

Comparison of Σ LMW Utilization Rate from Saline Wastewater in SBR Reactors with Granular and Flocked Activated Sludge [†]

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Abstract: Paper discusses changes in utilization rate of Low Molecular Weight polycyclic aromatic hydrocarbons PAHs in sequencing bath reactors (SBR) operating with flocked and aerobic granular activated sludge. Studies were carried out in laboratory scale SBR reactors filled with model wastewater characterized by salinity at level $4.00 \text{ g}\cdot\text{dm}^{-3}$. Wastewater inflowing to laboratory reactors was characterized by varying biological oxygen demand (BOD) load in the range of $0.05\text{--}1.60 \text{ kg BOD}\cdot\text{kg}^{-1}\cdot\text{d}^{-1}$.

Keywords: Σ LMW; saline wastewater; aerobic granular activated sludge

1. Introduction

Saline wastewater treatment with activated sludge method is still a current problem. In addition to known so far wastewater from industries, this type of wastewater may also arise as a result of shale gas extraction by hydraulic fracturing. The chemical composition of these wastewater varies in different extraction area and results from different proportions and types of chemical additives, varying water parameters that forms the basis of fracturing fluid and, above all, the diversified chemical structure of the rocks in which shale gas is trapped [1]. Parameters often quantified in this kind of wastewater are biological oxygen demand (BOD), chemical oxygen demand (COD), concentrations of nitrogen and phosphorus forms, salinity, amount of heavy metals and macroelements, as well as hydrocarbons, including polycyclic aromatic hydrocarbons.

As by-products formed in result of incomplete organic substances combustion [2], polycyclic aromatic hydrocarbons (PAHs) can be divided into a lighter and heavier fraction due to their molecular weight. The light PAHs fraction defined by the abbreviation LMW (Low Molecular Weight) describes the sum of hydrocarbons consisting of 2 and 3 aromatic rings, while the heavier fraction, abbreviated HMW (High Molecular Weight) describes the total concentration of hydrocarbons with four or more aromatic rings [3].

The aim of the study was to analyze the utilization rate of LMW PAHs from saline wastewater in sequencing bath reactors (SBR) operating with granular and flocked activated sludge. The reactors were supplied with model wastewater with salinity equal to $4.00 \text{ g}\cdot\text{dm}^{-3}$.

2. Materials and Methods

The laboratory SBR reactors used in studies were made of hardened polyethylene (HDPE). SBR laboratory model was supplied with an aerator of $550 \text{ dm}^3\cdot\text{h}^{-1}$ capacity. The total chamber volume was 16 dm^3 , while active reactor volume was 15 dm^3 . Studies were carried out in 12-hour operation

cycle, with 30 minutes filling phase duration, 90 minutes of mixing (anaerobic) phase, 540 minutes of mixing and aeration (aerobic) phase, 60 minutes of sedimentation phase and 30 minutes of decantation phase. Studies were carried out in simultaneously in two SBR reactor, one with aerobic granular activated sludge (R1) and one with flocculated activated sludge (R2).

Wastewater used in studies was prepared from peptone K (0.113–4.520 g·dm⁻³), enriched dry broth (0.076–3.040 g·dm⁻³), NH₄Cl (0.010–0.400 g·dm⁻³), NaCl (6.59 ± 0.01 g·dm⁻³), CaCl₂·6H₂O (0.004–0.160 g·dm⁻³), MgSO₄·7H₂O (0.001–0.040 g·dm⁻³), KH₂PO₄ (0.008–0.320 g·dm⁻³) and K₂HPO₄ (0.020–0.800 g·dm⁻³).

Sum of low molecular weight hydrocarbons ΣLMW included PAHs containing in their structure from 2 to 4 rings, that is: naphthalene, acenaphthene, acenaphthylene, fluorene, phenanthrene and anthracene. ΣLMW quantitative analysis was performed by chromatography using a gas chromatograph coupled with a mass detector GC/MS Agilent 7890B in the column DB-5MS. The stationary phase of the column was polydimethylsiloxane with a 5% share of phenyl groups. For the studied PAHs, analysis scanning mode of single ion monitoring (SIM) was chosen. Carrier gas was Helium with 6.0 purity with flow rate 1 mL·min⁻¹ (splitless). Injected sample volume was 1 µL. Temperature of dispenser, ion source and transfer line were respectively equal to 260 °C, 230 °C and 300 °C. The initial furnace temperature was 60 °C with 2 min isotherm. Temperature increase to 120 °C was 30 °C·min⁻¹; above 120 °C to 300 °C was 5 °C·min⁻¹. The final furnace temperature was 300 °C, with 15 min isotherm [4]. Described method validation results are given in Table 1.

Table 1. Gas chromatography (GC) method validation results.

Substance	Jon	Limit of Detection (LOD) ng·dm ⁻³	Limit of Quantification (LOQ) µg·dm ⁻³	Relative Standard Deviation (RSD)	Linear fit Coefficient R ² n = 5	Recovery %	Concentration Range µg·dm ⁻³
naphthalene	128	0.21	0.1340	0.04	0.995	96.00	0–1000
acenaphthalene	152	0.11	0.1340	0.02	0.999	95.00	0–1000
acenaphthene	154	0.15	0.5120	0.03	0.993	95.00	0–1000
fluorene	166	0.12	0.0530	0.02	0.993	93.00	0–1000
phenanthrene	178	0.10	0.1900	0.02	0.993	92.00	0–1000
anthracene	178	0.13	0.1210	0.04	0.997	97.00	0–1000

The ΣLMW utilization rate was calculated according to the following equation:

$$S_x = \frac{C_{pf} - C_{kf}}{t \cdot sdm} [\mu\text{g} \cdot \text{g}_{sdm}^{-1} \cdot \text{h}^{-1}] \tag{1}$$

S_x- ΣLMW utilization rate in µg·g_{sdm}⁻¹·h⁻¹, C_{pf}- concentration of ΣLMW at the beginning of anaerobic or aerobic SBR phase in µg·dm⁻³, C_{kf}- concentration of ΣLMW at the end of anaerobic or aerobic SBR phase in µg·dm⁻³, t- duration of the unit phase (anaerobic or aerobic) of the SBR reactor in h and sdm- activated sludge dry mass, which in the experiment was a constant value of 4.00 g·m⁻³.

On the basis conducted studies, a variance analysis was carried out, aimed at indicating statistically significant differences between the rate of ΣLMW removal in the anaerobic and aerobic phase of SBR reactors operating with granular and flocculated sludge. The factor relative to the ΣLMW utilization rate was SBR reactor process phase and BOD load inflowing to reactor. The Tukey test was selected to assess the statistical significance (α = 0.05) of observed phenomena. The statistical analysis was carried out using the Statistica 13.1 software on the Windows 10 platform. A total of 1624 measurement results were used for statistical analysis.

3. Results and Discussion

At the initial research stage, the efficiency of ΣLMW removal reached around 40%. Then, a gradual decrease in the removal efficiency for this group was observed, which depended on the BOD load inflowing to reactor. The decrease in ΣLMW removal efficiency was observed from 34th experiment day (above the BOD load of 1.00 kg BOD·kg⁻¹·d⁻¹) until the end of studies in both reactors.

During aeration phase, ΣLMW removal effect had a (Figures 1 and 2) similar changes trend in both reactors. In the granular sludge reactor, the removal effect was about 70%. From day 26 (BOD load 0.80 kg BOD·kg⁻¹·d⁻¹), a gradual decrease in removal effect of discussed ΣLMW was observed

(to 20%), which lasted until 46 experiment day (BOD load 1.20 kg BOD·kg⁻¹·d⁻¹). In contrast, in the reactor with flocced activated sludge, a gradual decrease in the removal effect of studied LMW PAHs was observed. At the initial research stage, the removal efficiency of this group was about 60%, while at the final stage of the study, it did not exceed 10%.

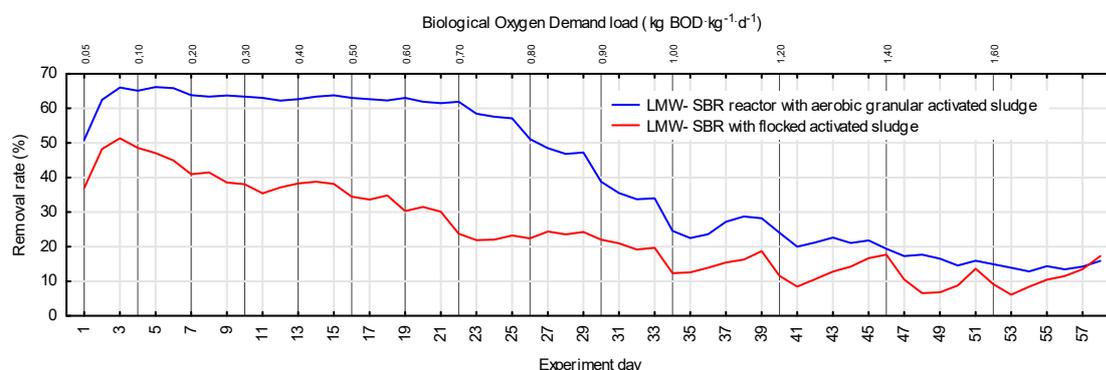


Figure 1. Sum of low molecular weight polycyclic aromatic hydrocarbons (ΣLMW) removal rate in sequencing bath reactor (SBR) anaerobic phase.

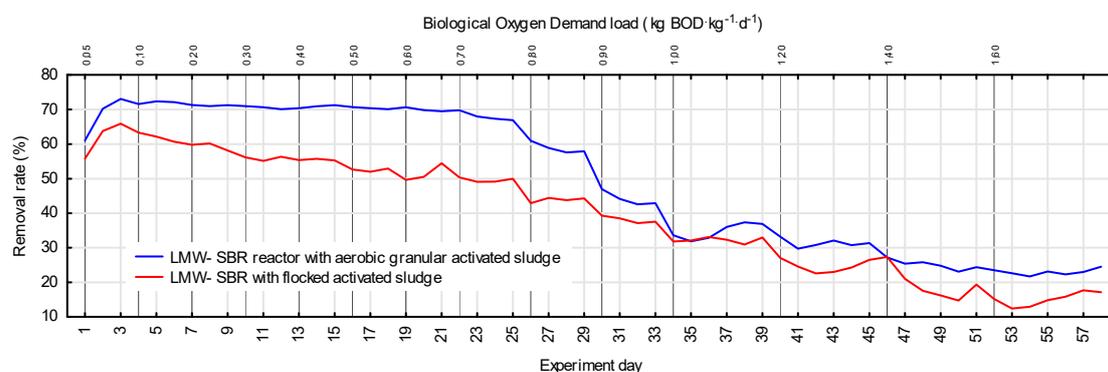


Figure 2. Sum of low molecular weight polycyclic aromatic hydrocarbons (ΣLMW) removal rate in sequencing bath reactor (SBR) aerobic phase.

ΣLMW utilization rate (Figure 3) during the first 25 days (to BOD load = 0.70 kg BOD·kg⁻¹·d⁻¹) was removed at the highest rate, which was 6.75 μg·g_{sdm}⁻¹·h⁻¹. After 25 days (BOD load above 0.70 kg BOD·kg⁻¹·d⁻¹) a gradual decrease in the utilization rate was observed which at the final stage of the study was about 0.75 μg·g_{sdm}⁻¹·h⁻¹. In reactor with flocced activated sludge ΣLMW utilization rate was lower and its maximum value was equal to 6.00 μg·g_{sdm}⁻¹·h⁻¹.

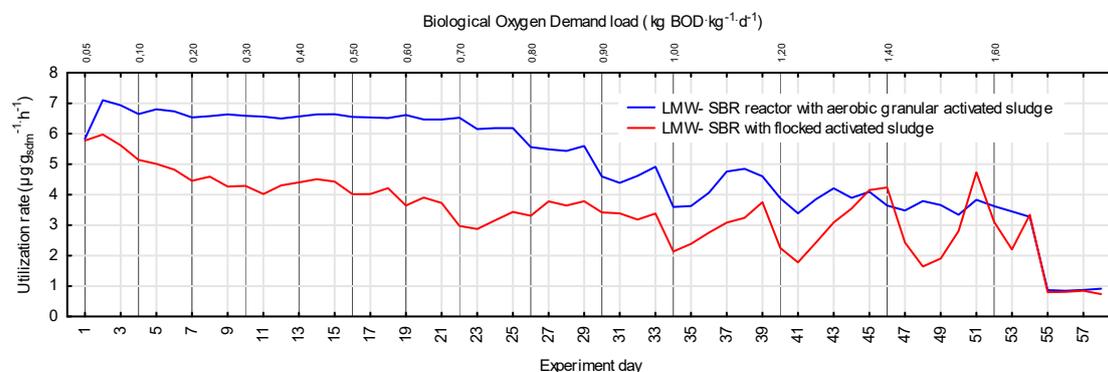


Figure 3. Sum of low molecular weight polycyclic aromatic hydrocarbons (ΣLMW) utilization rate in anaerobic phase.

Σ LMW utilization rate in the aeration phase was similar in both reactors (Figure 4). No effect on Σ LMW utilization rate was observed when increasing the BOD load. During the research period, Σ LMW was removed at a similar rate on both activated sludge types and was equal to $0.79 \mu\text{g}\cdot\text{g}_{\text{sdm}}^{-1}\cdot\text{h}^{-1}$.

Pugazhendi and others [5] showed that the halothermophilic consortium degrade to 90% of LMW PAHs at their initial concentration of $1500.00 \text{ mg}\cdot\text{dm}^{-3}$ in wastewater with salinity from 4–30%. PAH removal effectiveness that was observed in conducted studies was smaller, which may be caused by usage of different kind of microorganisms to those present in activated sludge.

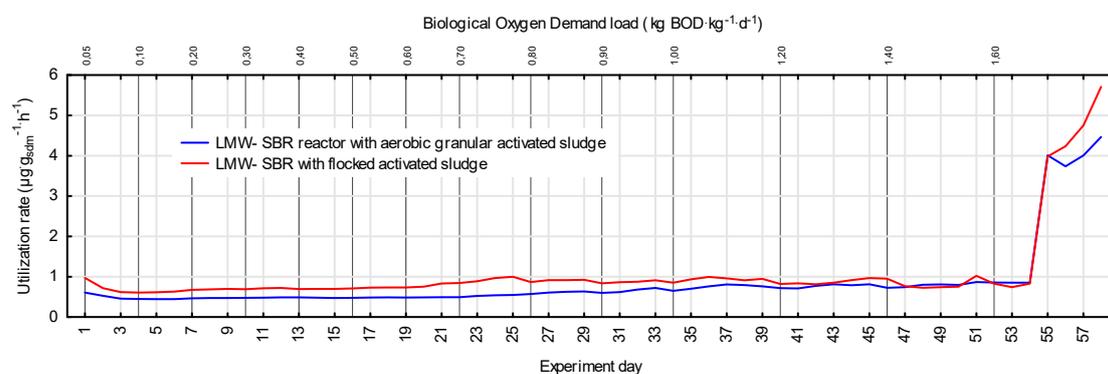


Figure 4. Sum of low molecular weight polycyclic aromatic hydrocarbons (Σ LMW) utilization rate in aerobic phase.

5. Conclusions

1. The efficiency of Σ LMW removal in the anaerobic and aerobic phase decreased with the increase of activated sludge BOD load.
2. The LMW removal rate decreased in anaerobic phase as the activated sludge BOD load increased.
3. The utilization rate of Σ LMW in the aerobic phase slightly increased with the increase of the activated sludge BOD load. This phenomenon may have been due to the length of the aeration phase and the higher activity of microorganisms in the aerobic phase compared to the anaerobic phase.

Authors Contribution: P.O. and I.S. conceived and designed the experiments; P.O. performed the experiments; P.O. analyzed the data; I.S. contributed reagents/materials/analysis tools; P.O. wrote the paper.

Conflicts of Interest: The authors declare no conflict of interest.

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