogen increased as a result of nitrification, reaching the value of 12 mg/dm^3 before the settling phase. Before the decantation phase the concentration of nitrate(V) nitrogen decreased to the value of 9.6 mg/dm^3, which may result from denitrification effected by denitrificators which contain organic matter in their cells. When the accumulated organic matter was exhausted, the nitrification process took place until the end of the decantation process, in the presence of oxygen.

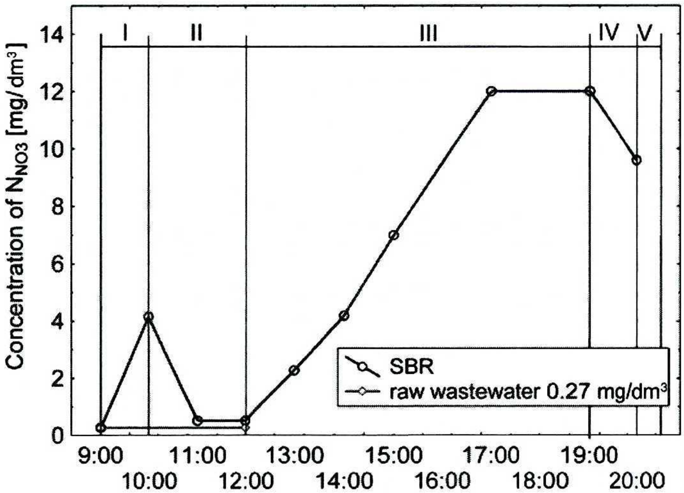

Fig. 2. Concentration of nitrate(V) nitrogen during individual phases of the SBR system operation

The kinetics of ammonium nitrogen concentration during different phases of the SBR operation is presented in Figure 3. As a result of nitrification, ammonium nitrogen was oxidized to nitrates(III) and nitrates(V). A considerable decrease in the concentration of ammonium nitrogen and the concurrent increase in the concentration of nitrate(V) nitrogen were observed during the first three hours of the aeration phase (III) – Figure 2. After about 3 hours of aeration, the concentration of ammonium nitrogen reached its minimum value of ca. 2 mg/dm^3 and remained so until the end of the decantation phase. Concentration of ammonium nitrogen in the reactor increased during the phase of static (I) and dynamic (II) filling as a result of the introduction to the reactor of raw wastewater containing a larger load of nitrogen compounds.

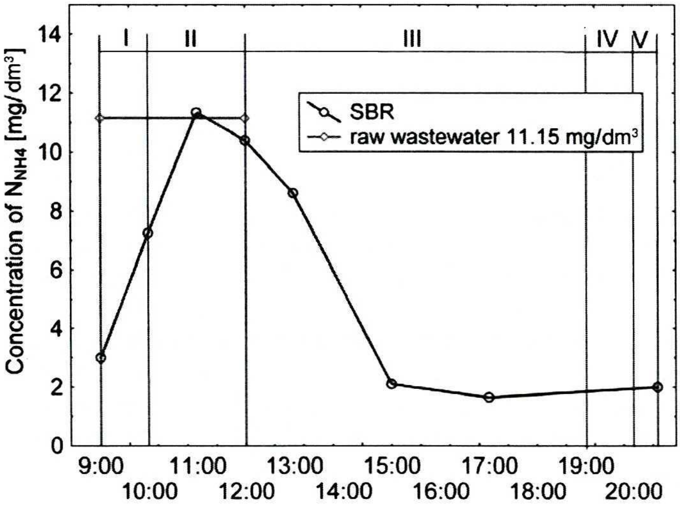

Fig. 3. Concentration of ammonium nitrogen during different phases of the SBR system operation

Removal of total organic carbon

Figure 4 shows the kinetics of total organic carbon concentration in the wastewater under treatment during different phases of the SBR operation. During the anoxic phase (I + II) as a result of the reactor filling up with raw wastewater at a concentration of 329 mg C/dm³, TOC concentration in reactor slowly increased to reach 19 mg C/dm³ during the final stage of the anoxic phase. Such a slight increase in concentration (despite a considerable difference in the concentration of raw and purified wastewater) was caused by carbon assimilation by heterotrophic organisms – Figure 2. Organic matter can also be precipitated and adsorbed in activated sludge. At the beginning of the aeration phase (III) organic carbon concentration was recorded to have decreased to the level of 8–9 mg C/dm³. The denitrification process was still going on – anoxic conditions still prevail inside the floccules. As aeration continued, the concentration of dissolved oxygen increased; it got inside the floccules and full nitrification occurred, and the TOC concentration remained at 8–9 mg C/dm³ since the nitrification organisms in a majority are autotrophs. They do not need organic carbon – they can assimilate carbon from inorganic compounds (carbonates, CO_2). The concentration of TOC decreased to the value of 7.5 mg C/dm³ during the settling and decantation phase, which may have been caused by carbon consumption by denitrificators – Figure 2.

Phosphorus compounds removal

The kinetics of phosphate removal is presented in Figure 5; for total phosphorus – in Figure 6. The mechanism is the same in both cases. In order to remove phosphorus biologically, alternate aerobic and anaerobic conditions have to be ensured. During the anoxic phase, phosphate concentration in the wastewater under treatment increased from 8 mg/dm³ to 54 mg/dm³ (to 17 mg/dm³ for total phosphorus) as a result of introducing raw wastewater with a concentration of 28.98 mg P_{PO4}/dm³ (15.42 mg/dm³ for total phospho-

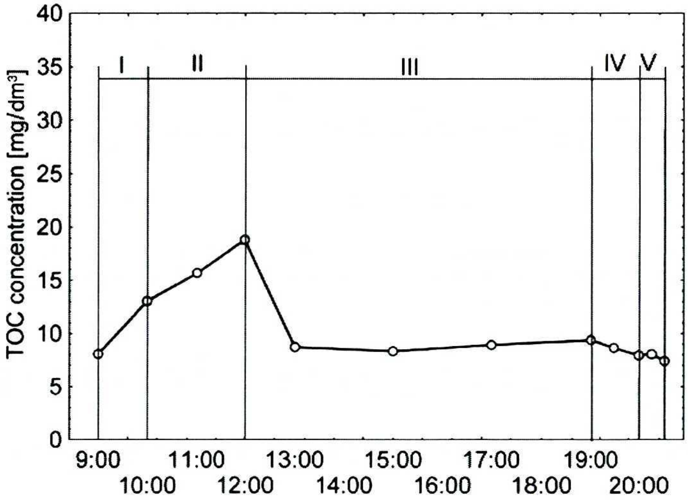

Fig. 4. TOC concentration during different phases of the SBR operation

rus) and as a result of secondary phosphorus release to the liquid under anaerobic conditions. As the time of aeration increased, the phosphorus and phosphate concentration decreased, as they were assimilated by certain bacteria strains (e.g., *Acinetobacter* sp., *Arthrobacter globiformis*) in as much as 25% of dry cell weight [7]. The concentration of phosphates at the end of the reactor work cycle was 5 mg/dm^3 and that of total phosphorus – 3 mg/dm^3. During the decantation phase the concentration of total phosphorus was recorded to increase by ca. 1 mg/dm^3 as a result of the phosphorus being released to the liquid from the precipitate.

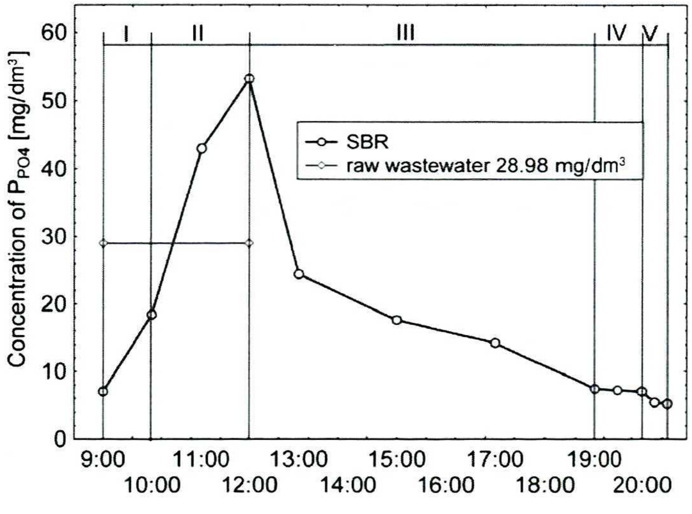

Fig. 5. Phosphate concentration during different phases of the SBR operation

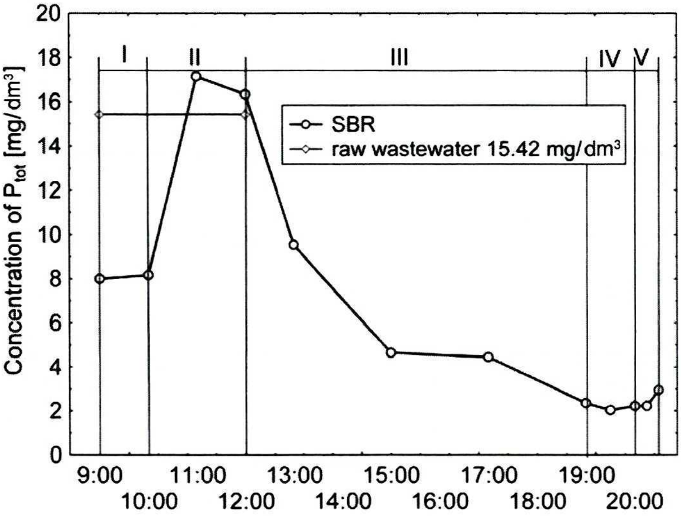

Fig. 6. Total phosphorus concentration during different phases of the SBR operation

The changes in the concentration of dissolved oxygen during different process phases in the reactor are shown in Figure 7. During the stage of static filling, the oxygen that was introduced into the system during the aeration phase was consumed by autotrophic nitrification organisms. No air was introduced into the system during the dynamic filling phase and the concentration of dissolved oxygen was close to zero (0.03 mg O_2/dm^3 on average). As has already been said, the denitrification took place and the process of secondary phosphorus release to the liquid at that time. Wastewater was aerated during phase III and the concentration of dissolved oxygen steadily increased up to the level of

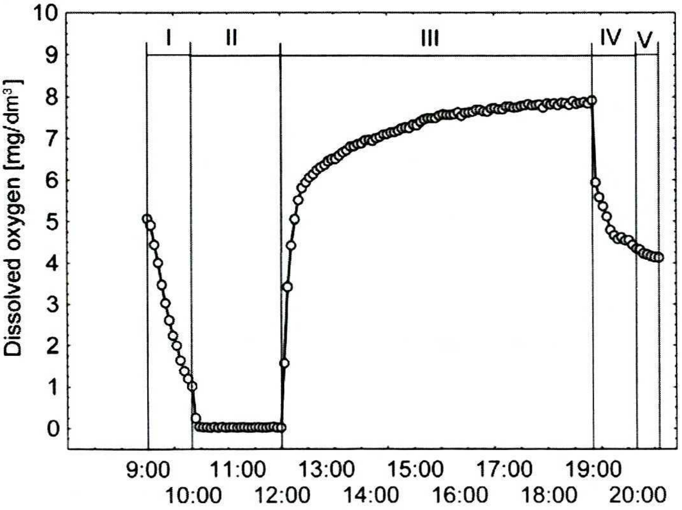

Fig. 7. Concentration of dissolved oxygen during different phases of the SBR system operation

8 mg O_2/dm^3. At this time, nitrification and biological dephosphatation took place. During phase IV and V the remaining oxygen, dissolved during the nitrification phase, was gradually consumed down to the concentration of 4 mg/dm^3 at the end of the decantation process (V).

Dissolved oxygen concentration is directly related to the redox potential, whose kinetics during the SBR system operation is presented in Figure 8. During the initial phase of static filling, the redox potential rapidly decreased from 11.7 mV to -211.6 mV, reaching the value of -332.2 mV at the end of the anoxic phase. The rapid decrease in the redox potential at the beginning of the anoxic phase was probably caused by denitrification. Raw wastewater introduced to the reactor has provided the necessary organic carbon to the system. The denitrification process, which requires reducing conditions, lasted until the end of the anoxic phase (during which time the concentration of nitrate(V) nitrogen and total organic carbon in the purified wastewater decreased – Figure 2 and Figure 4). With the beginning of the aeration phase, the redox potential began to increase steadily, reaching its maximum value (20 mV) at the end of decantation. When the redox potential increased during the aeration process, oxidation conditions prevailed and nitrification occurred – Figure 3.

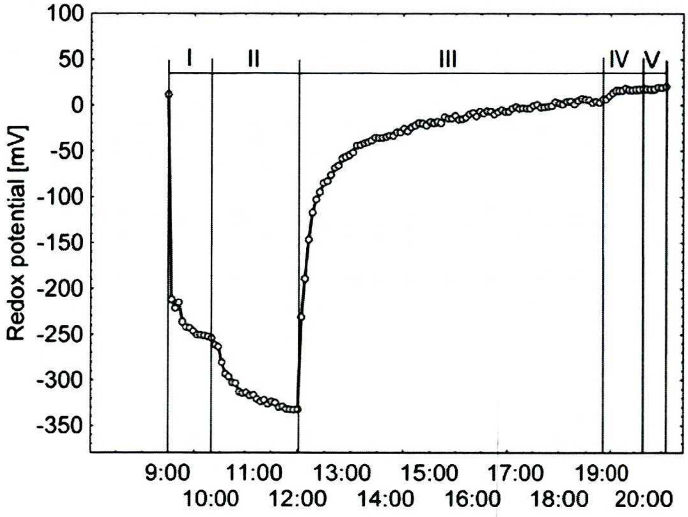

Fig. 8. The value of redox potential during different phases of the SBR system operation

Changes to the wastewater pH in the SBR reactor are shown in Figure 9. During the anoxic phase, pH of wastewater decreased due to the mixing of wastewater in the reactor (pH = 7.66) with neutral (pH = 7.25) raw wastewater. Further decrease in wastewater pH (to 6.85) was caused by increasing the amount of carbon dioxide, which was produced by decomposition of organic compounds in the denitrification process. Hydrolysis of organic substances and fermentation in phase I produced carbon dioxide and other acidic products, such as volatile fatty acids (VFA) that affected phosphorus compounds removal during phase III. After stirring was switched on, a slight pH increase to 7.2 was observed; when the wastewater in the reactor was thoroughly mixed, pH decreased to 6.85. The pH value increased during the oxidation phase and reaches a value of 7.97 at its end. An increase in the pH value during the oxidation phase resulted from consumption of carbon dioxide (carbonates) by nitrification organisms and removal of VFA.

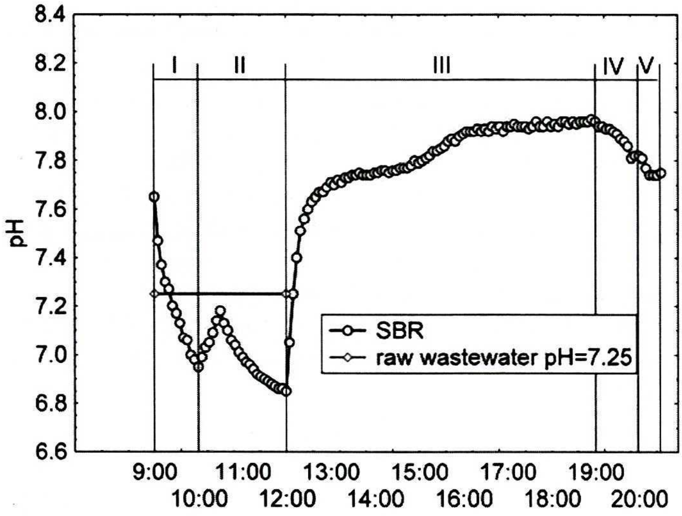

Fig. 9. Changes to wastewater pH during different phases of the SBR operation

SUMMARY

The 12-hour work cycle of the SBR reactor has ensured high effectiveness of contaminants removal from modeled dairy wastewater. Earlier research [17] indicated that a sludge age of 15 days was the optimum age for removal of most contaminants. The effectiveness of ammonium nitrogen removal was about 82%, which is similar to that of phosphorus (81.5% on average); TOC removal ratio was high – 97.75%. Only the concentration of nitrate(V) nitrogen increased, being higher after than before the purification process. Exploring the kinetics of the wastewater treatment process in an SBR reactor reveals characteristic changes in ammonium and nitrate(V) nitrogen concentrations for the nitrification and denitrification processes. Moreover, changes typical of phosphorus removal by phosphate microorganisms are also observable; during the anoxic phase the process of secondary phosphorus release to the liquid takes place.

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KINETYKA PROCESU OCZYSZCZANIA ŚCIEKÓW PRZEMYSŁU MLECZARSKIEGO W SYSTEMIE SBR

Na terenie zakładów mleczarskich powstają dwa rodzaje ścieków: poprodukcyjne i nieprodukcyjne. Oczyszczanie ścieków przemysłu mleczarskiego przebiega kilkuetapowo. W oczyszczaniu wstępnym ze ścieków usuwane są min. tłuszcze i piasek. Oczyszczanie drugiego stopnia to głównie oczyszczanie tlenowe metodą osadu czynnego, ale również metody pogłębionego utlenienia, a także oczyszczanie beztlenowe. W ostatnich latach coraz więcej zakładów decyduje się na oczyszczanie ścieków w sekwencyjnych reaktorach biologicznych (SBR), ponieważ wykazują się wysokim stopniem elastyczności w działaniu, pozwalając użytkownikowi zmieniać warunki, tak, aby dopasować je do zmieniającej się jakości ścieków surowych. W przeprowadzonych badania prześledzono kinetykę oczyszczania syntetycznych ścieków przemysłu mleczarskiego w systemie SBR. Analizowano usunięcie związków azotu, fosforu, węgla organicznego a także kinetykę stężenia tlenu rozpuszczonego i potencjału redoks. Badania przeprowadzono w skali laboratoryjnej w dwóch reaktorach o pojemności 12 dm^3 każdy. Reaktory pracowały w cyklu 12-godzinnym, z czego napełnianie trwało 3 godziny, napowietrzanie 7 godzin, następnie była godzinna sedymentacja, półgodzinna dekantacja i półgodzinna przerwa techniczna. W prezentowanych badaniach średnie stężenie zanieczyszczeń w ściekach surowych wynosiło: OWO 329 mg C/dm^3, azotu amonowego 11,15 mg N_{NH4}/dm^3, a fosforu ogólnego 15,42 mg P/dm^3.