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Reduction of Alkali Supplement in a Pilot-Scale Thermophilic Multi-Staged UASB Reactor Treating Alcohol Distillery Wastewater

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ABSTRACT: One of the main disadvantages of anaerobic wastewater treatment at a low pH is the significant operational cost due to the addition of necessary alkali. To reduce alkali supplement and thus the cost, this study proposes a sequential multi-feed (SqMF) mode (distributed feeding) and effluent recycle (ER) mode. Experiments were conducted with a pilot-scale (2.5 m^3) thermophilic (55°C) multi-staged up-flow anaerobic sludge blanket reactor. Alcohol distillery wastewater (*shochu*), a major source of industrial wastewater in Japan, was used for the study. The SqMF mode of operation (influent pH: 5.0; organic loading rate: 45 kgCOD/m^3/day; HRT: 12 hours; influent COD concentration: 20,900 mgCOD/L) successfully reduced the alkali supplement (24% NaOH solution) requirement by 67.2% compared with the single-feed mode. For the ER mode operation (organic loading rate: 35 kgCOD/m^3/day; HRT: 12 hours; influent COD concentration: 17,400 mgCOD/L), operation was possible without any alkali supplement since the system uses the alkalinity generated during microbial metabolism.

Key words: Alkalinity, Sequential multi-feed, Effluent recycle, Alcohol, Distillery, Wastewater

INTRODUCTION

In the thirty years since the development of the up-flow anaerobic sludge blanket (UASB) process by Lettinga *et al.*, 1979, it has become one of the most popular alternatives for the treatment of both municipal and industrial wastewaters (Frankin, 2001). There are currently more than 1,000 full-scale UASB reactors treating industrial wastewater (Frankin, 2001; Kassam *et al.*, 2003). Initial research on the thermophilic UASB process in the 1980s was related to applications that generated high-temperature wastewater, such as alcohol distillation and industrial pulping. Studies showed that in the thermophilic process, both the treatment efficiency and the loading could be enhanced 2- to 3-fold compared with the mesophilic UASB process (Wiegant *et al.*, 1985; van Lier, 1996; Syutsubo *et al.*, 1998). In 1990s, various high organic loading rate (OLR) reactors, such as the expanded granular sludge bed (EGSB) reactor, internal circulation (IC) reactor, and multi-staged UASB (MS-UASB) reactor, were developed (Pereboom & Vereijken, 1994; Pereboom, 1994; van Lier *et al.*, 1994; Harada *et al.*, 1997; Yamada *et al.*, 2006).

Although applied as a mainstream technology, most UASB processes that treat industrial wastewaters require a supply of alkali to maintain the appropriate pH in the reactor. This may increase the overall operational cost and make the system less attractive. The problem is especially serious in wastewaters containing high amounts of carbohydrates (Ferguson *et al.*, 1984; Romli *et al.*, 1994; Lettinga, 1985). Therefore, it is worthwhile to estimate the alkalinity requirement for the specific treatment and then manipulate the reactor design or the operational conditions to meet the requirement. For instance,

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*Corresponding author E-mail:m-yamada@kagoshima-ct.ac.jp studies have shown that the alkalinity demand for a process can be partially reduced via effluent recycling (ER) (Romli *et al.*, 1994; Shin *et al.*, 1992; Nishimura & Yoda, 1996).

In this study, we applied an ER mode as well as a sequential multi-feed (SqMF) mode to a thermophilic MS-UASB treating alcohol distillery wastewater and examined the alkalinity requirement for the process. It was hypothesized that the selected modes of operation might enhance the metabolism-derived alkalinity within the system.

MATERIALS & METHODS

An overview of the flow diagram of the pilot-scale MS-UASB reactor used in this study is shown in Fig. 1. The reactor had a volume (water filled) of 2.5 m^3, a height of 6.3 m, and an internal diameter of 0.8 m. The entire reactor shell was insulated to maintain the thermophilic condition (55°C±3°C). A total of six gas-solid separators (GSSs) were installed along the reactor height. The inlets were positioned at three different points along the height of the MS-UASB reactor (Inlet 1: 0.40 m, Inlet 2: 1.48 m, Inlet 3: 2.40 m), and installed just under GSS 1, GSS 2 and GSS 3, respectively. The organic loading rate (OLR) and hydraulic retention time (HRT) were calculated on the basis of the water-filled volume of the reactor. Various re-circulation ratios were tested for the system, and are discussed in detail below. The diluted wastewater was fed to the three inlets in a sequential manner. The operating conditions for the SqMF and ER modes are shown in Table 1 for the entire test period of 860 days: the SqMF mode was carried out for 24 days and the ER mode for 78 days. Results for the SqMF mode from day 643 to 681 and for the ER mode from day 759 to 836 are presented in this paper. The single-feed (SF) operational results are used for comparison with the SqMF and ER modes. The conditions for the SF, SqMF, and ER modes are shown in Fig. 2. The SqMF mode diluted feed wastewater with well-water by sequentially feeding the wastewater to inputs 1, 2 and 3 for 6, 5, and 4 minutes, respectively. This feeding cycle was continued throughout the SqMF run. Influent pH conditions were maintained between 6.3 and 5.0 in the dilution tank using alkali supplement. Barley-based *shochu* distillery wastewater was used throughout the study. The liquid fraction obtained after centrifugation (screw decanter type centrifuge: Ishikawajima-Harima Heavy Industries, Co.,Ltd. model HS-204L with centrifugal force of 3,500 G) was used for the treatment. The composition of this wastewater is shown in Table 2.

Parameters such as the COD, volatile fatty acids (VFAs), suspended solids (SS), and volatile suspended solids (VSS) of the influent and effluent were analyzed every week in triplicate. The water temperature and pH were continuously recorded. Similarly, biogas

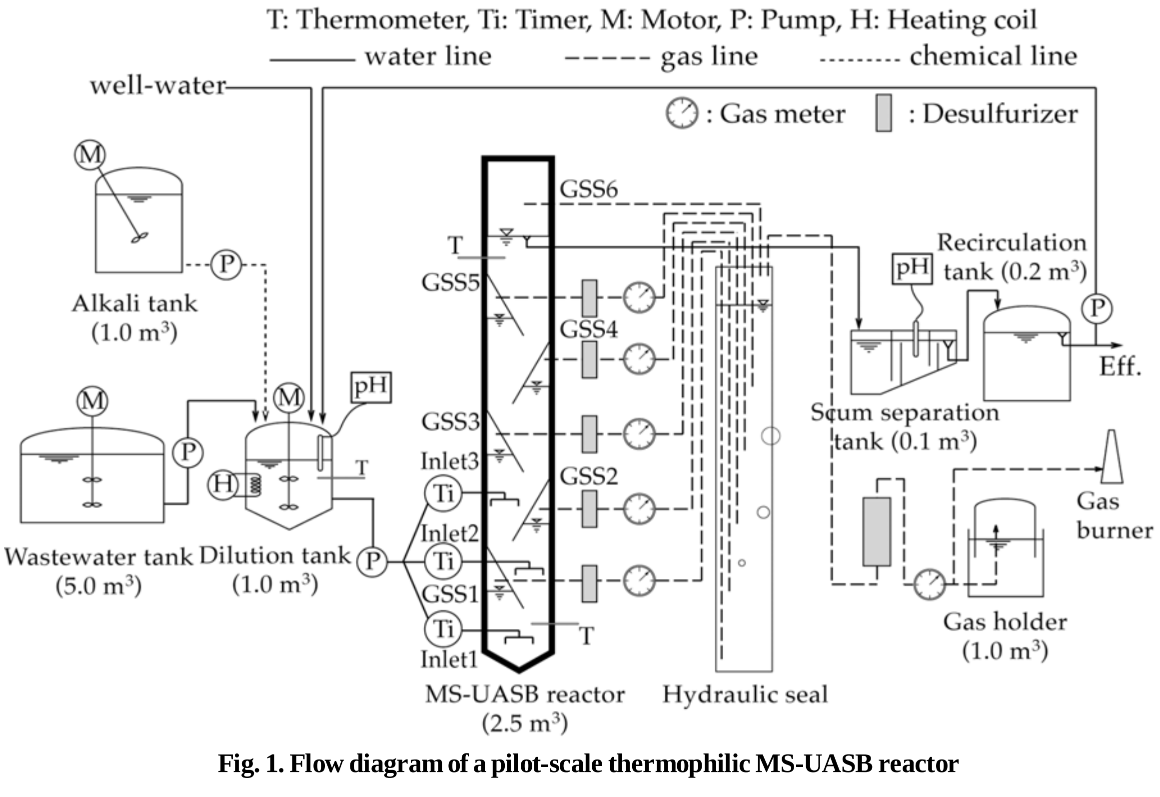

Fig. 1. Flow diagram of a pilot-scale thermophilic MS-UASB reactor

Table 1. Operating conditions in this study

Run	Experimental period	Inf.-pH	F:W:E	Dilution	Recycle ratio	OLR	Inf.-COD	HRT
	[d]	[-]	[-]	[times]	[times]	[kgCOD/m^3/day]	[mg/L]	[h]
SF	9	6.9	1:5.3:0	6.3	0	41.7	13900	8
SqMF 1	4	6.3	1:5.3:0	6.3	0	41.7	13900	8
SqMF 2	5	5.9	1:5.3:0	6.3	0	41.7	13900	8
SqMF 3	5	5.5	1:5.3:0	6.3	0	41.7	13900	8
SqMF 4	5	5.3	1:2.9:0	3.9	0	45.2	20900	12
SqMF 5	5	5.0	1:2.9:0	3.9	0	45.2	20900	12
ER 1	22	6.2	1:1:5.5	2	5	34.8	43450	24
ER 2	21	6.2	1:2:4.5	3	4.5	34.8	29000	20
ER 3	14	6.1	1:4:5	5	5	34.8	17380	12
ER 4	21	6.3	1:4:10	5	10	34.8	17380	12

SF: single feed mode, SqMF: sequential multi-feed mode, ER: effluent recycle mode
F: feed, W: well-water, E: effluent

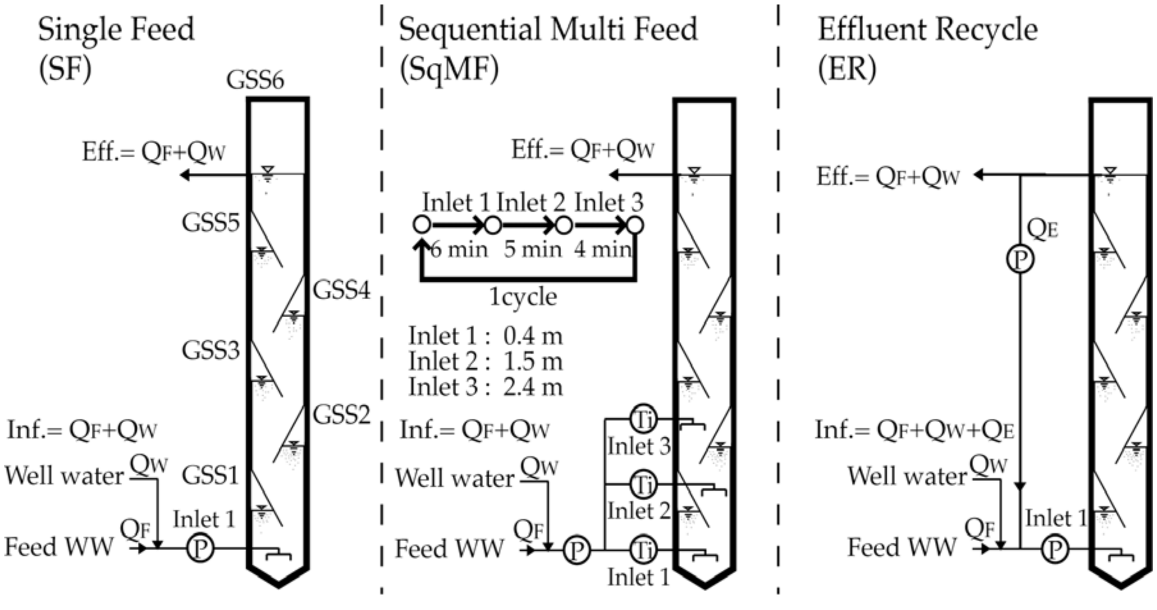

Fig. 2. Illustration of feed patterns used in this study

production and its composition were measured daily. Details on the analytical methods for COD, SS, and VSS are described elsewhere (APHA, 1998). Biogas and VFA analysis methods are provided by Harada *et al.*, 1996. True bicarbonate alkalinity (TBA5.75) was titrated to pH 5.75 as proposed by Jenkins *et al.*, 1983 and Ripley *et al.*, 1986, at which point it exhibits the alkali supplement reduction effect. When VFA accumulation occurs during process deterioration, accurate measurement of bicarbonate alkalinity is difficult if titration is done to pH 4.3. When titrated to pH 5.75, about 80% of bicarbonate is titrated, though about 20% or less is contributed by VFAs. Therefore, multiplying the titrated alkalinity at pH 5.75 by 1.25 can be used to theoretically calculate TBA5.75 (1), i.e.,

$$TBA5.75 = Alk5.75 \times 1.25 \qquad (1)$$

where TBA5.75 is the true bicarbonate alkalinity at pH 5.75, Alk5.75 is the titrated alkalinity at pH 5.75, and the factor 1.25:1 accounts for the fact that 80 % of the HCO_3^- is titrated at pH 5.75.

Table 2. Characteristics of alcohol distillery wastewater used in this study

Parameters		Unit	
pH		[-]	3.9
SS		[mg/L]	3,900
COD_{Cr}	Total	[mgCOD/L]	86,900
	Soluble	[mgCOD/L]	79,600
Carbohydrate	Total	[mgCOD/L]	11,680
	Soluble	[mgCOD/L]	9,730
VFA	Acetate	[mgCOD/L]	5,170
	Propionate	[mgCOD/L]	580
	i-Butyrate	[mgCOD/L]	170
	n-Butyrate	[mgCOD/L]	59
	i-Valerate	[mgCOD/L]	83
	n-Valerate	[mgCOD/L]	22
	i-Caproic acid	[mgCOD/L]	630
	n-Caproic acid	[mgCOD/L]	19
TKN		[mgN/L]	4,100
NH_4^+-N		[mgN/L]	600

RESULTS & DISCUSSION

The relationship between removed COD and alkalinity production during one thermophilic MS-UASB experiment is shown in Fig. 3. A linear relationship (R^2= 0.72) was found between removed COD and alkalinity production. Alkalinity production was 0.17 $kgCaCO_3$ per kg of removed COD. The methane fermentation of malt whisky distillery pot ale is consistent with that reported by Goodwin *et al*., 2001. The alkalinity increase was variable, but was typically around 0.16 $kgCaCO_3$ per kg of removed COD (Goodwin *et al*., 2001). Other researchers have reported alkalinity increases in a UASB reactor that averaged 0.17, 0.16, and 0.13 $kgCaCO_3$ per kg of removed COD for the three experimental conditions treating tomato-canning waste (Gohil *et al*., 2006). The relationship between influent pH and the alkalinity requirement for the influent COD concentration is shown in Fig. 4. Methanogens generally prefer nearly neutral pH conditions, with an optimum range of about 6.5 to 8.5. The alkalinity requirement for influent COD is 0.083 $kgCaCO_3$ for a pH of 6.5. Thus, operation is possible without any additional alkali supplement as the system reuses the alkalinity generated during microbial metabolism.

The experimental results obtained using the SqMF mode are shown in Fig. 5. The system was operated with an OLR of 40 $kgCOD/m^3$/day for about 24 days to evaluate the alkali requirement, which was then compared with the requirements for the SF mode conditions. The comparison shows that the COD removal efficiency dropped from 90% to 60-70% during SqMF 1 operation. After the Eff.-TBA5.75 dropped from 2 $gCaCO_3$/L to 1 $gCaCO_3$/L during SqMF 3, the HRT was changed to 12 hours, which raised the Eff-TBA5.75 concentration. The increase in alkalinity generated during microbial metabolism was suggested by the SqMF mode.

Compared to the SF mode baseline, the alkali requirement decreased for all SqMF operation modes (SqMF 1 - 5), as shown in Fig. 6. The SqMF operation mode (SqMF 5; influent pH: 5.0; COD loading rate: 45 $kgCOD/m^3$/day; HRT: 12 hours; influent COD concentration: 20,900 mg COD/L) successfully facilitated operation with a 67.2% reduction in alkali supplement (24% NaOH solution) compared to the SF mode. Under these conditions the alkalinity demand per kg of COD removal was 0.175 $kgCaCO_3$. The SqMF mode of operation was impossible without some alkali supplement, probably because although the system reused the alkalinity generated during microbial metabolism, some of this alkalinity likely exited with the effluent.

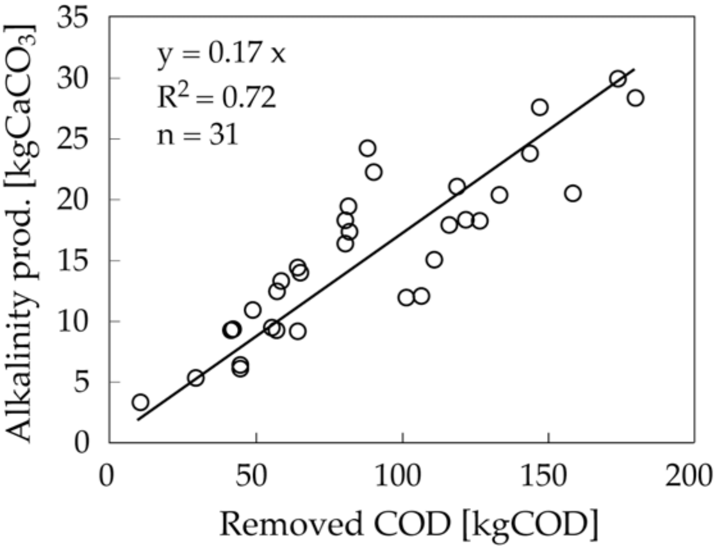

Fig. 3. Relationship between removed COD and alkalinity production during thermophilic MS-UASB experiment

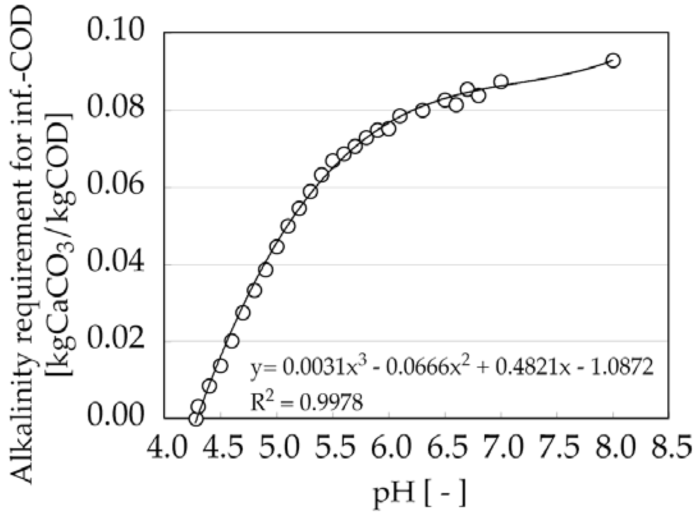

Fig. 4. Relationship between influent pH and alkalinity requirement for influent COD concentration

The SqMF mode is more effective than ER for wastewaters that contain high concentrations of nitrogenous compounds (such as free ammonium ion), which inhibit the methanogenic process. With *shochu* distillery wastewater, since the above-mentioned compounds are present in low concentrations, ER is preferred over SqMF.

The experimental results for the ER mode are shown in Fig. 7. The effluent was recycled for 78 days at an OLR of 35 kgCOD/m^3/day. For the ER 1 - 4 conditions, the well-water volume was increased in the influent to determine the required alkali dose. The effluent circulation was then increased from 5 to 10 times dilution, which is denoted as ER 4. The high recycle ratios reduced the alkalinity requirements to a more economically viable level; this may be described as the factor $Alk_{advantage}$= n/(1+n), where n is the recycle ratio. The operating conditions of ER 4 included a liquid velocity (L_v) of ~~a~~ 1.25 m/hour. The settling velocity of the granules in the UASB was significantly higher than the up-flow velocity under the operational conditions in this study. The influents for ER 1 and ER 2 were diluted by a factor of two (influent COD concentration: 43,450 mgCOD/L) and three (influent COD concentration: 29,000 mgCOD/L), respectively. It was observed that the effluent VFA concentration wasn't maintained at **a** low level and the COD removal was decreased around 60%. Therefore, the dilution times were increased by a factor of five for ER 3 and ER 4, and the effluent VFA concentration was decreased, under which conditions the process performance was good.

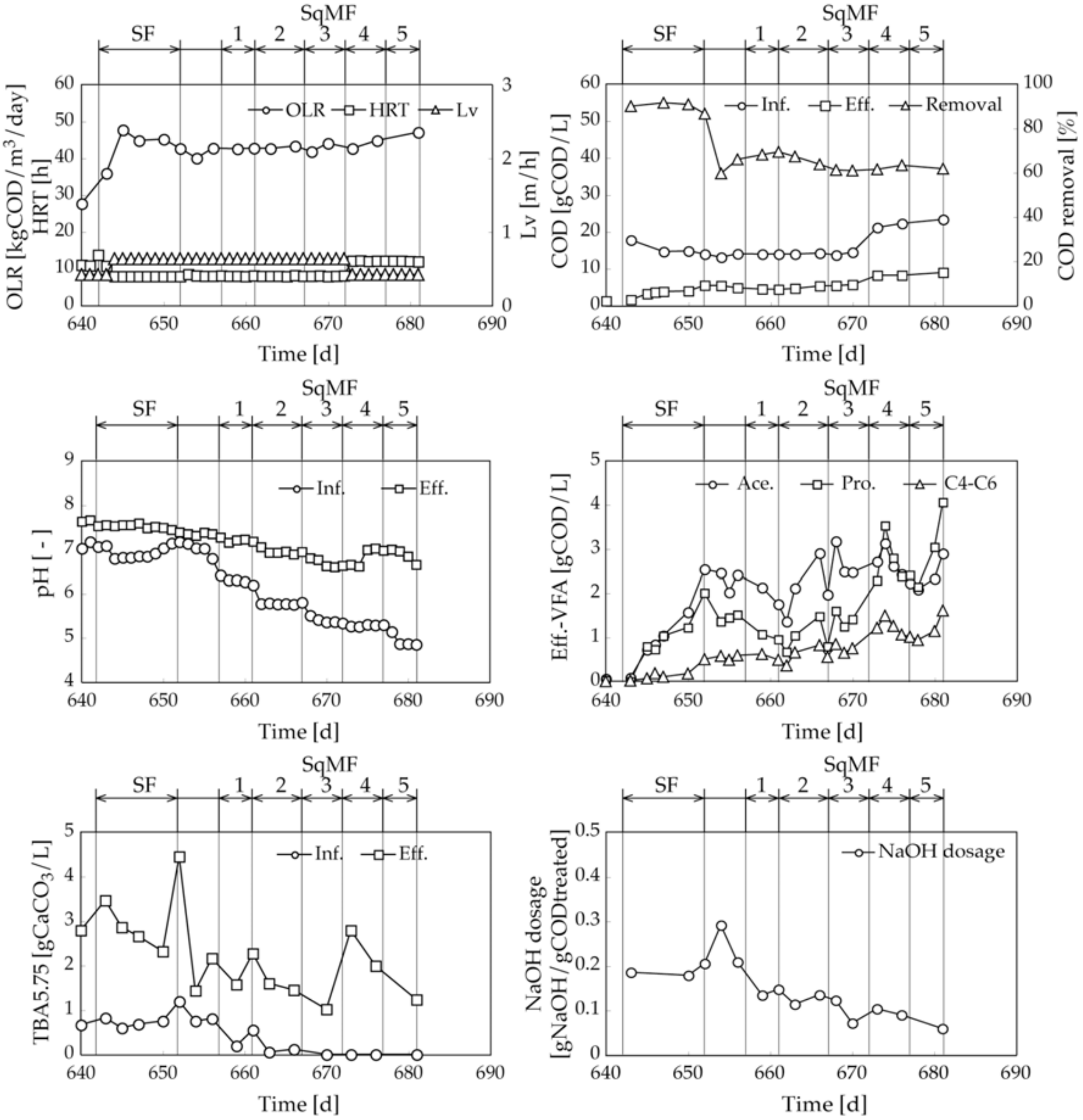

Fig. 5. Time course of process performance during SqMF mode experimental period

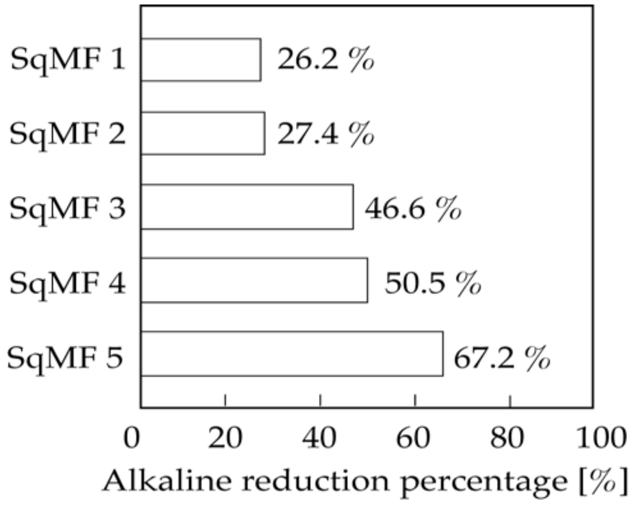

Fig. 6. Alkaline reduction percentage during SqMF mode operation

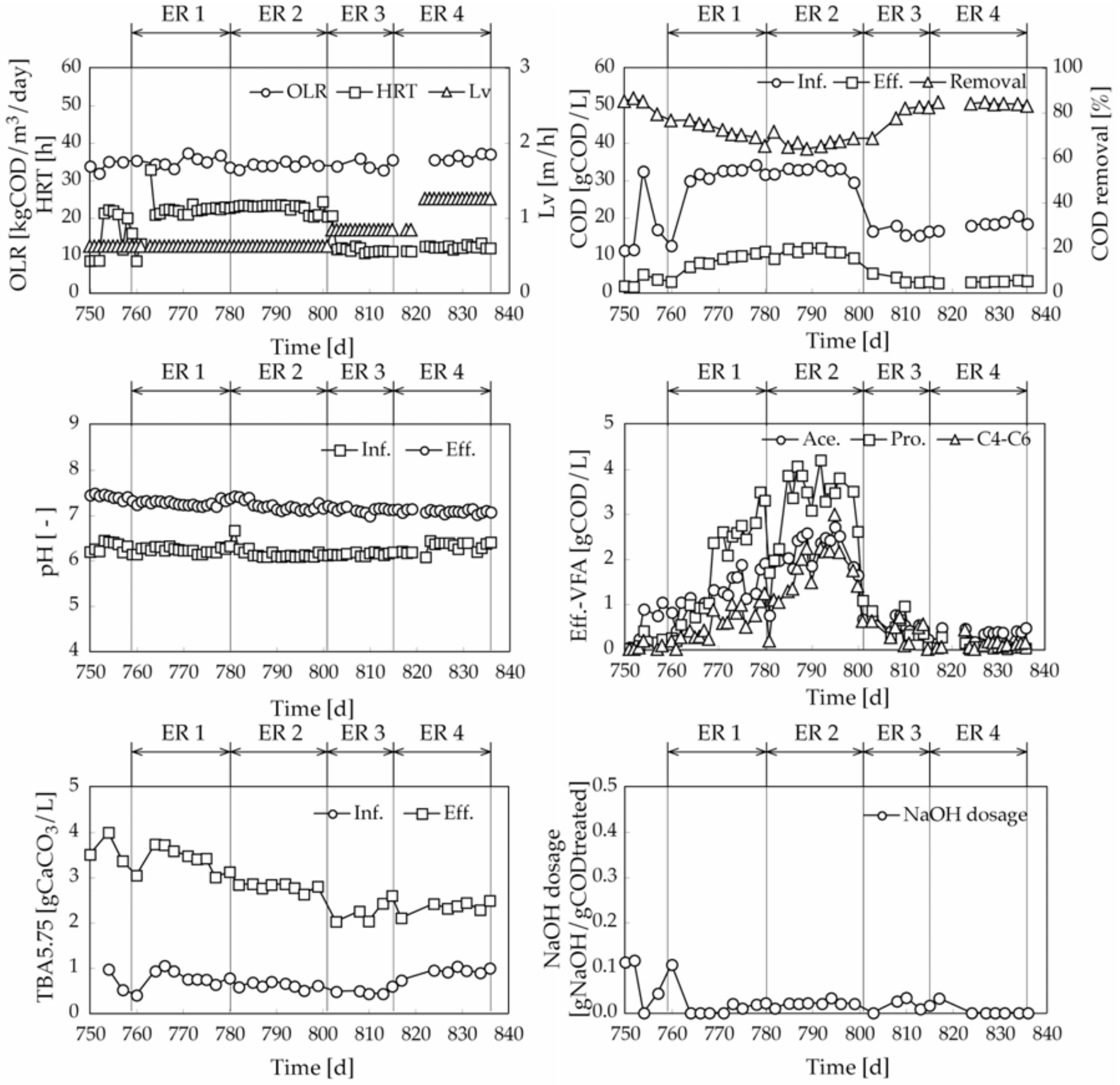

Fig. 7. Time course of process performance during ER mode experimental period

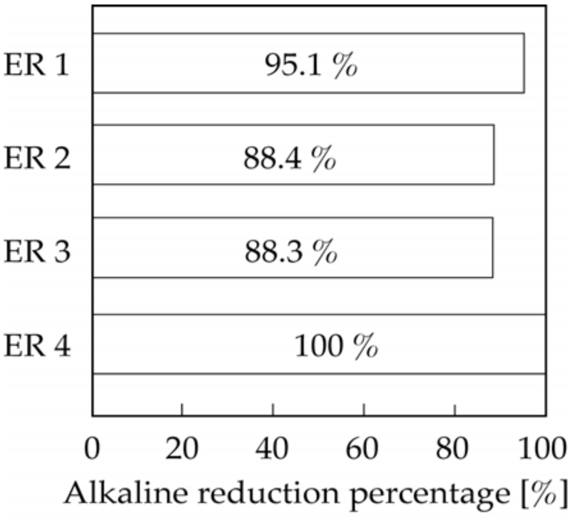

Fig. 8. Alkaline reduction percentage for ER mode

In comparison with the SF mode, the required alkali supplement drastically decreased for the ER 1 - 4 circulation operations, as shown in Fig. 8 (alkaline supplement reductions were ER 1: 95.1%, ER 2: 88.4%, ER 3: 88.3%, and ER 4: 100%). There was no need for alkali addition in ER 4. For ER 2, the COD removal dropped as a result of the alkalinity requirement and was similar to ER 3. Compared with the results obtained by Nishimura & Yoda, 1996 (0.020 kgCaCO$_3$/kgCOD treated) the alkalinity requirement in this system was reduced by 55%. For ER 4 (effluent recycle ratio: 10 times dilution), alkali was not added and an 80% COD removal was obtained. There was also a calculated alkalinity production of 14.8 kgCaCO$_3$ per unit of removed COD for the barley-based *shochu* distillery wastewater. For ER mode 4 (F:W:E = 1:4:10; COD loading rate: 35 kgCOD/m^3/day; HRT: 12 hours; influent COD concentration: 17,400 mgCOD/L), operation was possible without any alkali addition, since the system reuses the alkalinity generated from microbial metabolism.

CONCLUSION

Operation of a thermophilic MS-UASB treatment process via the SqMF mode resulted in 60% COD removal for an influent pH and HRT of 5.0 and 8 hours, respectively. Using this mode, it was possible to limit the alkali supplement to 0.075 kgCaCO$_3$/kgCODtreated. The COD removal was 83.8% for ER 4 (F:W:E=1:4:10), and alkali addition was not necessary. From the above observations, we can conclude that for wastewater containing inhibitory substances, the SqMF mode with appropriate influent dilution performs well. However, for other wastewater types, ER is more effective than SqMF and can reduce the alkali supplement.

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