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Anaerobic Degradation of Molasses Stillage in a Pilot UASB Reactor

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The feasibility of a mesophilic anaerobic treatment of an alcohol distillery wastewater (beet molasses stillage) was studied in a 1300 l Upflow Anaerobic Sludge Blanket (UASB) reactor for a period of 180 days. The system was seeded with 600 L of mesophilic anaerobic sludge harvested from the bottom of a dairy anaerobic lagoon. Nutrients were added to acidified effluent and after adjusting the pH in an equalization tank, the system was fed with a diluted effluent containing COD in the range of 1000-11000 mg/L at 30°C. Initially, the system had an OLR of 1 kg COD m^{-3} d^{-1} and upflow velocity was maintained at 0.6 m/h (HRT= 6 h) throughout the study. A gradual increase in OLR, through increased feed concentration, resulted in an excessive sludge washout necessitating the addition of calcium carbonate to act as a nuclei for granule formation. After 20 days of operation and at an OLR of 5.3 kg COD m^{-3} d^{-1}, signs of granule formation were observed, as indicated by increased VSS at the bottom of the reactor and reduced effluent VSS. At this point, the loading to the system was increased in four stages up to 16 kg COD m^{-3} d^{-1} (COD removal efficiency of 95%) to evaluate the optimum operational conditions of the system. During this period, the VSS/SS ratio remained constant at 0.83 and the SLR varied from 0.14 to 0.81 kg COD kg^{-1} VSS d^{-1}. The performance of the system, based on unit reactor volume and unit microbial mass, was 10 kg SCOD m^{-3} d^{-1} and 0.25 kg SCOD kg^{-1} VSS d^{-1}, respectively.

INTRODUCTION

Anaerobic degradation of high-strength effluents has become more prevalent, due to technological developments as well as improved process knowledge. Introduction of high-rate treatment systems, such as an Upflow Anaerobic Sludge Blanket (UASB), provided further interest in this type of process because it made high loading and sustainable operation possible, resulting in smaller footprints. Since its introduction in the early 1980s [1], this system has gone through a lot of improvement in both design and operational details and has been used to treat a variety of industrial effluents [2].

Effluent from molasses stillage results from the fermentation of beet or cane molasses in the process of alcohol production. It has a distinct characteristic of being low in pH, high in temperature and rich in organic and inorganic matter, making its treatment complicated [3]. Volatile acid accumulation is a common problem hindering anaerobic treatment of these effluents and the dominant constituent is either propionic acid [4] or acetic acid [5]. The presence of inorganic constituents, such as potassium and sulphates, can also be inhibitory.

A range of organic and hydraulic loading can be successfully accommodated by UASB reactors, depending on the substrate used and the quality and quantity of microbial community. Syutsubo [6] reports a COD loading of 30 kg COD m^{-3} d^{-1}, with a COD removal efficiency of 85%. According to Soto [7], excellent stability and high treatment efficiency was achieved with hydraulic residence times as low as 2 hours at an OLR of 6 kg COD m^{-3} d^{-1}, the percentage of COD removals being 95% (30°C) and 92% (20°C), while the percentage of COD converted to methane reached 67% (30°C) and 48% (20°C). The digester, operated at 20°C, maintained similar efficiencies when the OLR was increased up to 9 kg COD m^{-3} d^{-1}, at an HRT of only 1.3 hours. When more easily degradable substrate, such as glucose, is used, removal efficiencies of up to 90% can be obtained [8]. In another study,

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Ruiz et al. [9] reported a better performance of UASB at OLRs of 1-6.5 compared to anaerobic filters. Neither of these studies report indications of granule formation, and organic loadings were relatively low. While thermophilically grown sludge has an intrinsically higher methanogenic activity than mesophilic granules, COD removals reported by Hideki et al. [10] for thermophilic (55°C) treatment of cane molasses stillage was 39-67% at an organic loading rate of 28 kg COD m^{-3} d^{-1}.

In this study, an alcohol distillery stillage containing high COD content was used to investigate the feasibility of a mesophilic UASB process in treating these type of effluents. The experiments were conducted at different organic loadings and the capacity of the systems in biodegrading organics was evaluated. This paper describes the reactor performance with respect to COD removal efficiencies and sludge activity.

MATERIALS AND METHODS

Experimental Set Up

The 1300-L effective volume UASB reactor used in this study is shown in Figure 1. The pilot had a cross-sectional area of 0.63 m^2 and an effective height of 4.25 m. A perforated piping system was used at the bottom of the reactor to ensure a homogeneous distribution of flow into the reactor. Six sampling ports were provided along the height of the reactor to monitor sludge gradient throughout the experiment. The system was set up in open space with wide temperature fluctuations but reactor temperature was maintained constant at different operational conditions.

The system was set up to allow a combination of operational schemes to be tested during the start up and throughout the study period while maintaining favorable conditions within the reactor. Necessary equipment was provided for dilution, heating and flow recycle. Three possible schemes are described below:

1. Feed dilution but not heating and flow recycle:
   A dosing pump (2) was used to send the flow through valves 3, 7 and 8, while keeping valve 17 closed. Dilution water was provided by opening valves 15 and 4. Dilution flow was measured by timing the volume collected over time in a small container;
2. Feed dilution and heating, no flow recycle:
   A dosing pump (2) was used to send the flow to the heater by keeping valve 7 closed and 4 open. Dilution water was provided by opening valve 15. Pump 6 remained off and valves 17 and 8 were open;
3. Feed dilution, heating and flow recycle:
   A dosing pump (2) was used to send the flow through valves 3, 7 and 8, while keeping valve 4 closed. Dilution water was provided by opening valve 15. Pump 6, heater 16 and valves 5, 17 and 8 remained open.

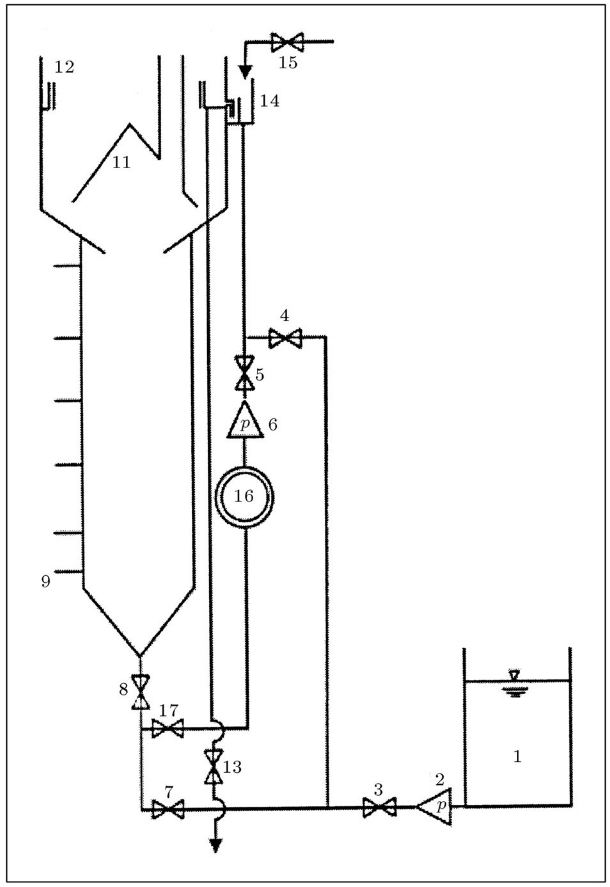

Figure 1. Schematics diagram of the pilot UASB system (see text for explanation).

Feed

A high strength beet molasses stillage used in this study was obtained from a local alcohol distillery plant (Table 1). Acidified effluent (pH = 4.5) was neutralized by 10 M sodium hydroxide to bring the pH in the range of 7-7.5. Buffering capacity was provided by $NaHCO_3$ and alkalinity was maintained in the 700-1000 mg/L (as $CaCO_3$) range. Ammonium phosphate, at a concentration of 320 mg/L, was used as a source of nutrient in an equalization tank, prior to entering into the UASB reactor, to provide a COD/N/P ratio of 200:5:1.

Operation

The reactor was inoculated with 600 L sludge from a dairy anaerobic lagoon. The solid content of seed sludge, in terms of SS and VSS, was 18.5 and 13.8 g/L, respectively. It occupied about 40% of the reactor volume. The system was started at 30°C and the

Table 1. Characteristics of undiluted beet molasses stillage effluent used in the study.

Parameter	Value
pH	4-6
Total COD, mg/L	70000-120000
Soluble COD, mg/L	11-17
Total BOD_5, mg/L	62000-105000
Suspended Solids, mg/L	500-700
Total Nitrogen, mg/L	1100-1200
Phosphorus as P_2O_5, mg/L	20-25
Potassium as K_2SO_4, mg/L	12000-15000
Sulfate as K_2SO_4, mg/L	2300-2600
Total Alkalinity as $CaCO_3$, mg/L	2800-3300
Temperature,°C	80-90

temperature was maintained constant throughout the study. The sludge was initially fed with a low load of 0.05-0.10 kg SCOD m^{-3} d^{-1} by a dilution of raw wastewater with tap water to the desired concentration. Influent feed strength was gradually increased to the desired organic loading rate, while maintaining upflow velocity constant at 0.6 m/h.

Analytical Methods

Routine physiochemical analyses (pH, COD, SS, VSS) were performed using procedures outlined in Standard Methods [11]. Sufficient time was allowed after any change in conditions prior to sampling and conducting analyses. The soluble COD was determined by the dichromate reflux method after passing through a 0.45 membrane filter. A wet-test gas meter was used to measure biogas volume. Gas composition was determined using a modified gas chromatography previously described [12].

Experimental Design

The experimental protocol was designed to examine the effect of different organic loading rates on the operational (e.g., efficiency of COD removal) and performance (e.g., volumetric and microbial elimination capacity as defined in the next section below) indicators. All experiments were performed under steady state conditions. The attainment of the steady state was verified by checking whether the mean of the effluent characteristics for the last two measurements done within 3 x HRT were remaining relatively constant. All the performance and operation results reported are the average values of at least two measurement data.

Operational and Performance Parameters

Operational and performance parameters include organic loading rate, sludge loading rate, elimination capacity and detention time. Loading rates can be looked at from the pollution indicator, empty reactor bed volume and microbial mass. Organic Loading Rate (OLR) takes into account the liquid flow rate and contaminant concentration and is defined as the mass of pollutant introduced in a unit volume of UASB reactor per unit time (e.g., kg COD m^{-3} s^{-1}). As such, this parameter integrates reactor characteristics, operational characteristics and biofilm mass and activity into the volume of media. Sludge Loading Rate (SLR) or food to microorganism ratio (F/M) integrates contaminant concentration and microbial mass and is the mass of pollutant applied to a unit mass of microbial mass per unit time (e.g., kg COD kg^{-1} VSS d^{-1}).

Elimination Capacity (EC) can be used as a performance indicator. Elimination capacity is related to organic loading rate and sludge loading rate in that it is defined as the fraction of the organic load biodegraded in a unit volume of the UASB reactor or a unit mass of microbial mass. This parameter can be expressed either volumetrically (EC_V, kg pollutant removed per unit volume of reactor per day) or on the basis of microbial mass (EC_m, kg pollutant removed per unit mass of microorganisms in the reactor per day). It differs from removal efficiency (η), an operational parameter, which is a measure of the effectiveness of the reactor in degrading a contaminant. EC_m is an indicator for microbial activity and is a measure of the substrate degradation capacity of the microbial mass of the reactor as a whole, regardless of the respective growth phase. It is a useful parameter in that it reduces the chance of overestimating reactor capability by considering microbial mass only. Elimination capacity is a useful parameter for design purposes and removal efficiency helps the operator determine if his system is complying with regulatory effluent requirements.

Mass loading rate (kg m^{-3} d^{-1}), sludge loading rate (kg kg^{-1} d^{-1}) and elimination capacity (kg m^{-3} d^{-1} or kg kg^{-1}VSS d^{-1}) were determined using the relationships between influent and effluent contaminant concentration, effluent flow rate, the effective volume of UASB reactor and the application of appropriate conversion factors, as follows:

$$\mathrm{OLR} = \left(\frac{\mathrm{Q}}{\mathrm{V}_r}\mathrm{C}_{\mathrm{in}}\right), \tag{1}$$

$$\mathrm{SLR} = \mathrm{Q}\left(\frac{\mathrm{C}_{\mathrm{in}}}{\mathrm{VSS}}\right), \tag{2}$$

$$EC_V = \left(\frac{Q}{V_r}\right)(C_{in} - C_{out}), \quad (3)$$

$$EC_m = \frac{EC_V}{VSS}, \quad (4)$$

where Q is the effluent flow rate (m^3 h^{-1}), V_r is the effective volume of reactor bed (m^3), VSS is the microbial concentration of the reactor (mg VSS L^{-1}) and C_{in} and C_{out} are the contaminant concentrations (mg SCOD L^{-1}) in the influent and effluent streams, respectively.

RESULTS AND DISCUSSION

Start up

During the start up, low strength feed was supplied to the reactor to allow the adaptation of the sludge to the new conditions. The organic loading rate for start up was adjusted to 0.05 and was gradually increased during the two weeks period to 0.1 kg SCOD m^{-3} d^{-1}. It should be noted that the time of operation, indicated in the figures to follow, was after initial troubleshooting and the fine tuning of the operations, which lasted two weeks.

There was no gradient in solids concentration throughout the depth of the reactor. The difference in average VSS concentrations at the bottom and top (18.5 and 18.1 g/L, respectively) were insignificant and no sludge gradation seemed obvious throughout the whole reactor.

Steady State Performance

Sludge Proliferation and Maturation

The trend of sludge behavior with time is illustrated in Figure 2. As shown in the figure, there was no major difference in volatile solids content between bottom port (S1) and top port (S6) in the beginning days of the study. In order to promote granulation, calcium carbonate was added to the reactor, beginning with phase 2 (day 5) at a concentration of 2 g/L. This resulted in a decrease in the VSS/SS ratio from 0.74 to 0.47 for the sludge bed as shown in Table 2. The effect was a gradual increase in VSS concentration as S1 relative to S6. After 2 months of operation, the differentiation in the nature of the sludge became more significant and remained stable for a month.

Beginning with day 88, for unexplained reasons, there was an even larger increase in VSS concentration at S1. The VSS content of S6 also showed a decrease at this time but the rate was comparable to the previous periods. As shown in Figure 3 and Table 1, the variability of the data during this phase also increased greatly compared to the previous phases. Nonetheless, the difference in mean concentrations is statistically significant. The increase in VSS/SS ratio from 0.59 to 0.77 indicates an enhancement in viable sludge population in the blanket but, as shown later, there is no significant increase in unit sludge activity.

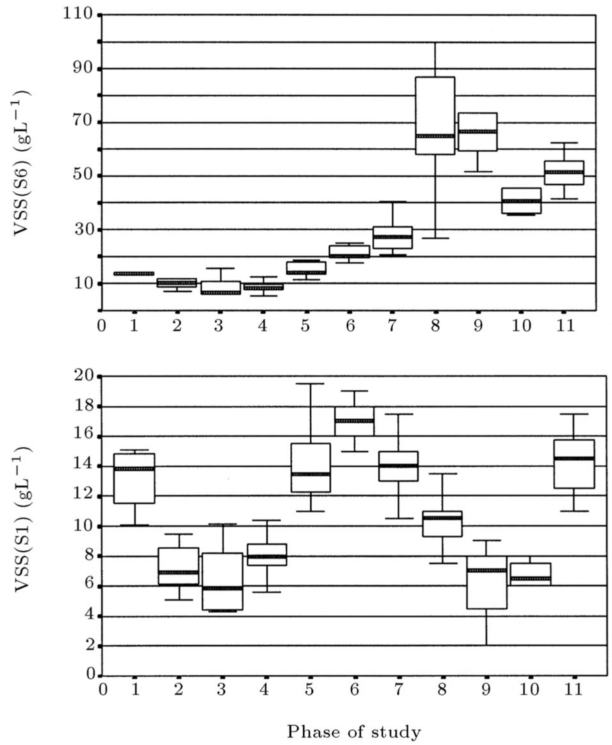

Figure 2. Average volatile suspended solids concentration at the bottom (S1) and top (S6) sampling ports of the UASB reactor during different phases of the study. Values are in g L^{-1} and the bars represent 95% confidence interval.

With the beginning of phase 9 of the study (day 103), the granulated sludge started to show signs of deterioration, as indicated by a sudden drop in concentration. Further increase of OLR to 13.3 kg SCOD m^{-3} d^{-1} at phase 10, did not result in further decrease in VSS concentration as expected. Surprisingly, there was an increase in VSS at S6, despite an even higher OLR value of 16 kg SCOD m^{-3} d^{-1} at phase 11 and the system seemed to be recovering from the initial shocks of the phase 9 increase of OLR. However, this apparent recovery was not followed by a concurrent decrease in VSS content at S6. Examination of the VSS/SS ratio during this period showed no unusual change in either a positive or negative direction. As such, the notion of system recovery has some uncertainty associated with it and needs to be substantiated with additional experimental data.

Overall COD Removal

The relationship between SCOD removal efficiency and ORL is illustrated in Figure 3. It can be seen that removal efficiencies are always above 80% and generally increase with increasing OLR. As mentioned above, in

Table 2. Operational and performance data for different phases of the study.

Phase	Days	SCOD mg/L	VSS, mg/L Blanket	VSS, mg/L Bed	OLR kg SCOD m^{-3}	SLR d^{-1}	SCOD rem, %	VSS/SS Bed	VSS/SS Blanket
1	1-4	94	13763 ± 375	13189 ± 2270	0.13	-	80.2	0.74	0.73
2	5-10	935	10012 ± 1931	7173 ± 1651	1.3	0.14	80.9	0.47	0.46
3	11-17	1869	8975 ± 379	7074 ± 3766	2.6	0.31	89.6	0.51	0.45
4	18-39	2803	8845 ± 2046	8167 ± 1350	3.9	0.42	92.1	0.49	0.53
5	40-48	3338	15942 ± 3769	14208 ± 2595	5.3	0.32	93.6	0.66	0.67
6	49-57	4672	21444 ± 2899	16944 ± 1402	6.6	0.35	95.1	0.66	0.62
7	58-87	5607	28883 ± 7572	14100 ± 2023	7.9	0.42	95.7	0.66	0.59
8	88-102	7250	70209 ± 20259	10467 ± 2446	10.2	0.38	96	0.82	0.7
9	103-111	7854	71722 ± 17612	6167 ± 2462	11.1	0.47	95.3	0.85	0.77
10	112-117	9667	44250 ± 11733	6750 ± 822	13.6	0.81	95	0.82	0.87
11	118-124	11118	51571 ± 7508	14214 ± 2307	15.7	0.62	95.4	0.84	0.86

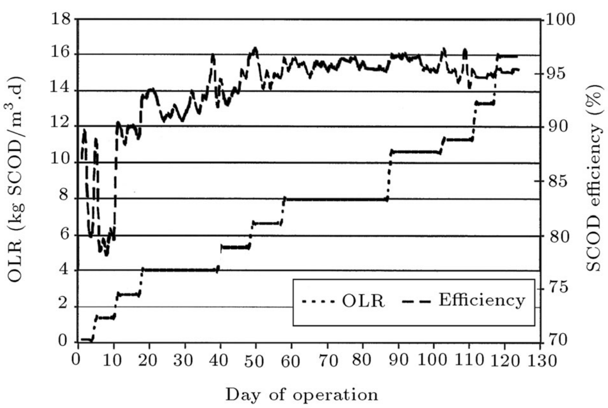

Figure 3. SCOD removal efficiencies at different organic loading rates.

phase 1 of the study, calcium carbonate was added to the reactor to promote granulation. The effect is seen as a transient reduction in removal efficiencies during days 5-10. The system recovered thereafter and removal efficiencies started to increase and became stable. The rate of increase in removal efficiencies was steady as OLR was increased up to around 8 kg SCOD m^{-3} d^{-1}, reaching a stable value of about 97%.

Examination of the trend for removal efficiency indicates three stages of increase, no change and an apparent decrease. It is conceivable that a higher substrate concentration available to the microbial mass is beneficial to biodegradation, assuming Monod kinetics apply. Nonetheless, a point is reached where all the enzyme sites of the microbial population become saturated and there is no further benefit in increased influent concentration. Higher sulfide concentrations at higher OLRs can also be inhibitory. The fact that the system started to show signs of decreased removal efficiencies as OLR was increased to above 11 kg SCOD m^{-3} d^{-1} may point to the saturation conditions, even though a satisfactory SCOD removal efficiency of around 95% was still maintained. The trend of reduced efficiencies at a higher OLR value may be regarded as an onset of performance limitations but further examination of the data in the following sections suggests otherwise.

Elimination Capacity as a Function of Organic Loading Rate

As mentioned above, an apparent performance limitation was suggested with reduced efficiencies observed at increased OLR. Elimination capacity as a performance indicator can be used to examine this hypothesis. Experimental data can be analyzed by focusing on the system performance, either from a unit reactor volume point of view or a unit mass of microbial population.

As illustrated in Figure 4, there is a strong linear relationship between elimination capacity and organic loading rate. The fact that the trend remains linear even at high OLR values suggests that for the range of organic loading rates applied, there was no limiting OLR for which the system performance showed any sign of deterioration. This is not in conformity with the conclusions reached by looking at the SCOD removal efficiency data alone. Nevertheless, it can be expected that the continuing trend of increased EC with increasing OLR will have to cease at higher OLRs, unless there is a corresponding increase in mass

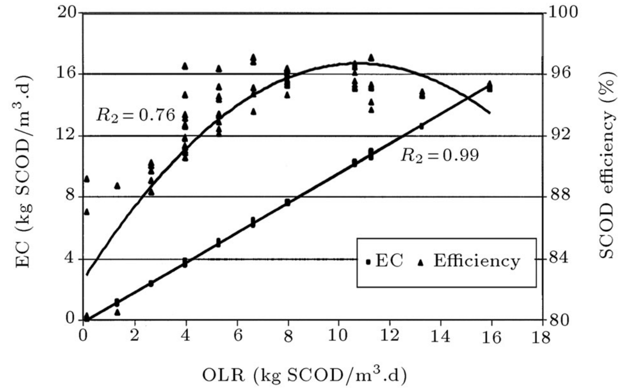

Figure 4. Reactor performance as a function of organic loading rate.

and/or the specific activity of microbial population in the reactor.

To further examine the experimental data from the microbial point of view, a sludge profile of the reactor under different operating conditions can be analyzed. Since most of the biodegradation occurs in the lower portions of the reactor where microbial mass is the greatest, results from the bottom Sample Port (S1) will be used as a representative area for microbial mass and activity. As shown in Figure 5, there is an increase in microbial mass, as indicated in VSS concentration at the bottom of the reactor. The increasing trend is more uniform in the beginning, up to the closing days of phase 7 of the study (days 57-88), corresponding to an OLR value of around 10 kg SCOD m^{-3} d^{-1}. This uniformity begins to break down at higher OLR values and increased data scatter is observed.

Microbial activity represented by the Elimination Capacity of the biomass (EC_m), is low at the beginning but starts to increase rapidly. It stabilizes around day 40 and remains so until the end of phase 7. Thereafter, signs of a decreasing trend start indicating deteriorating conditions. Initiation of this condition corresponds to the increased data scatter for microbial

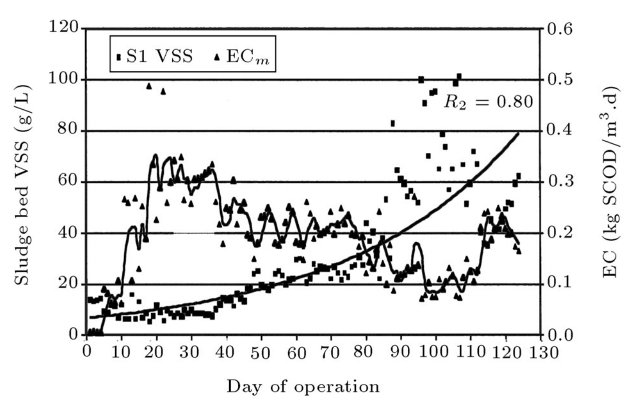

Figure 5. Microbial mass and activity during different phases of the study.

mass. These results suggest that the UASB reactor used may not be able to consistently treat organic loading rates higher than 10 kg SCOD m^{-3} d^{-1} for this type of wastewater and under these conditions. This is in line with the ranges of the reported values of stable operation at an OLR value of 5.46 or less [13], 13.8 [14], and 12.2 kg SCOD m^{-3} d^{-1} [15] from conventional and cellulosic feedstocks.

CONCLUSIONS

Results from this study confirm the suitability of a UASB reactor in treating stillage effluent from alcohol production facilities. Satisfactory SCOD removal efficiencies of above 90% were obtained at a constant HRT value of 6 h and organic loading rates of around 10 kg SCOD m^{-3} d^{-1}. The performance of the system, based on unit reactor volume and unit microbial mass, was 10 kg SCOD m^{-3} d^{-1} and 0.25 kg SCOD kg^{-1} VSS d^{-1}, respectively.

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