

Treatment of sulphate containing yeast wastewater in an anaerobic sequence batch reactor

Marina Krapivina^a, Tõnu Kurissoo^b, Viktoria Blonskaja^{c*}, Sergei Zub^d,
and Raivo Vilu^a

^a Department of Chemistry, Tallinn University of Technology, Ehitajate tee 5, 19086 Tallinn, Estonia

^b BimKemi Eesti AS, Akadeemia tee 21G, 12618 Tallinn, Estonia

^c Department of Environmental Engineering, Tallinn University of Technology, Ehitajate tee 5, 19086 Tallinn, Estonia

^d AS Salutaguse Pärmitehas, Kohila, 79702 Raplamaa, Estonia

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Abstract. Anaerobic mesophilic fermentation of sulphate containing yeast industry wastewaters at laboratory scale with anaerobic sequence batch reactors (ASBR) was studied. Three different treatment schemes were investigated – ASBR with and without a polymeric filler and coupled micro-aerophilic/anaerobic SBR (CSBR). The optimal concentration of sludge (total solids 17.3 g L^{-1}) in the reactor and the optimal reaction time (22 h) were determined. It was shown that in the case of ASBR efficient treatment characterized by chemical oxygen demand (COD) removal of 75–82% took place at volume loading rates up to $7.7\text{--}8.0 \text{ kgCOD m}^{-3} \text{ d}^{-1}$ and at COD/ $(\text{SO}_4)^{2-}$ ratio 8.0. In optimal conditions the methane content of the biogas was 60%. The best results for sulphate removal (99%) were achieved in the CSBR with the concentration of sulphide in the reactor effluent being about 10 mg L^{-1} . Decreasing treatment efficiency after a long-time exploitation of these reactors occurred as a result of the formation of insoluble sediment (presumably CaCO_3 and $\text{Ca}_3(\text{PO}_4)_2$).

Key words: anaerobic sequence batch reactor (ASBR), calcium precipitates, high strength wastewater, sulphate reduction, yeast industry.

INTRODUCTION

Wastewater from the yeast industry contains extremely high concentrations of COD (up to 30 g L^{-1}) and sulphate (up to 4.5 g L^{-1}). For the treatment of high strength wastewaters anaerobic digestion appears to be economically more

* Corresponding author, viktoria.blonskaja@ttu.ee

attractive than aerobic processes. Two important goals are achieved simultaneously in anaerobic processes: removal of organic matter and sulphates.

Advantages of anaerobic digestion include also relatively low sludge production and low energy need compared with aerobic treatment. However, a high sulphate content can lead to the destabilization of the anaerobic treatment processes due to the hydrogen sulphide formation [1], especially if $\text{COD}/(\text{SO}_4)^{2-}$ is below 10 [2]. Despite these difficulties anaerobic digestion has been successfully applied for the treatment of a variety of sulphate-rich wastewaters both at laboratory and full-scale levels [1]. In comparison with continuous anaerobic methods, anaerobic digestion is a more flexible and cost-effective treatment technology [3]. However, there are no reports in the literature on the treatment of sulphate-rich wastewaters using anaerobic sequence batch reactors (ASBR).

The main aim of this research work was to study the treatment process of sulphate-rich high strength wastewaters from a yeast production plant using ASBR technologies.

MATERIALS AND METHODS

Experimental set-ups

Three different schemes of laboratory-scale experimental set-ups of ASBR were used. In the first experimental set-up (Fig. 1) a stand-alone ASBR was used. The ASBR with an active liquid volume of 0.7 L was made of glass tubing of $0.145 \text{ m} \times 0.075 \text{ m}$ (diameter). Plastic tubes were attached to the filling and

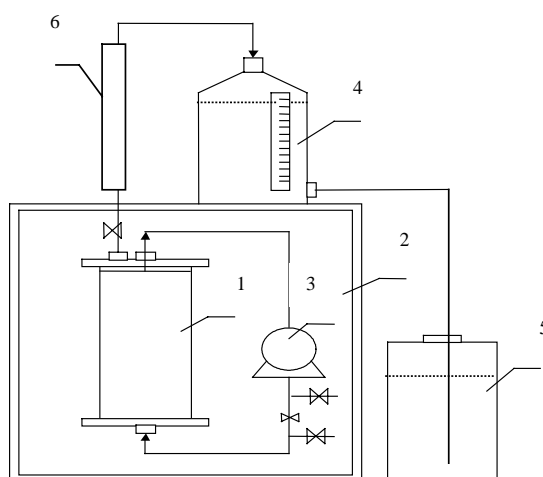


Fig. 1. Laboratory set-up for an anaerobic sequencing batch reactor. 1 – ASBR, 2 – thermostat, 3 – peristaltic pump, 4 – wet gas meter, 5 – water collector, 6 – alkali lock.

drawing ports. Peristaltic inflow pumps (Zalimp, Poland) were used at rates of $0.48\text{--}0.51\text{ L h}^{-1}$ to fill the reactor, draw off the effluent, and to mix the suspension during the treatment process. The temperature was maintained constant ($35 \pm 2^\circ\text{C}$) during the operation by a thermostat. Methane gas production was measured using a wet gas meter after absorption of CO_2 and H_2S in a scrubber with 10% NaOH solution.

In the second scheme the ASBR was loaded with a polymeric filler (Water Group, Germany): $0.8\text{ cm} \times 1.0\text{ cm}$ diameter, with a conditional surface area of $640\text{ m}^2\text{ m}^{-3}$. The volume of carriers was 0.5 L. Otherwise the experimental set-up was as in the first case.

In the third set-up, a coupled sequence batch reactor (CSBR) where the anaerobic effluent from the ASBR was recycled through a microaerophilic system was applied. Mixing in the microaerophilic reactor was carried out using a magnetic stirrer with regulated stirring speed (Beco, MM-5, 220 W). The biogas from the anaerobic reactor was passed to the microaerophilic reactor with the recycling effluent. The anoxic reactor was open and the temperature of the water was the same as the temperature of the air in the room ($20 \pm 2^\circ\text{C}$). The oxygen concentration was kept at $0.1\text{--}0.15\text{ mg L}^{-1}$.

Operating cycle parameters

The operating cycles of the ASBRs in all three set-ups consisted of three stages: (1) filling and decanting stage – this was accomplished by replacing the upper layer of the liquid in the reactors (effluent) with the lower layer adding influent to the bottom of the reactor, (2) reaction stage with uninterrupted agitation (by suspension recycling), and (3) sludge settling stage. The total cycle length was 24 h made up of 23 h of reaction–agitation, 0.5 h at rest for settling, and 0.5 h for filling and drawing (Fig. 2).

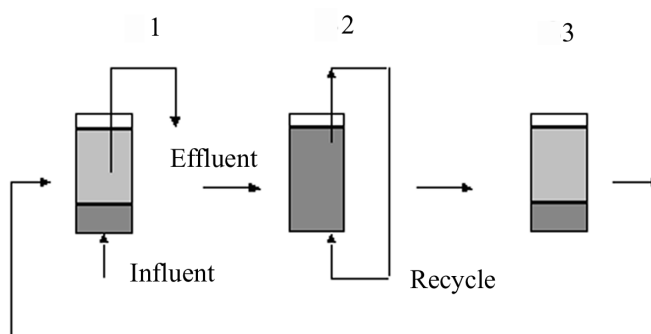


Fig. 2. Operation cycles of an ASBR. 1 – filling and decanting cycle, 2 – reaction cycle, 3 – sludge settling.

Sludge used

Two types of seed sludge were used for comparing the efficiencies of the processes. Anaerobic sludge from the anaerobic digester of the municipal wastewater treatment plant (WWTP), Tallinn, Estonia, which was not adapted for the treatment of sulphates, was used in the first two experimental set-ups, and sulphate adapted anaerobic sludge from full-scale anaerobic digesters of a yeast plant (AS Salutaguse Pärmitehas, Estonia) was used in the case of the CSBR.

Morphology of the sludge

The morphology of the seed sludge and of the sludge at the end of the experiments was investigated using microscopy. Sludge samples of 10 mL were washed with 10 mL of distilled water and allowed to settle while the turbid layer was drained. The procedure was repeated until the water became transparent. The washed sludge samples were placed into a 3.5 cm Petry dish and studied.

Microscopy of the structure of the seed anaerobic sludge from Tallinn WWTP showed that the sludge was of granulated type. The approximate size of granules was 1.7–2.0 mm. The sludge was mixed with sand, which seemed to be a good carrier of the sludge granules.

Investigation of the structure of the adapted to the sulphates seed anaerobic sludge from the Salutaguse yeast plant showed that the sludge was of flocculated type with a small percentage of single granules. The approximate size of granules was 0.5 mm. The activated sludge used in the CSBR experiment for seeding the microaerophilic reactor was completely flocculated.

Sulphate-rich high strength yeast production wastewaters

The reactors were fed with wastewater from the full-scale yeast production plant of Salutaguse (Estonia). The chemical composition of the wastewater was as follows: total COD 14.4–25.7 g L⁻¹, SO₄²⁻ 3.5–5.3 g L⁻¹, COD/SO₄²⁻ 2.71–7.63, total solids 12.9–21.6 g L⁻¹, total N 250–350 mg L⁻¹, total P 17.3–48.2 mg L⁻¹, trimethylglycine 3.7–4.0 g L⁻¹. Prior to treatment the wastewater was stored at 4 °C to prevent premature denaturation.

Sampling and monitoring

The production of biogas in anaerobic reactors, the influent and effluent pH, and the temperature of the sludge were measured daily. For the pH determinations a pH meter (E6121, Evicon) was used. Dissolved oxygen concentration in the microaerophilic reservoir was controlled twice a day by a conductivity and dissolved-oxygen meter (WTW.GMBH, M325/Oxi-L5). The COD, total solids (TS), sulphate, and total sulphides concentrations in the effluent were measured weekly, dissolved phosphorous and total nitrogen contents were analysed twice a

month. In all cases standard procedures described in standard methods [4] for wastewater examination were used. Effluent samples were drawn from the ASBR upon completion of the 30 min decant cycle. Sulphide and sulphate contents were determined immediately. The COD and phosphorous samples were frozen before analysis. Completely mixed samples were taken from the ASBR reactor before and after the end of the experiments and used for TS determination. The biogas composition was determined with gas chromatography.

RESULTS AND DISCUSSIONS

The optimal concentration of sludge for the start-up in usual anaerobic processes is 30–40% of the volume of the reactor, about 15 g L^{-1} of the sludge [5].

The start-up experiments with three different amounts of seed sludge were carried out during 47 days. Three identical reactors (first scheme) were seeded with 30% (TS 12.9 g L^{-1}) of anaerobic sludge obtained from the anaerobic digester (municipal WWTP, Tallinn, Estonia), 40% (TS 17.3 g L^{-1}), and 50% (TS 21.6 g L^{-1}), respectively. To allow biomass to adapt to sulphate-rich wastewater the sludge load was increased step-by-step (5% weekly). During the start-up period the organic load rate (OLR) was gradually increased from $1.4 \text{ kgCOD m}^{-3} \text{ d}^{-1}$ to $7.1 \text{ kgCOD m}^{-3} \text{ d}^{-1}$ (Fig. 3) and hydraulic retention time (HRT) was changed from 10 and to 2.5 days, respectively.

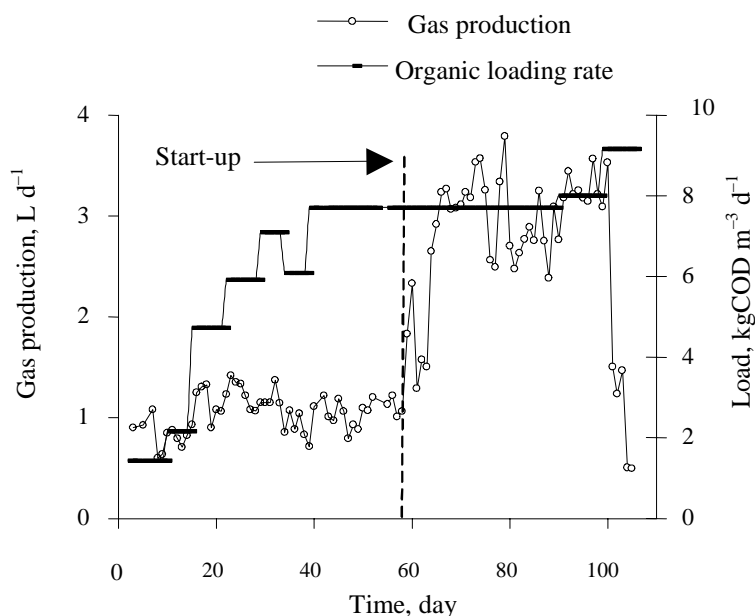


Fig. 3. Organic load and gas production during the experiment.

During a month following seeding the OLR of $7.7 \text{ kgCOD m}^{-3} \text{ d}^{-1}$ was maintained and then the reactors were operated at a constant OLR value. The efficiency of the treatment process during the start-up was monitored by biogas production (Fig. 4). A faster start-up of the reactor inoculated with 40% of sludge than of those inoculated with 30% and 50% of sludge was observed. The average gas production rates were 0.96 , 0.6 , and 0.4 L d^{-1} , respectively. Maximum gas production of 1.6 L d^{-1} was detected for the reactor with 40% sludge on the 27th day of experiments. On the basis of these results the reactor with the sludge concentration of 17.3 g L^{-1} was selected for the subsequent experiments.

As seen from Table 1, during the start-up period the COD removal efficiency in the reactor was rather low – 10–33%, but it increased toward the end of the

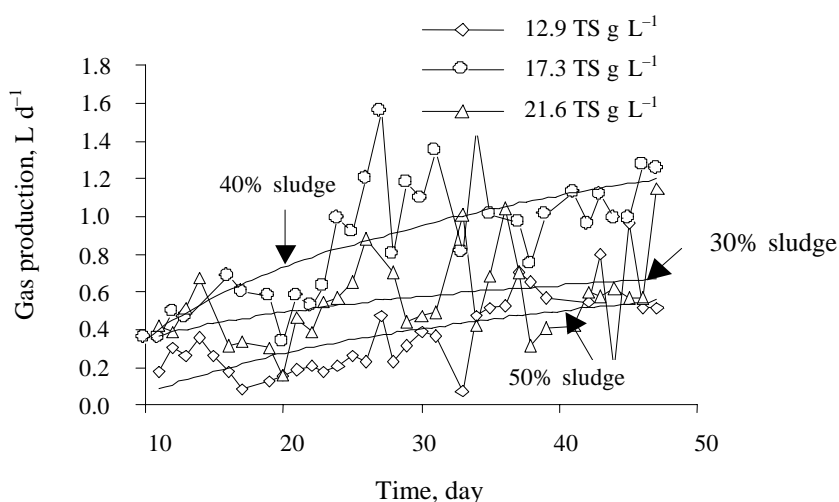


Fig. 4. Gas production at different seed sludge contents.

Table 1. Results of the experiment with the organic load TS 17.3 g L^{-1}

Day	COD in influent, mg L^{-1}	COD in effluent, mg L^{-1}	Organics removal efficiency, %	Gas production, $\text{m}^3 \text{ kg}^{-1} \text{ COD removal}$	Sulphate in influent, $\text{mgSO}_4^{2-} \text{ L}^{-1}$	Sulphate in effluent, $\text{mgSO}_4^{2-} \text{ L}^{-1}$	Sulphate removal efficiency, %	Sulphide in effluent, $\text{mg S}^{2-} \text{ L}^{-1}$
Start-up								
11	14 380	12 880	10	0.243	5 300	840	84	6.2
22	23 660	15 840	33	0.157	5 300	40	99	41.4
39	20 280	17 200	15	0.178	3 100	320	90	7.3
47	20 280	13 960	31	0.232	3 600	10	100	18.3
Steady state								
68	20 540	5 030	80	0.126	4 800	40	99	10.5
75	20 540	3 970	81	0.165	3 000	20	99	2.3
88	22 890	3 670	84	0.187	3 000	10	100	36.7
100	22 890	11 040	52	0.161	3 500	340	90	28.1

start-up period. The change of the operational parameters during the start-up could be explained by the process of adaptation of bacteria to a gradual increase of OLR (from 2.16 to 7.7 kgCOD m⁻³ d⁻¹).

Study of the ASBR process in the treatment of high strength sulphate containing yeast production wastewaters

The selected reactor with 40% sludge was operated during the start-up stage until day 39 and then a constant OLR value (7.7 kgCOD m⁻³ d⁻¹) was applied from 39th to 89th day of the experiment (see Fig. 3). On the 89th–105th days of operation the amount of the feedstock was increased to 0.35 L in order to check the maximum possible loading rate. The maximum OLR applied during this phase was 9.16 kgCOD m⁻³ d⁻¹ on the 98th day of operation. At this OLR inhibition of the treatment process was observed. Gas production decreased from 3.5 to 0.4 L d⁻¹ and the pH of the effluent fell to 6.01. The experiment was stopped after the process was destabilized (see data in Table 1).

Stabilization of the pH in the ASBR during the operations is shown in Fig. 5. During the first month of the ASBR experiment the pH of the influent was adjusted using 10% NaOH solution. Afterwards the reactor was operated without any adjustment and the average pH value of the reactor effluent was 7.4, which indicated a high efficiency of the anaerobic digestion process. Alkalinity did not vary much during the study, the average values always remained above 118 mEq L⁻¹. Alkalinity was presumably produced as a result of the reduction of sulphates to H₂S in the presence of organic carbon sources, which supplied the necessary energy in accordance with the following equation [6]:

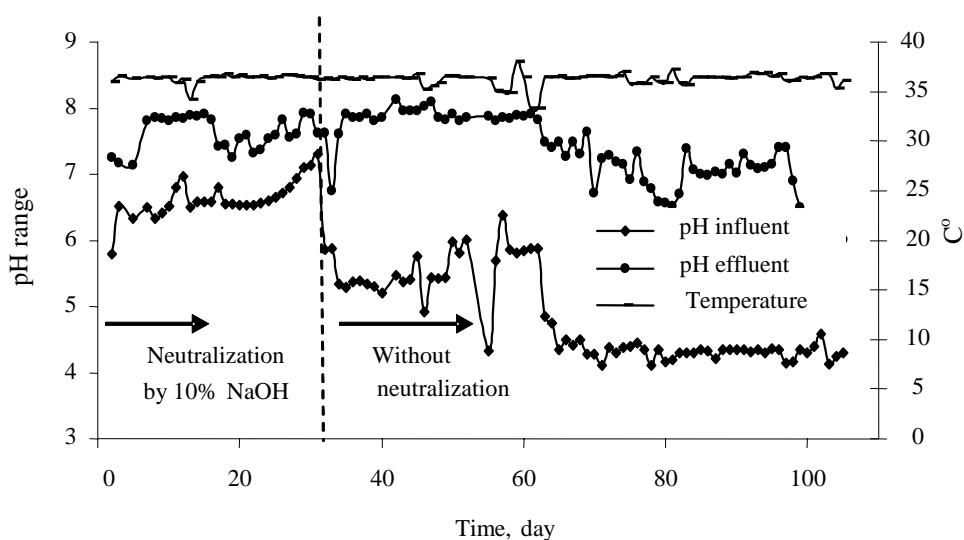


Fig. 5. Differences in the pH of the influent and effluent.

During the operation at a constant OLR of $7.7 \text{ kgCOD m}^{-3} \text{ d}^{-1}$ a significant increase in the removal efficiency to over 80% was observed. The maximum treatment efficiency (removal of 84% of COD) and the maximum biogas production of 3.79 L d^{-1} was reached at OLR values between 7.7 and $8.0 \text{ kgCOD m}^{-3} \text{ d}^{-1}$. At higher OLR (over $8.01 \text{ kgCOD m}^{-3} \text{ d}^{-1}$, days 89–105) the treatment efficiency decreased.

The data obtained on the treatment efficiency in COD removal were in agreement with the data published for yeast wastewater treatment process in [7].

The average sulphate removal efficiency was 95% in the experiment. Sulphate conversion to sulphide was greater than 80% during the start-up period. Then during days 39–89 when the OLR was constant no inhibition was detected and a nearly 100% removal efficiency was observed. Furthermore, the concentration of sulphates in the effluent did not exceed 40 mg L^{-1} . Due to the high OLR ($9.2 \text{ kgCOD m}^{-3} \text{ d}^{-1}$, day 98) the conversion efficiency decreased after day 100 to 90%. The data indicated that sulphate reduction was limited at higher OLR, and higher sulphate concentrations were observed in the influent. In fact, it has been supposed that for a successful anaerobic treatment a COD/SO₄²⁻ ratio higher than 10 is necessary [8]. Lower ratios were thought to be detrimental to methanogenesis because they led to the production of excessive sulphide concentrations ($>150\text{--}200 \text{ mg L}^{-1}$). In the experiment the sulphide concentrations in the effluents of neither ASBR nor CSBR exceeded the inhibitory levels (150 mg L^{-1} , [9]) despite the fact that the COD/SO₄²⁻ ratio of the influent was always lower than 8. The effluent sulphide concentration was lower than $41.4 \text{ mg S}_2\text{L}^{-1}$.

During the steady state period of operation (days 39–89) the rate of biogas production varied between 2.30 and 3.85 L d^{-1} . This indicated that the performance and functioning of the reactor were rather variable. The variability observed was caused most probably by competition between sulphidogens and methanogens and possible inhibitory influence of sulphides (average value $18.85 \text{ mg S}_2 \text{ L}^{-1}$), although they did not exceed the inhibitory level.

The composition of biogas was measured on the 68th day of the experiment and was as follows: 60% CH₄, 35% CO₂, 2.7% H₂S. This composition indicated that mainly methanogenic mineralization of organic matter was taking place in the ASBR. The biogas production rate during the operation cycle was measured on the 50th day of the experiment. The data obtained showed that the rate of biogas production was the greatest at the start of the cycle (during the first 7 h after the period of raw water input), and then slowly decreased with time, reaching very low and relatively stable levels at the end of the reaction stage. Biogas production completely stopped in the reactor on the 22nd–23rd hour of the cycle. The data showed that the lengths of the stages of the treatment cycle had been chosen correctly.

Previous results have indicated that inoculation of UASB with non-sulphate-adapted sludge could lead to complete inhibition of the treatment process [2] because bacterial groups, especially methanogens, could not adapt to the high levels of sulphide present in the influent. However, in our research full inhibition

of the process did not take place. This could be explained by the presence of non-competitive substrates for methanogens (trimethylglycine) in yeast wastewater. Since trimethylglycine remains undetected by a COD dichromate assay, its concentration can be underestimated, which in turn may lead to a significant overloading of WWTPs. It is known that sugarbeet molasses used as a component of the growth medium for baker's yeast [5] in the Salutaguse yeast plant contains up to 6% w/w trimethylglycine. In anaerobic treatment plants, trimethylglycine is practically totally degraded through a multistep degradation process with the formation of nitrogen-containing intermediates – trimethylamine and other methylated amines [10]. These intermediates are further degraded by methanogenic bacteria, yielding CO₂, ammonium, and methane. The presence of trimethylglycine could allow methanogens to maintain a significant population in a sulphate containing environment, which stimulates the growth of sulphate reducing bacteria (SRB), competitors of methanogens for the same substrates in the anaerobic treatment processes. Degradation of trimethylglycine (trimethylglycine is a nitrogenous compound, whose complete anaerobic degradation can result in an increase of the effluent ammonia concentration) and formation of amines can explain also accumulation of N_{tot} during the experiments carried out by us (see Table 2).

As seen from Table 2, the effluent concentrations of N_{tot} increased on average from 236 to 570 mgN L⁻¹. It should be noted that removal of all nitrogen compounds would require anaerobic, microaerophilic, and aerobic conditions established simultaneously in different locations of the anaerobic reactor, which is highly improbable in the case of the small-scale laboratory vessels used in our experiments.

The results of the present study (Table 2) demonstrate the ability of the ASBR process to achieve a good phosphorus removal efficiency – up to 61%. As calcium chloride is used in the technological process of yeast production, wastewaters are characterized by a rather high content of calcium ions. Under these conditions the high phosphorous removal efficiency could be explained by precipitation as a result of the formation of insoluble Ca₃(PO₄)₂.

Table 2. Change of phosphorus and nitrogen content in the ASBR during the steady-state period

Day	N _{tot} in influent, mg L ⁻¹	N _{tot} in effluent, mg L ⁻¹	N accumulation, %	P _{tot} in influent, PO ₄ ³⁻ mg L ⁻¹	P _{tot} in effluent, PO ₄ ³⁻ mg L ⁻¹	P removal efficiency, %
39	245	275	12	32.2	13.9	56.9
47	475	870	83	48.2	24.3	49.6
68	325	650	100	28.5	22.2	22.1
75	345	550	59	17.3	15.3	10.7
88	255	690	170	32.6	19.2	41.1
100	250	270	8	34.2	13.3	61.1

Despite the high sulphate treatment efficiency achieved in the ASBR, sulphide production during the process was significant, and this led to the observed instability of the process. In the large-scale experiments the instability of the processes could create significant difficulties in applying the ASBR technology for the treatment of yeast wastewaters. In addition to the inhibition of the process, sulphide formation caused also major malodour problems and corrosion of equipment during the experiment. In the further experimental work two modifications of the ASBR technique were investigated to reduce the problems noted. Accumulation of sulphides was an indication that competition between methanogens and SRB was won by the latter.

The aim of the further investigation was to find experimental conditions where methanogens would prevail, and the reduction of sulphate would stop at the level of elemental sulphur. An ASBR with a polymeric filler and coupled microaerophilic/anaerobic sequence batch reactor (CSBR) were investigated.

ASBR with a polymeric filler

Experiments with a polymeric filler used as a support material for micro-organisms were performed in order to study the influence of an artificial filler on the efficiency of the process. Previous studies [11] had shown that the use of a support material favours the adherence of methanogenic bacteria and accelerates the washout of SRB. A poor attachment ability of SRB was demonstrated. It was concluded on the basis of the experimental results that in the presence of a filler SRB are washed out of the reactor providing acetotrophic methanogenic bacteria with a sufficient growth advantage. These data suggest that an artificial carrier could stimulate methanogenic activity in the anaerobic digester and increase the efficiency and stability of the treatment processes.

Two reactors were operated in our series of experiments during 68 days. One was loaded with a polymeric filler and the other was operated like the first one but without the filler. The operational conditions were the same as described in the previous experiments. The COD and sulphate removal efficiencies were not significantly different between the two reactors studied; however, in the reactor without the carrier a slightly higher average treatment efficiency was observed, sulphate removal efficiencies varied from 85% to 100%. The sulphide concentrations in the effluents of either reactors did not exceed inhibitory levels and were not higher than 123 and 110 mg L⁻¹, respectively. These data are in agreement with the results of our previous experiment. The efficiency of phosphorous removal in the reactor with the carrier was significantly higher (up to 79%) than in the control reactor (57%). It can be assumed that the carrier promoted deposition of insoluble materials, for example precipitation of Ca₃(PO₄)₂. This conclusion was supported by the observation that scaling of the carrier beads was observed in the experiment. The fast clogging of the system with a carrier when treating sulphate-rich wastewaters has been described also in several other studies [12, 13]. In addition to facilitating scaling, a carrier could hamper equal

distribution of wastewater over the sections of the reactor, which could result in a lower COD and sulphate treatment efficiency. Therefore it can be concluded that the application of the carrier for the given treatment system was not effective and cannot be recommended.

Coupled microaerophilic/anaerobic system (CSBR)

In the CSBR the effluent from the anaerobic reactor was recycled through an aeration system. The content of oxygen in the microaerophilic reservoir was kept at the level of 0.1–0.15 mg L⁻¹ to prevent sulphate formation in the oxidation of the sulphide formed in the anaerobic stage of the process leaving sulphur in the form of elemental sulphur (S⁰) [14]. It was assumed to be the best for simultaneous solution of two problems: sulphate and sulphide removal. The formation of elemental sulphur is an advantage because sulphur is a colloid, inert solid and can be removed from the wastewater for example by gravity sedimentation. The anaerobic reactor was seeded with sulphate adapted anaerobic sludge, and the microaerophilic reactor was seeded with activated sludge obtained from the full-scale aerobic reactor of the Salutaguse yeast plant, Estonia.

The CSBR was operated during 68 days under the operational conditions described in previous experiments. The maximum OLR achieved was 7.74 kgCOD m⁻³ d⁻¹. The average pH value of the final effluent was 8.2 and the alkalinity always remained up to 177 mEq L⁻¹ at the average pH of the influent 4.2. No attempts were made to adjust the pH of the influent. High pH values could be explained by the formation of hydroxide ion during the following biological overall reaction, taking place in a microaerophilic sulphide removal system [15]:



The results obtained allow us to conclude that a rather good COD removal efficiency (50–70%) was achieved during the experiment. Since the sludge had been well adapted to wastewater a very quick start-up was observed. Only a few days after seeding, the COD removal significantly increased and reached 70%.

The optimal COD loading found for the ASBR was 6–8 kgCOD m⁻³ d⁻¹. The highest COD removal efficiencies, exceeding 65% in the CSBR, were observed at the same (from 6 to 8 kgCOD m⁻³ d⁻¹) OLR values (Fig. 6).

Taking into consideration that the optimal ORL value reported in the literature [1] for different methanogenic reactors varies remarkably – from 4 to 12 kgCOD m⁻³ d⁻¹ – the results obtained in our experiments were quite good for the treatment of high strength sulphate-rich wastewaters. The sulphate removal efficiency achieved in our experiments was excellent – more than 98%. Due to the low dissolved oxygen concentration (0.1–0.15 mg L⁻¹) there were almost no sulphides and sulphates in the effluent (Fig. 7). Only approximately 0.5 mg L⁻¹ of H₂S and 0–30 mg L⁻¹ of SO₄²⁻ were present in the effluent while up to 3.6 g L⁻¹ of sulphate had been reduced.

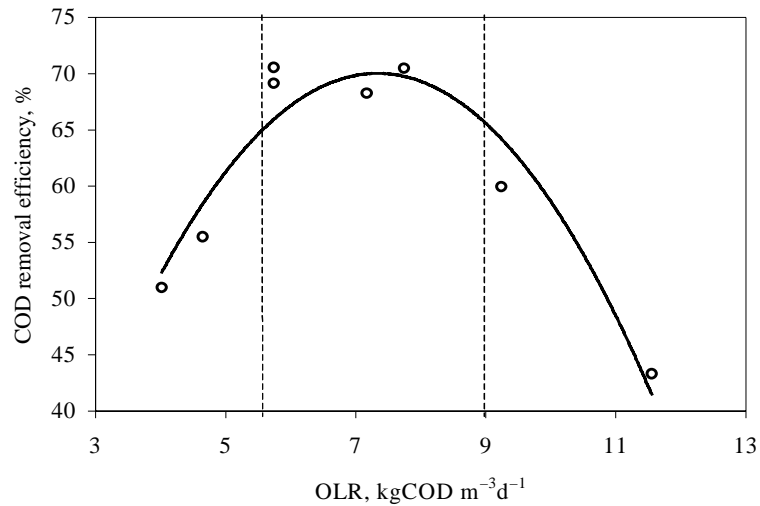


Fig. 6. Relationship between OLR and the efficiency of COD removal.

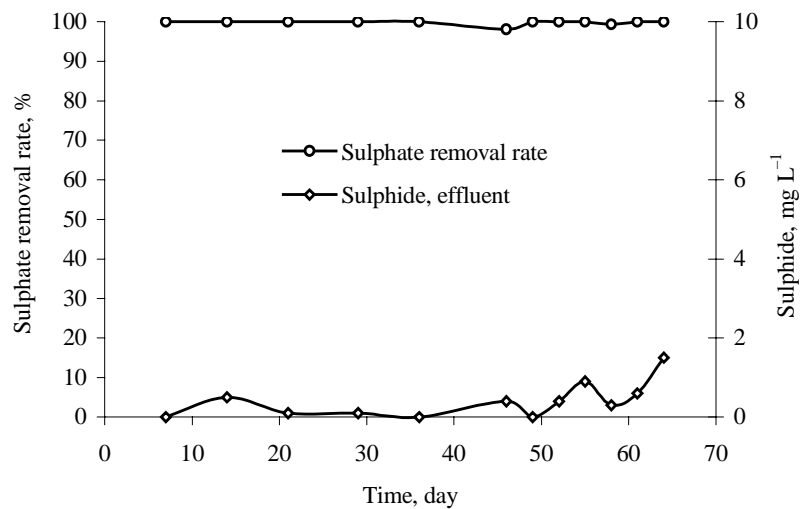


Fig. 7. Concentration of sulphide and the rate of sulphate removal.

Our data suggest that keeping a low level of the dissolved oxygen concentration in the microaerophilic part of the treatment system helps to poise the treatment process towards the formation of elemental sulphur and that the coupled microaerophilic/anaerobic treatment processes of sulphate-containing wastewaters were effective in alleviating sulphide inhibition of both methanogenesis and sulphate reduction. Last but not least, the exceptional stability of the CSBR process should be noted. The operational conditions worked out in the

laboratory-scale experiments were successfully applied at full scale in the Salu-taguse yeast plant, where the process has been applied by now for more than a year.

Final sludge tests

Microscopic examination of the sludge and of the biomass concentration were performed at the beginning and at the end of each experiment. In none of our experiments granulation was detected. However, significant changes in the structure of the sludge were recorded.

Serious scaling of biomass by inorganic precipitation was observed already during 3.5 months of operation. Measurements of biomass concentration showed that the density of the sludge had also significantly changed since the start of the experiments. The sludge concentration varied between 43.2 g TS L^{-1} at the beginning of the experiment and 62 g TS L^{-1} in the ASBR and 65.2 g TS L^{-1} in the CSBR at the end of the study (Fig. 8). The difference between the values of total solids and volatile suspended solids indicated the presence of inorganic salts in suspension, possibly calcium carbonate and phosphates. Due to the formation of elemental sulphur in the CSBR a faster accumulation rate of inorganic compounds was observed than in the ASBR. With all advantages of this type of reactor the fast accumulation of inorganic compounds is an essential disadvantage. Precipitation of inorganic salts, as for example calcium carbonate, can indirectly upset the reactor performance by scaling [6, 16], which interferes with a good mass transport of substrate and reaction products. Scaling of biomass by Ca precipitates (CaCO_3 and/or $\text{Ca}_3(\text{PO}_4)_2$) may already occur at Ca^{2+} concentrations of 400 mg L^{-1} [17]. Also clogging problems can arise from precipitates in the piping system. Unfortunately, the concentration of calcium in the influent and effluent was not measured in the present study and the problem of the formation and removal of inorganic precipitate requires more detailed study in the future.

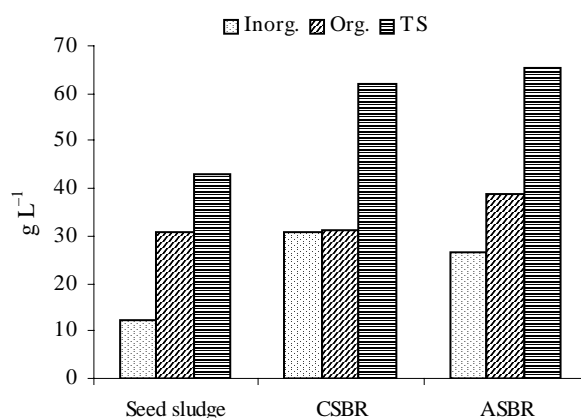


Fig. 8. Changes in the sludge composition during the CSBR and the ASBR processes.

CONCLUSIONS

The results of the study carried out demonstrated that the anaerobic sequencing batch reactor (ASBR) is a suitable and effective tool for anaerobic treatment of sulphate-rich wastewaters from baker's yeast production plants. Optimal parameters of the process were determined. However, sulphide formation caused significant malodour problems and corrosion of equipment during the experiment.

Experiments with two additional schemes developed for solving the sulphide formation problem showed that use of plastic carriers in the reactor led to a decrease of the treatment efficiency due to the accumulation of insoluble sediment (presumably CaCO_3 and $\text{Ca}_3(\text{PO}_4)_2$) on the surface of the carriers. So this technology cannot be recommended for large-scale application.

Combination of anaerobic sulphate reduction with biological oxidation of sulphide in a coupled microaerophilic/anaerobic SBR (CSBR) showed the best results and might be preferable for the treatment of sulphate-rich yeast wastewaters. As the scaling of biomass and fast accumulation of inorganic compounds were observed also in this case, successful application of the CSBR technology requires finding a solution for the removal of the inorganic precipitate from the reactor. The data obtained by us will be useful in designing full-scale ASBR and CSBR processes.

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REFERENCES

1. Lens, P. N. L., Omil, F., Lema, J. M. & Hulshoff-Pol, L. W. Biological treatment of organic sulphate-rich wastewaters. In *Environmental Technologies to Treat Sulphur Pollution* (Lens, P. & Hulshoff-Pol, L., eds). IWA Publishing, London, Alliance, 2000, 467–489.
2. O'Flaherty, V. & Colleran, E. Effect of sulphate addition on volatile fatty acid and ethanol degradation in an anaerobic hybrid reactor, I: process disturbance and remediation. *Biores. Tehnol.*, 1999, **68**, 101–110.
3. Sung, S. & Dague, R. R. Laboratory studies on the anaerobic sequencing batch reactor process. *Water Environ. Res.*, 1995, **67**, 291–294.
4. Clesceri, L. C., Breenberg, A. E. & Trussel, R. R. *Standard Methods for the Examination of Water and Wastewater*. Washington, DC, USA, 1989.
5. Blonskaja, V., Menert, A., Kurisoo, T. & Vilu, R. Use of biological oxidation in the operation of anaerobic digester with sulphate-rich wastewaters. In *Proc. 9th World Congress Anaerobic Digestion*. Antwerpen, Belgium, 2001, Part 1, 713–718.
6. Maree, J. P., Hulse, G., Dods, D. & Schutte, C. E. Pilot plant studies on biological sulphate removal from industrial effluent. *Water Sci. Technol.*, 1991, **23**, 1293–1300.

7. Doorn, M., Strait, R. & Barnard, W. In *Estimates of Global Greenhouse Gas Emissions from Industrial and Domestic Wastewater Treatment*. Environmental Protection Agency Office of Research and Development, Washington, 1997, 148.
8. Rinzema, A. & Lettinga, G. Anaerobic treatment of sulphate containing wastewater. In *Bio-treatment Systems* (Wise, D. L., ed.). CRC Press, Boca Ration, 1988, 65–109.
9. Lens, P. N. L., Visser, A., Janssen, A. J. H., Hulshoff-Pol, L. W. & Lettinga, G. Biotechnological treatment of sulfate-rich wastewaters. *Crit. Rev. Environ. Sci. Technol.*, 1998, **28**(1), 41–88.
10. Welsh, D. T. Ecological significance of compatible solute accumulation by microorganisms: from single cells to global climate. *FEMS Microbiol. Rev.*, 2000, **24**, 263–290.
11. Isa, Z., Grusenmeyer, S. & Vertraete, W. Sulfate reduction relative to methane production in high rate anaerobic digestion: technical aspects. *Appl. Environ. Microbiol.*, 1986, **51**, 580–587.
12. Matuzevičius, A. & Dilba, A. Experience in using anaerobic reactors for treating highly polluted wastewater. *Environ. Engin.*, 1999, **4**, 206–208.
13. Thalasso, F., Van Der Burght, J., O'Flaherty, V. & Colleran, E. Large-scale anaerobic degradation of betaine. *J. Chem. Technol. Biotechnol.*, 1999, **74**(12), 1176–1182.
14. Buisman, C. J. N., Bert, G. G., Lispeert, P. & Lettinga, G. Optimisation of sulphur production in a biotechnological sulphide-removing reactor. *Biotechnol. Bioeng.*, 1990, **35**, 50–56.
15. Buisman, C. N. J., Stams, A. J., Meijer, H. & Lettinga, G. Sulphur and sulphate reduction with acetate and propionate in an anaerobic process for sulphide removal. *Appl. Microbiol. Biotechnol.*, 1989, **32**, 363–370.
16. Lettinga, G. Anaerobic wastewater treatment systems. *Ant. Leeuw.*, 1995, **67**, 3–28.
17. Hulshoff Pol, L., Lens, P., Stams, A. J. M. & Lettinga, G. Anaerobic treatment of sulphate-rich wastewaters. *Biodegradation*, 1998, **9**(3–4), 213–224.

Pärmitööstuse sulfaate sisaldavate reovete töötlemine anaeroobse annuspuhasti reaktoris

Marina Krapivina, Tõnu Kurisoo, Viktoria Blonskaja, Sergei Zub
ja Raivo Vilu

Laboratoorse annuspuhastina töötava anaeroobse reaktori (ASBR) vahendusel on uuritud pärmitööstuse mesofiilsel temperatuurirežiimil sulfaate sisaldavate reovete puhastusprotsessi. On kasutatud kolme erinevat režiimi: puhastusprotsessi läbiviimist vabalt elunevate anaeroobsete bakterite suspensiooniga, polümeerse täidise pinnale kinnitunud anaeroobsete bakteritega ja mikroaerofiilset/anaeroobset töötlust annuspuhastis (CSBR). Anaeroobsete bakterite suspensiooni optimaalseks kontsentratsiooniks on leitud $17,3 \text{ g L}^{-1}$ kuivaine järgi ja reaktsioonijaks 22 tundi. ASBR-i režiimis töötavas seadmes alaneb KHT 75–82% mahukoormuse $7,7\text{--}8,0 \text{ kgKHT m}^{-3} \text{ d}^{-1}$ ja KHT/(SO₄)²⁻ suhte 8,0 korral. Eralduvas biogaasis on metaanisisaldus optimaalsete tingimuste korral 60%. Parim tulemus (99%) sulfaatide sisalduse alandamisel saavutatakse CSBR-i režiimil, kusjuures reaktorist väljunud reovees on sulfiidioonide sisaldus 10 mg L^{-1} piires. Annuspuhastina töötava anaeroobse reaktori pikaajalisel töös hoidmisel väheneb puhastusprotsessi efektiivsus, mis on autorite hinnangul tingitud lahustumatu mineraalse sette moodustumisest, mis võib koosneda kaltsiumkarbonaadist (CaCO₃) ja kaltsiumfosfaadist (Ca₃(PO₄)₂).