Treatment and Biogas Production of Sulfate Containing Low-Strength Industrial Wastewater in Upflow Anaerobic Sludge Blanket (UASB) Reactors

著者	LU XUEQIN
学位授与機関	Tohoku University
学位授与番号	11301甲第17222号
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リク　ユキキン
氏　　　　　　　名　陸　　雪琴
研究科，専攻の名称　東北大学大学院工学研究科（博士課程）土木工学　専攻

学 位 論 文 題 目　Treatment and Biogas Production of Sulfate Containing Low-Strength Industrial Wastewater in Upflow Anaerobic Sludge Blanket (UASB) Reactors（硫酸塩含有低濃度産業廃水の UASB 処理およびバイオガス生成に関する研究）

論 文 審 査 委 員　主査　東北大学教授　李　玉友
東北大学教授　西村　修　東北大学准教授　久保田 健吾
東北大学准教授　坂巻 隆史

論文内容要約

As per Ministry of the Environment's statistics, the produced industry wastewater in Japan was estimated to be around 1160 million m^3 in 2014. The power plant wastewater represents the largest component with 58% in terms of the total wastewater discharge, while the chemical industry (CI), paper & pulp industry (PPI) and food industry wastewater (FIW) represents 5.7%, 1.5% and 1.1 %, respectively. In this regard, to date, one of the main challenges is to develop appropriate technologies treating industry wastewater, with the great potential to minimize the risks for human health and to maximize sustainable bio-energy generation. Industry wastewater contains organic matter and sulfate discharge into surface water; all contribute to the serious environmental problems.

Among the multifarious alternatives, the Upflow Anaerobic Sludge Blanket (UASB) reactor is by far one of the most widely adopted anaerobic options for treatment of various wastewaters due to its high efficiency, flexibility, energy generation in the form of biogas and low sludge production. However, when UASB treatment is applied to high-strength sulfate containing wastewater, the competition between sulfate reducing bacteria (SRB) and methane producing archaea (MPA) to utilize the carbon sources often leads to a decrease in the methane production and even failure of the treatment process. Consequently, it is very important to understand the interaction between SRB and MPA.

Therefore, one of the most attractive challenges for extension of the UASB process may be its application to treatment of low-strength industrial wastewaters containing high sulfate concentrations; the application of biological treatments in industrial effluent containing high-strength sulfate was carried out in a UASB reactor with starch, methanol as the sole carbon source. This study focused on how to promote the organics and sulfate removals as well as simultaneous methane production, advancing the applications of the technology in water industry from basic science.

The performances of UASB reactor in COD and sulfate removals and biogas production under different HRT and OLR were studied. The balance of COD and sulfate conversion during the running were also investigated. At the same time, according to methane production and sulfide conversion, the competition between MPA and SRB in electron flow utilization at different HRT and OLR were analyzed. To elucidate the pathways of COD and sulfate removals and conversion, SMA (specific methanogenic activity) and SSA (specific sulfidogenic activity) of the granular sludge were determined with batch experiments, and the communities of microorganisms were analyzed with FISH and 16S rRNA gene.

The whole thesis consisted of 7 chapters along with acknowledgement and publications. The whole thesis structure is illustrated in Fig.1. In Chapter 1, it introduced the background of industry wastewater discharge and global energy crisis; meanwhile, the objectives of the thesis were also described. In Chapter 2, we provided a literature review on recently developed technologies for industrial wastewater treatment. The Chapters 3 to 6 were the main part of the research for the thesis. In Chapter 7, the important conclusions were obtained based on the research results from this study. Besides, recommendations for further investigation of recommendations were also given as well.

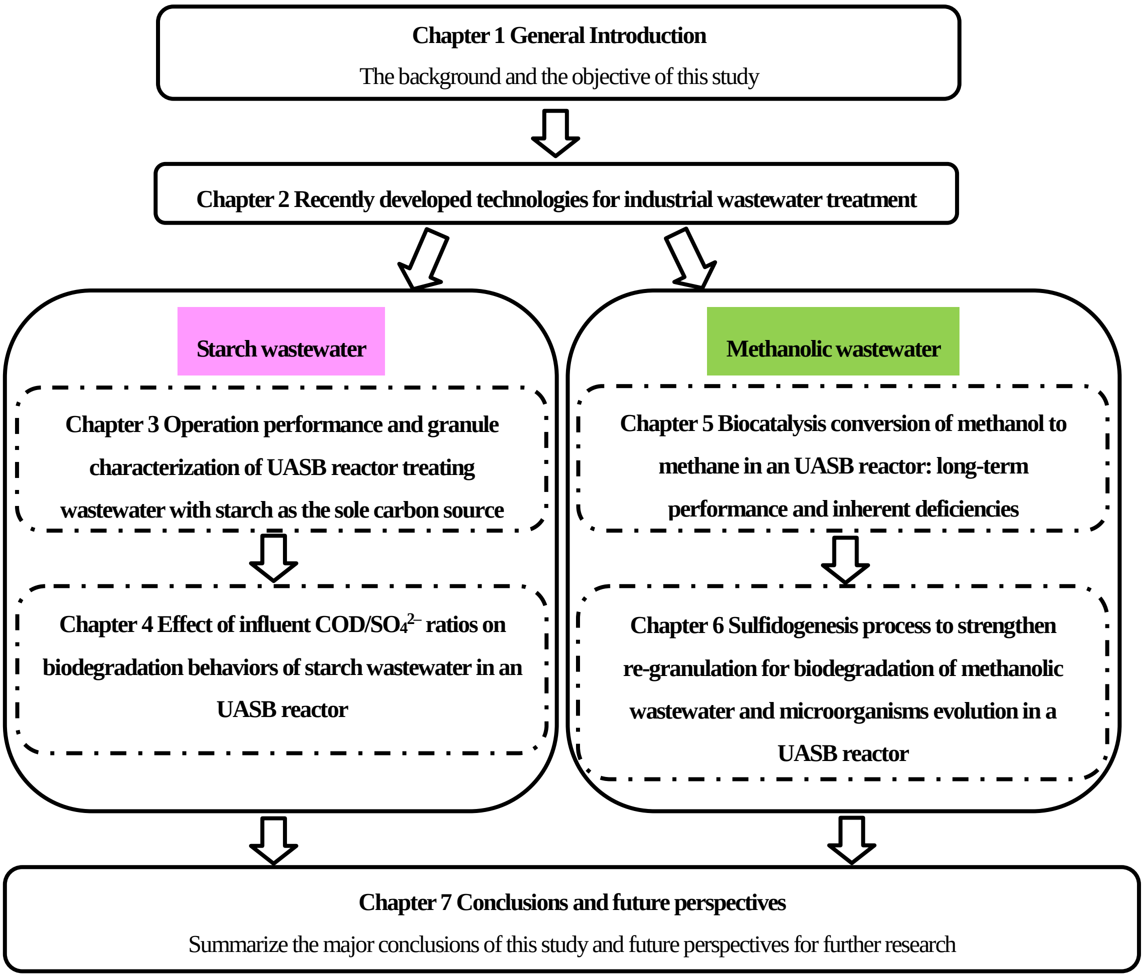

Figure 1 The whole thesis structure.

The studies were conducted step by step from 2013 to now, with the following outcomes to be achieved.

(1) To evaluate the long-term performance of UASB reactor in starch wastewater treatment. A lab-scale UASB reactor has been constructed and operated for more than 200 days to comprehensively evaluate the long-term performance of the reactor in treating starch wastewater. The effects of organic loading rates (OLR) on the overall stability were examined by varying hydraulic retention times (HRT) (from 24 to 3 h) to optimize the operating condition. In order to elucidate the responsible pathway for starch biodegradation, the specific methanogenic activity (SMA) of granules by feeding seven different substrates

were also determined. Besides, the possible changes of water qualities (i.e. pH, ORP, COD, acetate, etc.) and granule characteristics (i.e. morphological and microbial structure, EPS distribution, settling velocity, etc.) along the reactor height were detected, hoping to map the core degradation dynamics occurred in the interior of UASB.

(2) To understand how the COD/SO_4^{2-} ratio affects the biodegradation routes of starch wastewater as well as subsequent methane production and sulfate reduction. The balance of COD and sulfate conversion under different scenarios were calculated to explore the relative portion of electron donor transferred into MPA and SRB. Activity tests were performed to clearly map the biodegradation kinetics of starch. Furthermore, morphological and microbial structures of granular sludge were characterized by scanning electron microscopy (SEM) and fluorescence in situ hybridization (FISH). Finally, the energy conversion efficiencies of the reactor under different COD/SO_4^{2-} ratios were calculated, with the purpose of providing more basic data and theoretical guidance for advancing its practical application.

(3) To assess the long-term performance of UASB reactor in treating methanolic wastewater and to in-depth explore the granulation/dispersion mechanisms of granular sludge. The effects of OLR on the overall stability were investigated by varying HRT from 48 to 2 h to optimize the operating conditions. The granule characteristics including morphological and microbial structure, extracellular polymeric substances (EPS) distribution and metal cations (Ca^{2+}, Mg^{2+}, Fe^{2+}, K^{+}, and Na^{+}) in different EPS fractions, and specific methane activities (SMAs) were researched, aiming to thoroughly elucidate the core methanol degradation dynamics occurred in the interior of UASB.

(4) To assess the introduction of sulfate with different COD/SO_4^{2-} ratios on the long-term performance of UASB reactor in treating methanolic wastewater by taking the performance, granulation and microbial community into account. Meanwhile, it also intended to gain deeper insight into the competitive and syntrophic interactions between the different bacterial trophic groups in the reactor, and to inspect and verify whether the dispersed sludge could be re-granulated or not if the sulfate was introduced. The reactor has been run continuously under mesophilic condition for around 235 days. The effects of sulfate on the overall stability were investigated by varying the influent COD/SO_4^{2-} ratio from 20 to 0.5 to optimize the conditions, and the granule characteristics (e.g. EPS, metal cations, and metabolic activity) as well as microbial community were discussed as well.

Fig. 2 shows the research routes of my doctor thesis. In general, this thesis can be divided into three parts: first, the effects of OLR on the overall stability were examined by varying HRT to optimize the operating condition; second, the core degradation dynamics occurred in the interior of UASB was analyzed; third, the influent COD/SO_4^{2-} ratios were optimized to promote the organic and sulfate removals as well as bioenergy production. My work would provide preliminary basis and theoretical guidance for the practical applications of UASB technology in the real world.

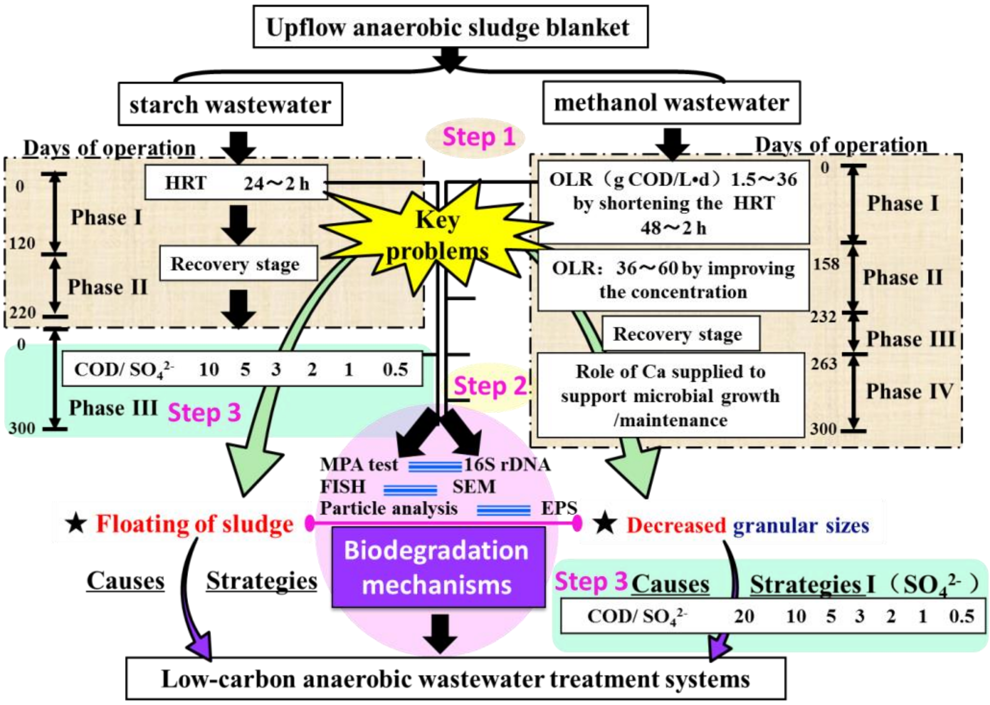

Figure 2 Research routes of the doctor thesis.

The long-term performances of UASB reactors in treatment and chemical energy harvest from low-strength industrial starch and methanolic wastewater were investigated systematically under different operational conditions (i.e. OLR, HRT, influent COD/SO_4^{2-} ratios, etc.). The main outcomes obtained in this thesis are as follows:

(1) The long-term performance of a lab-scale UASB reactor treating starch wastewater was investigated under different HRT. Successful start-up could be achieved after 15 days' operation. The optimal HRT was 6 h with OLR 4 g COD/L·d at COD concentration 1000 mg/L, attaining 81.1–98.7% total COD removal with methane production rate of 0.33 L CH_4/g $COD_{removed}$. Specific methane activity tests demonstrated that methane formation via H_2-CO_2 and acetate was the principal degradation pathways. Vertical characterizations revealed that main reactions including starch hydrolysis, acidification and methanogenesis occurred at the lower part of reactor ("main reaction zone"); comparatively, at the up converting acetate into methane predominated ("substrate-shortage zone"). Further reducing HRT to 3 h caused volatile fatty acids accumulation, sludge floating and performance deterioration. Sludge floating was ascribed to the excess polysaccharides in extracellular polymeric substances (EPS). More efforts are required to overcome sludge floating-related issues.

(2) A lab-scale UASB has been run for 250 days to investigate the influence of influent COD/SO_4^{2-} ratios on the biodegradation behavior of starch wastewater and process performance. Stepwise decreasing COD/SO_4^{2-} ratio enhanced sulfidogenesis, complicating starch degradation routes and improving process stability. The reactor exhibited satisfactory performance at a wide COD/SO_4^{2-} range ≥ 2, attaining stable biogas production of 1.15–1.17 L/L·d with efficient simultaneous removal of total COD (73.5–80.3%) and sulfate (82.6 ± 6.4%). Adding sulfate favored sulfidogenesis process and diversified microbial community, invoking hydrolysis-acidification of starch and propionate degradation and subsequent acetoclastic

methanogenesis; whereas excessively enhanced sulfidogenesis (COD/SO_4^{2-} ratios <2) would suppress methanogenesis through electrons competition and sulfide inhibition, deteriorating methane conversion. This research in-depth elucidated the role of sulfidogenesis in bioenergy recovery and sulfate removal, advancing the applications of UASB technology in water industry from basic science.

(3) The long-term performance of methanol biocatalysis conversion in a lab-scale UASB reactor was evaluated. Properties of granules were traced to examine the impact of methanol on granulation. Methanolic wastewater could be stably treated during initial 240 d with the highest biogas yield of 18.6 ± 5.7 L/L·d at OLR 48 g-COD/L·d. However, the reactor subsequently showed severe granule disintegration, inducing granule washout and process upsets. Some steps (e.g. increasing influent Ca^{2+} concentration, etc.) were taken to prevent rising dispersion, but no clear improvement was observed. Further characterizations in granules revealed that several biotic/abiotic factors all caused the dispersion: (1) depletion of EPS and imbalance of protein/polysaccharide ratio in EPS; (2) restricted formation of hard core and weak Ca-EPS bridge effect due to insufficient calcium supply; and (3) simplification of species with the methanol acclimation. More efforts are required to solve the technical deficiencies observed in methanolic wastewater treatment.

(4) The effect of sulfidogenesis process on sludge granulation was studied. The beneficial sulfidogenesis process invoked the significant increase in Fe iron and more EPS secretion that bound and immobilized in the sludge, which inspired the sludge re-granulation. The UASB reactor maintained the satisfactory performance at a wide COD/SO_4^{2-} range of ≥ 2, attaining high biogas production of 3.78 ± 0.32 L/L·d with efficient concurrent removal of total COD (96.54 ± 4.39%) and sulfate (56.34 ± 12.99%). Methane content in biogas kept a fairly stable level of 81.5 ± 1.6% at all COD/SO_4^{2-} ratios tested. Particle size of granules showed that a clear increase in the particle size as decreasing the COD/SO_4^{2-} ratios. Despite that the enhanced sulfidogenesis led to electron flow distributed into the SRB (20.00 ± 2.43%), but MPA (80.00 ± 2.43%) could out-compete sulfate reducers even at low COD/SO_4^{2-} ratio of 0.5 in organics removal and electrons utilization. Activity tests and microorganism results of low COD/SO_4^{2-} ratio suggested that the conversion of methanol into methane is not only depend on the less acetoclastic methanogen and hydrogenotrophic methanogenesis, but also depend on incomplete oxidizer SRB species (*Desulfovibrio* sp.) utilized H_2/CO_2 with acetate to achieve mineralize the methanol to methane. In consequence, the metabolic pathway of methanol was diversified. Further analysis through SEM, FISH and microorganism shift revealed that lower COD/SO_4^{2-} ratio favored sulfidogenesis process, diversified the microbial community and complicated metabolic pathway of methanol inside the reactor. The benefical sulfidogenesis process subsequently revealed that several biotic/abiotic factors all benefit the re-granulation: (i) form the EPS network due to sufficient Fe-EPS bridge; (ii) enhance microbial diversity by incomplete oxidizer SRB species (*Desulfovibrio* sp.) utilized H_2/CO_2 with acetate to achieve mineralize the methanol to methane; and (iii) complicate metabolic pathways of methanol, which was vital driving force to the sludge re-granulation. This research verified the favorable effect of sulfidogenesis in strengthening re-granulation and bioenergy recovery for

biodegradation of methanolic wastewater, providing the fundamental data and theoretical guidance for advancing the widespread applications of UASB technology in water industry from basic science.

UASB has showed great operation performance in treating synthetic industrial wastewater during the thesis. As a consequence, it is every suitable for the industrial wastewater treatment due to its numerous advantages such as higher up-flow velocity, low energy consumption, low sludge production, higher removal efficiency, vast potential of resource recovery, less equipment required and high operational simplicity. However, it is worth noting that due to the high sulfate concentration in the wastewater, a relatively high level of hydrogen sulfide gas can be produced. With increasing knowledge of sulfide toxicity, in order to achieve efficient use of biogas, it may well be possible in the future to develop a novel cost-effective desulfurization process to remove hydrogen sulfide from biogas (**issue i**). Sulfate-rich wastewater from industrial plants can be treated by anaerobic technology first, and then the produced biogas will be sent to the biological desulfurization reactor. It could get clean water, renewable energy and sulfur resource at the same time. Thus, a combined waste-to-energy system could be expected in the near future.

Furthermore, granular biomass has been proposed as a prerequisite for successful application of UASB for anaerobic treatment of industrial wastewater. However, when the UASB reactor was fed with starch, a large amount of foam was produced which filled gas holder, and this resulted in the escape of biogas from the outlet and reduce the recovery efficiency of biogas. In addition, floating of sludge also sometimes takes place. The limited results achieved previously still cannot effectively alleviate and avoid the granular sludge floating occurring in starch wastewater treatment by UASB process (**issue ii**). Moreover, there is a need to understand the microbial community and function with granules and to establish the links between the sludge granulation and microbial diversities using the combined involvement of several techniques

Besides sludge floating observed during starch wastewater treatment, there were some technical problems coming out in methanolic wastewater treatment, in particular granular sludge dispersion/disintegration, which resulted in the severe sludge washing out. In our previous research, several strategies including the addition of Ca^{2+}, varying influent COD/SO_4^{2-} ratios, etc., have been developed, and given positive results. Nonetheless, more efforts should be dedicated to this field to completely solve the inherent deficiencies of UASB process in treating methanolic wastewater (**issue iii**), such as co-digestion with other kinds of organic wastewater, etc. Also, there is also a further need for scientific research to clarify clearly competitive interactions between MPA and SRB as well as electron flow distribution (**issue iv**) when employing different substrates in UASB.