Highlights

- The S-SAD of animal residue permits to obtain renewable energy.
- The daily repeated percolate recirculation avoids inhibition phenomena.
- The chemical characteristics of WEOM affect the stability of the S-SAD.
- The recirculation frequency influences the quality of the final solid digestate.

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Optimization of solid-state anaerobic digestion through the percolate recirculation

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Abstract

Anaerobic digestion is an environmentally sustainable way to manage organic waste, and it is able to enhance the recovery of organic carbon and nutrients in agricultural soils and to produce renewable energy. Solid-state anaerobic digestion (S-SAD) is a technology that permits the treatment of different type of residues, but is characterized by inhibition phenomena, resulting in a low operational stability. An experimental apparatus, equipped with a recirculation system for the digestate liquid fraction (percolate), was used to optimize the S-SAD system. Different frequencies of recirculation, one, two or four per day, were carried out to investigate how recirculation might affect the quality of the liquid fraction as well as the possible effects on biogas production and on the obtained solid digestate quality. Biogas production was positively affected by percolate spreading, especially when recirculation was performed 4 times per day. As shown by percolate chemical analyses, recirculation avoided the accumulation of volatile fatty acids in the liquid fraction, resulting in a better process stability. In addition, recirculation induced a large consumption of readily available compounds in the percolate, as shown by the depletion of water extractable organic C and total reducing sugars. The quality of the digested solid fraction was also improved by percolate recirculation in terms of the C/N ratio and organic N parameters. These findings showed that daily repeated recirculation of the liquid fraction is suitable to avoid inhibition phenomena during S-SAD and to improve the quality of the digestate solid fraction.

1. Introduction

Anaerobic digestion (AD) is a sustainable solution combining recycling of organic materials with the production of renewable energy (biogas) [1,2,3,4,5]. Animal residues-AD is a process that is used very successfully in a large number of countries because of its contribution to the reduction of greenhouse gas emissions into the atmosphere [6,7]. In fact, compared to raw materials, the use of the biomass obtained after AD resulted in a stable and partially hygienized organic product, characterized by the presence of stable organic matter [8,9].

The most common AD is based on wet technology, operating with a total solids (TS) concentration of <15% (w/w) [10,11]. This type of process is characterized by some significant technical drawbacks, i.e., the need for pre-treatments, large use of water, and consequent production of sludge that needs to be disposed of [12,13]. For all of these reasons, solid-state anaerobic digestion (S-SAD) is becoming more common [5] and consists of treating biomass and residues that maintain their shape when managed in an open pile. This condition is usually achieved with a TS concentration of >25% (w/w) [14]. The use of S-SAD allows many types of residues to be treated**,** with different qualities and rates of biodegradability [15,16]. Despite these positive aspects, S-SAD is characterized by inhibition phenomena, resulting in a low efficiency of biogas production. It is well known that during the anaerobic process, large amounts of volatile fatty acids (VFAs) are produced, resulting in a decreased pH (acidogenic phase). In particular, this first stage of AD is driven by acidogenic microbes, which are faster than methanogenic microorganisms, often causing the accumulation of VFAs [16,17]. Hence, S-SAD is exposed to inhibition phenomena caused by VFA accumulation, resulting in a low operational stability and an alteration of organic material degradation, which affects the final digestate quality [11,18]. It is also true that the use of solid inoculum might guarantee optimal conditions for methanogenic species, avoiding the inhibition phenomena [13,16] due to VFA accumulation. The use of solid inoculum causes a loss in the volume capacity of the anaerobic reactor or biocell. This issue may be solved by spreading the

liquid fraction of the digestate, i.e., the percolate, on the material being treated (approximately 10% by weight of treated waste), improving the process stability and digestate quality [11,14].

Therefore, the use of percolate spreading has been proposed as a method to avoid inhibition phenomena [11,18]; but, it is also important to understand how the chemical characteristics of the percolate affect the S-SAD behaviour. Characterization of water extractable organic matter (WEOM) was widely studied to evaluate the composting process, showing that the quality of WEOM is a function of organic matter stability [19,20]. Even during S-SAD, it might be interesting to investigate how the quality of percolates changes during spreading in terms of WEOM and its influence on biogas production. To optimize S-SAD by percolate recirculation, the aim of the present study was to investigate how the frequency of recirculation might affect the quality of the liquid fraction as well as possible effects on biogas production and on the obtained solid digestate quality. Specifically, the hypotheses are as follows: i) the chemical characteristics of percolate, i.e., WEOM, may change with the frequency of recirculation, affecting the stability of S-SAD; ii) the recirculation of percolate induces the removal of inhibitor factors during S-SAD, improving the quality of the final solid digestate.

2. Materials and methods

2.1 Characteristics of the starting mixture

The initial mixture used for each trial consisted of pig slurry with straw added at a ratio of 3:1 (w/w); the inoculum, produced from previous S-SAD, was added at the same amount of pig slurry to the initial mixture. Prior to the start of the experiment, 2 L of demineralized water were added to the bottom part of the reactor, and the obtained mixture was analysed for its main chemical characteristics (Table 1).

(PLEASE INSERT TABLE 1)

2.2 Experimental apparatus

AD was carried out by means of laboratory reactors equipped with a recycling system for the liquid fraction (percolate) and a hydraulic gasometer to measure biogas production (Fig. 1).

(PLEASE INSERT FIGURE 1)

Three polyethylene reactors with a 15 L capacity were used for each test. In particular, the percolate was collected through a tapped hole at the bottom of the reactor, while on the top, an output that allowed the produced biogas to pass was present. To create a separation between the percolate and solid fraction, a polyethylene filter with a porosity of 3 mm was fitted to allow passage of the liquid fraction and to prevent any solid fragments from occluding the recirculation system. The gasometer consisted of a water tank that was sealed with a hermetic cap and connected to a second tank by a plastic tube (internal diameter 4 mm). The biogas leaving the reactor generates pressure on the water present in the former tank, causing a transfer of the liquid to the second tank. The cumulative volume of water in the latter tank was measured daily, and the biogas production was calculated. This parameter was measured for 50 days, and the results were expressed as Nm^3 of biogas/t of VS. Moreover, the biogas composition and concentration (CH_4, CO_2 and O_2) were evaluated at 20 days for each trial by using an infrared portable gas detector (ETG-MCA 100, ETG Risorse e Tecnologia, Montiglio, Italy). The trials were performed in a climatic chamber under mesophilic conditions (35± 2 °C), where the temperature was maintained constant throughout the entire experimental period. During the experiment, we compared two different AD technologies: with and without percolate recirculation, the latter of which was used as the control. In particular, the effect of a different frequency of recirculation was investigated: once per day, twice per day (every 12 hours), and four times per day (every 6 hours), namely, as 1 S-SAD, 2 S-SAD, and 4 S-SAD, respectively. The duration of each recirculation was 45 minutes. The percolates were collected from each reactor at specific sampling times and then analysed for their chemical characteristics.

2.3 Chemical analysis of the starting mixture and the final digestates

The starting mixture and final digestates resulting from the different treatments were analysed for their main chemical characteristics. The moisture content and total volatile solids (VS) were determined by weight loss upon drying at 105 °C in an oven for 24 h and ashing at 550 °C in a muffle furnace for 24 h, respectively. Electrical conductivity (EC) and pH were determined for the fresh samples at a 1:10 (w/v) solid/water suspension ratio. The total organic carbon (TOC) content was determined using the Springer-Klee wet dichromate oxidation method [21]. Fresh samples were used to determine the total Kjeldahl-N (TKN) and total ammonia nitrogen (TAN) by means of macro and micro-Kjeldahl distillation methods, respectively [22]. Total organic N was calculated by the difference between TKN and TAN. Total P was measured spectrophotometrically after digesting the dried samples with concentrated H_2SO_4/$HClO_4$ [22]. Total Cu and Zn were analysed by flame atomic absorption spectroscopy (AA 6800, Shimadzu Corp., Tokyo, Japan) after digesting the dried samples with concentrated HNO_3/$HClO_4$ [22]. All of the analyses were carried out in triplicate.

2.4 Percolates characterization

Samples of percolates were collected at 4, 8, 11, 15, 21, 28, 35, 42, and 50 days of AD from each laboratory reactor; the percolates were then analysed for the following parameters: process stability by means of the FOS/TAC (Flüchtige Organische Säuren/Totales Anorganisches Carbonat) ratio, water extractable organic C (WEOC), total phenolic compounds (TPC) and total reducing sugars (TRS).

The FOS/TAC parameter was used as an indicator of process stability and was evaluated as a ratio between the total VFAs (expressed as mg/L of CH_3COOH equivalent) and alkalinity (expressed as mg/L of $CaCO_3$) [23,24]. The FOS/TAC of percolates was determined in 20 mL of sample by

means of an automatic titration device (Hach Lange TIM 840, Hach Lange Italia, Lainate, Italy) as a two-step endpoint titration using a 0.05 M H_2SO_4 solution.

The VFAs were analysed in the percolates during the first two weeks at 4, 8, 11 and 15 days. To determine each VFA, 2 mL of percolate was acidified with 60 µL of 20% H_3PO_4 and centrifuged at 3000 rpm for 15 min. The supernatant was filtered through a 0.22-µm nylon filter and analysed with a gas chromatograph (Trace-GC Thermo, ThermoFisher Italia, Rodano, Italy) equipped with a flame ionization detector and a VF-WAX column (30 m length, 0.25 mm internal diameter, and 0.25 µm film thickness) as described by Massaccesi et al. [18]. Fatty acids, up to 7 C atoms, were investigated. WEOC was measured using Pt-catalysed, high temperature combustion (800 °C) followed by infrared detection of CO_2 (MULTI N/C 2100/2100S, Analyticjena AG, Jena, Germany). TRS in the percolates were determined using a phenol reagent [25] as described by Massaccesi et al. [18], and the results are expressed in mg glucose-C equivalents/L. TPC in the percolates were determined using a colorimetric method with a modified version of the Foline Ciocalteu method [26] as described by Said-Pullicino and Gigliotti [27], and the results are expressed in mg vanillic acid-C equivalents/L.

2.5 Statistical analysis

Two-way analysis of variance (ANOVA) was used to compare the WEOC, TRS and TPC results as a function of the recirculation rate and experimental time; significant differences were assessed by Tukey's Honest Significant Difference (HSD) test ($P = 0.05$), and the standard error of the mean (SEM) was reported. The correlations between the WEOC and TRS, and WEOC and TPC results, were evaluated by Pearson's correlation ($P \leq 0.05$), All data are expressed as the mean ± standard error ($n = 3$).

3. Results and discussion

3.1. Biogas production and process stability

Figure 2 shows the evolution of the daily and cumulative biogas production during the experiment.

(PLEASE INSERT FIGURE 2)

The effect of different recirculation frequencies on biogas production is evident, especially when the percolate is recirculated more than once a day. Previous studies demonstrated the effectiveness of leachate recirculation on biogas production [28,29,30,31]. In our study, it was observed that 2 and 4 recirculations per day led to an increase in biogas production, especially during the first 10 days of S-SAD. Afterwards, biogas production decreased in both 2 S-SAD and 4 S-SAD, reaching the same production of 1 S-SAD and the control on the 20^{th} day. The peak of biogas production in the 4 S-SAD also resulted in the highest cumulative biogas production at the end of experiment (240.8 Nm^3/t^-VS), whereas the percolate recirculated once a day did not improve biogas production, as shown by the similar evolution of the process between this test and the reactors without recirculation. This result suggests that the recirculation of percolate had a positive effect on S-SAD and on biogas production when recirculation was performed > 2 times per day. However, the percolate recirculation did not affect the biogas composition measured at after 20 days of S-SAD (data not shown).

This phenomenon was probably attributable to the removal of inhibitor factors from the solid biomass, which induced a better process stability and improvement in biogas production. It is also true that an increase in biogas production was evident, especially in the early stages of the anaerobic process, probably because of the fast digestion rate of the solid biomass in the reactor [31,32]. The liquid digestate, obtained from spreading the solid biomass, is likely able to create good conditions for the hydrolytic and methanogenic species during S-SAD [11,18]. However, the recycling of leachate can lead to the accumulation of VFAs or other factors that inhibit, in the liquid phase, the activity of methanogenic bacteria [13,33]. To study the possible inhibiting effects in the liquid phase, the behaviour of the FOS/TAC and VFAs were investigated in the percolates. The results of the FOS/TAC (Fig. 3) clearly show an increase at the beginning of the experiment, followed by a gradual decrease after 10 days in all tests.

(PLEASE INSERT FIGURE 3)

This trend was expected since the biochemical process during the first step of the AD led to a high production of VFAs, enhancing the acidity of the percolates. In fact, the peak of the FOS/TAC was observed after one week of AD, particularly in the control and 1 S-SAD tests, suggesting that the buffer capacity of the process, in the liquid fraction, was more suitable when recirculation was performed more than once a day. It is well known that the production of ammonia and bicarbonate during AD lead to an efficiency increase of the buffer system in the reactors, especially when the alkalinity, expressed as mg $CaCO_3$/L, ranged from 3,000-5,000 mg/L [34]. In fact, in our experiment, the recirculation of percolate had a positive effect on this parameter, as demonstrated by the highest concentration values detected at 10 days in the percolates collected in 2 and 4 S-SAD (4,366 and 3,800 mg $CaCO_3$/L, respectively). This result suggests that enhanced percolate recirculation induced a faster degradation of protein in the solid biomass, especially in the 2 and 4 S-SAD tests, as also demonstrated by the FOS/TAC values on the 10^{th} day (0.62 and 0.37, respectively). Afterwards, the FOS/TAC decreased, reaching the optimum conditions (ranged from 0.25 to approximately 0.5, as reported by Di Maria et al. [35]) for biogas production after 10 days only in run 4 S-SAD.

These results are supported by the determination of the VFAs in the percolate during the experiment. Figure 4 shows the concentration of each VFA produced during the first 15 days of the S-SAD test.

(PLEASE INSERT FIGURE 4)

The amount of VFAs reported in Fig. 4 is obtained by summing all of the concentrations detected at each sampling time. Not all of the investigated VFAs were detected in the percolates, only those with up to 4 C atoms, i.e., the acetic, propionic, isobutyric and butyric acids. As shown by the FOS/TAC results, the greatest amount of VFAs was produced from the control and 1 S-SAD, followed by the 2 S-SAD and 4 S-SAD tests. In particular, this increase was mainly attributed to acetic and propionic acids, which exhibited concentration values of 52 and 9 times higher,

respectively, in the control with respect to 4 S-SAD. While tests that recirculated percolate did not show any increase in the concentrations of both acetic and propionic acids, both acids exhibited a rise until 10 days in the control (data not shown). The lack of an increase in acetic and propionic acids was probably attributed to the faster consumption of VFAs in percolates derived from the 2 and 4 S-SAD tests.

The FOS/TAC parameter, supported by the total VFA results, suggests that the recirculation of percolate avoids the accumulation of VFAs, leading to better process stability and greater biogas production. During the first few days of AD, the repeated recirculation of percolate (more than once a day) accelerated hydrolysis and the conversion of VS into VFAs, as well as encouraged the formation of a buffer system that favoured the subsequent methanogenic activity. These findings were confirmed by the highest biogas production obtained from the 2 S-SAD and 4 S-SAD tests.

3.2. Evolution of WEOM and the quality of percolates

Figures 5 and 6 show the evolution of WEOC and TRS in the percolates. The trends of both parameters are similar, as the values were higher in S-SAD with recirculation of percolate than the control during all experiments.

(PLEASE INSERT FIGURES 5 AND 6)

In particular, Fig. 5 shows that the WEOC concentration was significantly higher with respect to the control in all tests, particularly in 4 S-SAD. In addition, in this test, the WEOC showed a rapid decrease during the first week, despite the other tests that showed a slow depletion rate. However, the WEOC concentration led to a significant decrease within 50 days in all tests in which the percolate was recirculated.

Figure 6 shows the TRS results during the S-SAD experiments. In all tests with recirculation of percolate, the TRS values were higher than that of the control until the end of the experiment. The initial highest concentration of TRS in 4 S-SAD was probably due to the faster hydroxylation of the

complex molecules in the solid biomass, as also observed by Massaccesi et al. [18]. However, a rapid decline of TRS was observed after 8 days of the experiment, as also observed in WEOC. Moreover, it is interesting to observe that only in 4 S-SAD did the TRS content show a significant decrease with respect to the beginning of the experiment. The behaviour of the TRS observed during the first two weeks demonstrated that 4 recirculations per day enhanced the degradation of the organic compounds of the solid biomass into readily available molecules, such as sugars. In addition, the significant depletion of the TRS observed after 20 days of AD was probably due to the use of these compounds in the liquid fraction as a source of energy by the microorganisms.

Both the WEOC and TRS parameters showed a similar trend, corresponding to a positive correlation value (r = 0.52), which indicated that the decrease in WEOC reflects overall the depletion of TRS. In particular, this was significant when 4 recirculations per day were adopted (r = 0.77). Whereas, the correlation was not significant for the 1 S-SAD, control and 2 S-SAD tests. These findings suggest that the decrease in WEOC and TRS was related to enhanced microorganism activity and the consumption of the readily available compounds, especially in the 4 S-SAD test. With regard to the 1 and 2 S-SAD tests, the correlation was less evident, probably because WEOC depletion by microorganisms was balanced by that released from the organic biomass in the reactor.

Figure 7 shows the TPC results during the S-SAD tests.

(PLEASE INSERT FIGURE 7)

The TPCs were significantly higher in the percolates collected at the beginning of the experiment in all tests with recirculation. Although the TPC concentrations were higher in the percolates collected from the 1 S-SAD, 2 S-SAD and 4 S-SAD tests with respect to the control, they did not show any decrease during the experiment. Even Massaccesi et al. [18] observed that a significant aliquot of TPC remained in the liquid fraction after 78 days of the anaerobic process.

Indeed, the correlations between the WEOC and TPC results were not significant for the 1 S-SAD, 4 S-SAD and control tests, except for 2 S-SAD (r = -0.83). However, the TPCs did not show any

significant differences in the in the time in the 4 tests, probably because the consumption rate of these compounds by microorganisms is slower, despite the times of daily recirculation.

3.3. Solid digestate characterization

The chemical characterization of the solid digestates obtained from each S-SAD test is reported in Table 2. The dry matter content led to a decrease with respect to the beginning of the experiment because of the effect of percolate recirculation, which makes the biomass in the reactors moister. The VS results show that the recirculation rate enhanced the decreasing amount of VS in the final digestate. The depletion of VS was particularly noticeable for the 2 S-SAD and 4 S-SAD tests, suggesting that the time of recirculation can improve the degradation of organic matter, as also demonstrated by a higher biogas production in these two tests with respect to the control and the 1 S-SAD test. The pH shows a small increase in all tests, except for 1 S-SAD, where the pH did not change. The EC did not change overall in all tests, except in the control, in which a significant decrease was observed. This suggests that when recirculation was not carried out, soluble salts accumulated in the liquid fraction (data not shown), i.e., percolate, likely contributing to the inhibition of the AD process. In fact, it was demonstrated that the slowdown of microorganism metabolism is due not only to the high concentration of ammonium nitrogen but also to the high concentration of soluble salts, which may cause osmotic shock in microbial cells [36]. With regard to the TOC content, a decrease was observed during the anaerobic process in all tests, in particular the 4 S-SAD test. Carbon loss is due to the degradation of organic matter and subsequent biogas production, which is more evident in our experiment for the 4 S-SAD test. The TKN only leads to a small increase in the 4 S-SAD test, probably due to the removal of VS and the consequent

concentration of the biomass. In addition, it is interesting to consider the percentage of organic N that is present in the final digestates, which is higher in all tests with respect to the initial content, which is particularly noticeable for the 4 S-SAD test. This result was probably due to the leaching of TAN into the percolates, contributing to the formation of the buffer system in the liquid fraction and, at the same time, to the stability of the S-SAD. The organic matter loss and constant content of TKN, led to a decrease in the C/N ratio with the enhancement of the recirculation rate (4 S-SAS > control > 2 S-SAD > 1 S-SAS). The decrease in the C/N ratio obtained with recirculation may be interesting from an agronomic point of view since the digestate would allow for agricultural use when the C/ N ratio is < 25.

(PLEASE INSERT TABLE 2)

4. Conclusions

The optimization of S-SAD through percolate recirculation has proven to be a suitable means to treat animal residues while avoiding inhibition phenomena, which frequently occur in this type of AD. In fact, it was demonstrated that the increase in the rate of percolate recirculation promoted hydrolysis in the solid fraction (e.g., animal residues) with the subsequent release of readily available organic compounds in the liquid fraction. In addition, the accelerated degradation led to faster protein mineralization in the solid fraction, causing the formation of a buffer system in the percolate. The enhanced alkalinity in the liquid fraction during the first stages of S-SAD was important in reducing the negative effect of VFA accumulation, promoting methanogenic activity and hence biogas production. These findings suggest that the chemical characterization of WEOM was important to better understanding the behaviour of S-SAD and to identify the main critical points during the anaerobic process. Moreover, recirculation of the percolate, repeated four times per day, was shown to have a positive effect on both the agronomical and environmental qualities of the digested solid fraction, even if further investigations are needed on the chemical and spectroscopic characteristics of the obtained solid fraction of digestate.

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Table 1. Main chemical characteristics of the starting mixture[a]

Parameter	**Starting mixture**
Dry matter (%)	20.7 ± 1.3
VS (g/kg)	877 ± 5.4
pH	8.22 ± 0.18
EC (dS/m)	5.54 ± 0.89
TOC (g/kg)	491.0 ± 5.7
TKN (g/kg)	11.9 ± 1.1
TAN (g/kg)	8.8 ± 0.7
Organic N (g/kg)	3.1
C/N	41.3

[a] All data are expressed on a dry weight basis.

Table 2. Main chemical characteristics of the final digestates[a]

Parameter	**Control**	**1 S-SAD**	**2 S-SAD**	**4 S-SAD**
Dry matter (%)	16.0 ± 0.3	14.0 ± 0.6	13.3 ± 0.3	12.2 ± 0.5
VS (g/kg)	854 ± 10.0	859 ± 26.0	841 ± 4.6	831 ± 5.4
pH	8.90 ± 0.10	8.22 ± 0.06	8.69 ± 0.06	8.82 ± 0.08
EC (dS/m)	1.80 ± 0.20	4.82 ± 0.15	4.18 ± 0.34	5.36 ± 0.38
TOC (g/kg)[b]	411.8 ± 2.8	417.7 ± 6.1	376.9 ± 6.7	230.9 ± 9.0
TKN (g/kg)	11.8 ± 0.2	10.8 ± 1.2	11.4 ± 3.9	16.4 ± 1.5
TAN (g/kg)	5.4 ± 0.4	2.9 ± 0.4	1.1 ± 0.6	0.4 ± 0.1
Organic N (g/kg)	6.4	7.9	10.3	16.0
C/N	34.9	38.7	33.1	14.1

[a] All data are expressed on a dry weight basis.
[b] TOC values were corrected on ash content.

Figure captions

Fig. 1. Schematic of the S-SAD experimental apparatus composed of a polyethylene reactor (15 L capacity) and a hydraulic gasometer.

Fig. 2. Daily and cumulative biogas production during the S-SAD tests at different frequencies of recirculation. Control: without recirculation; 1 S-SAD: once per day; 2 S-SAD: 2 per day; and 4 S-SAD, four per day.

Fig. 3. FOS/TAC evolution during the S-SAD tests at different frequencies of recirculation. Control: without recirculation; 1 S-SAD: once per day; 2 S-SAD: 2 per day; and 4 S-SAD, four per day.

Fig. 4. VFA production during the first 15 days at different frequencies of recirculation. Control: without recirculation; 1 S-SAD: once per day; 2 S-SAD: 2 per day; and 4 S-SAD, four per day.

Fig. 5. WEOC evolution during the S-SAD tests at different frequencies of recirculation. (SEM = 268.3)
Control: without recirculation; 1 S-SAD: once per day; 2 S-SAD: 2 per day; and 4 S-SAD, four per day.

Fig. 6. TRS evolution during the S-SAD tests at different frequencies of recirculation. (SEM = 62.4)
Control: without recirculation; 1 S-SAD: once per day; 2 S-SAD: 2 per day; and 4 S-SAD, four per day.

Fig. 7. TPC evolution during the S-SAD tests at different frequencies of recirculation. (SEM = 36.5)
Control: without recirculation; 1 S-SAD: once per day; 2 S-SAD: 2 per day; and 4 S-SAD, four per day.

Figure 1

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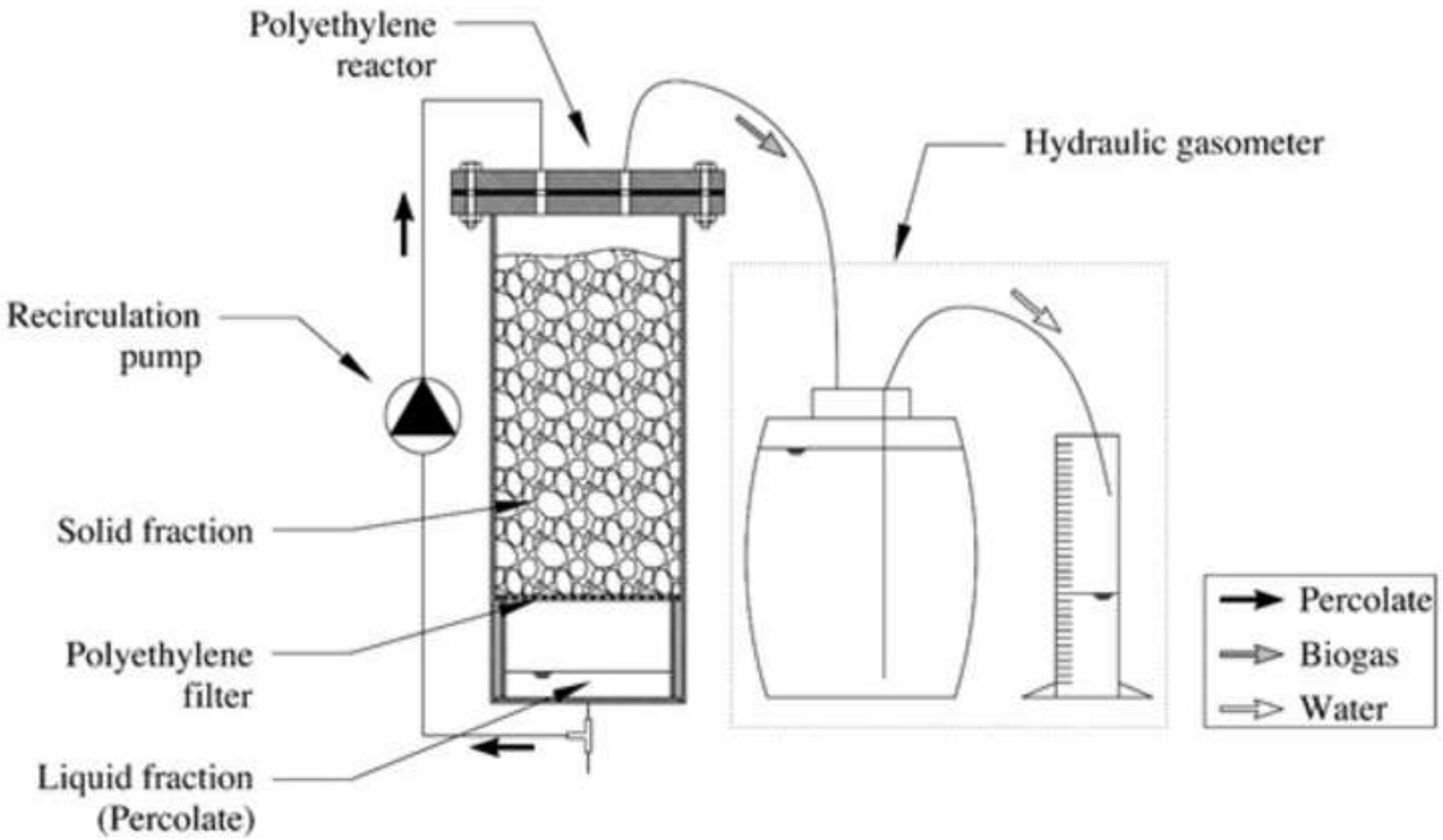

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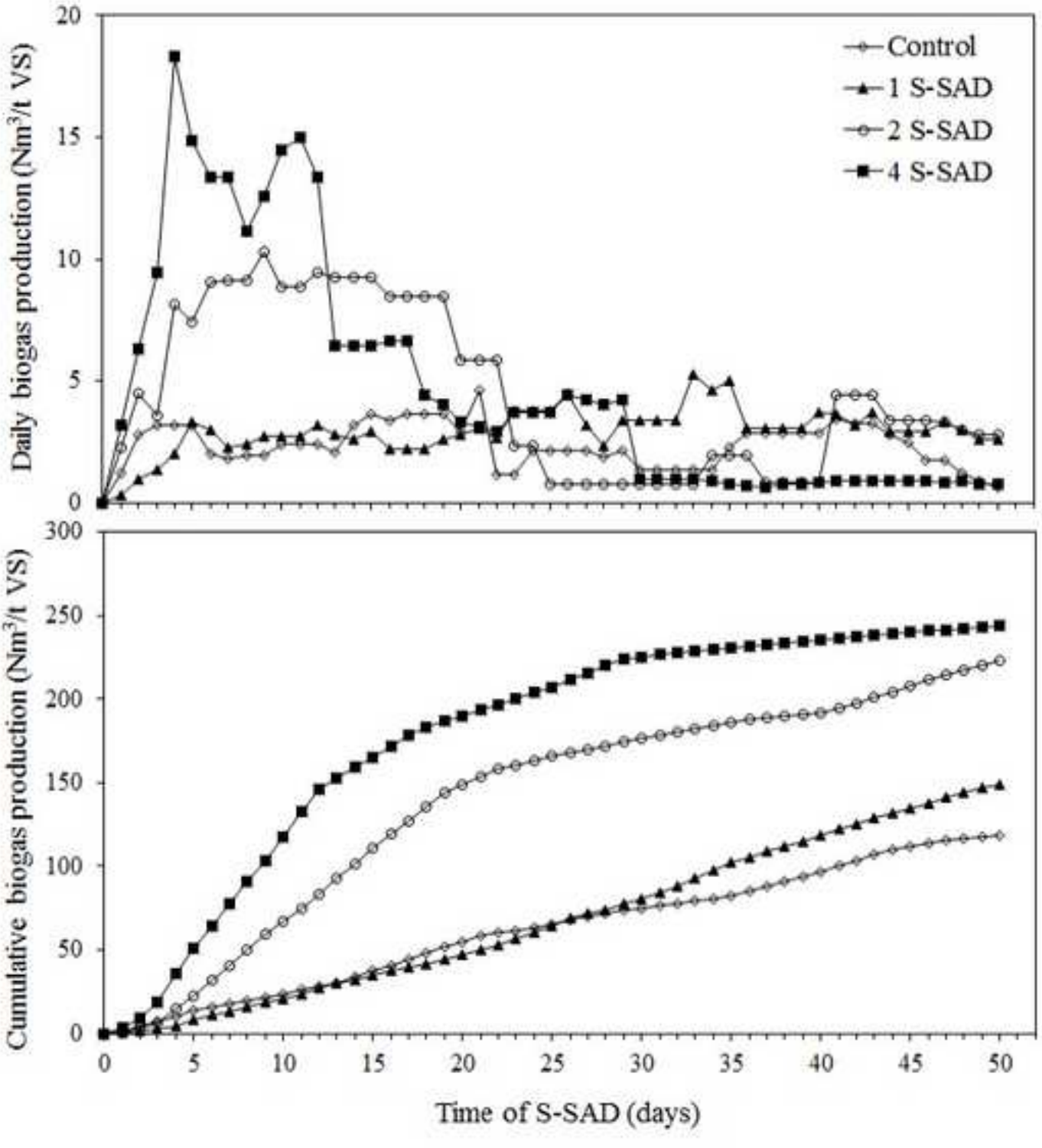

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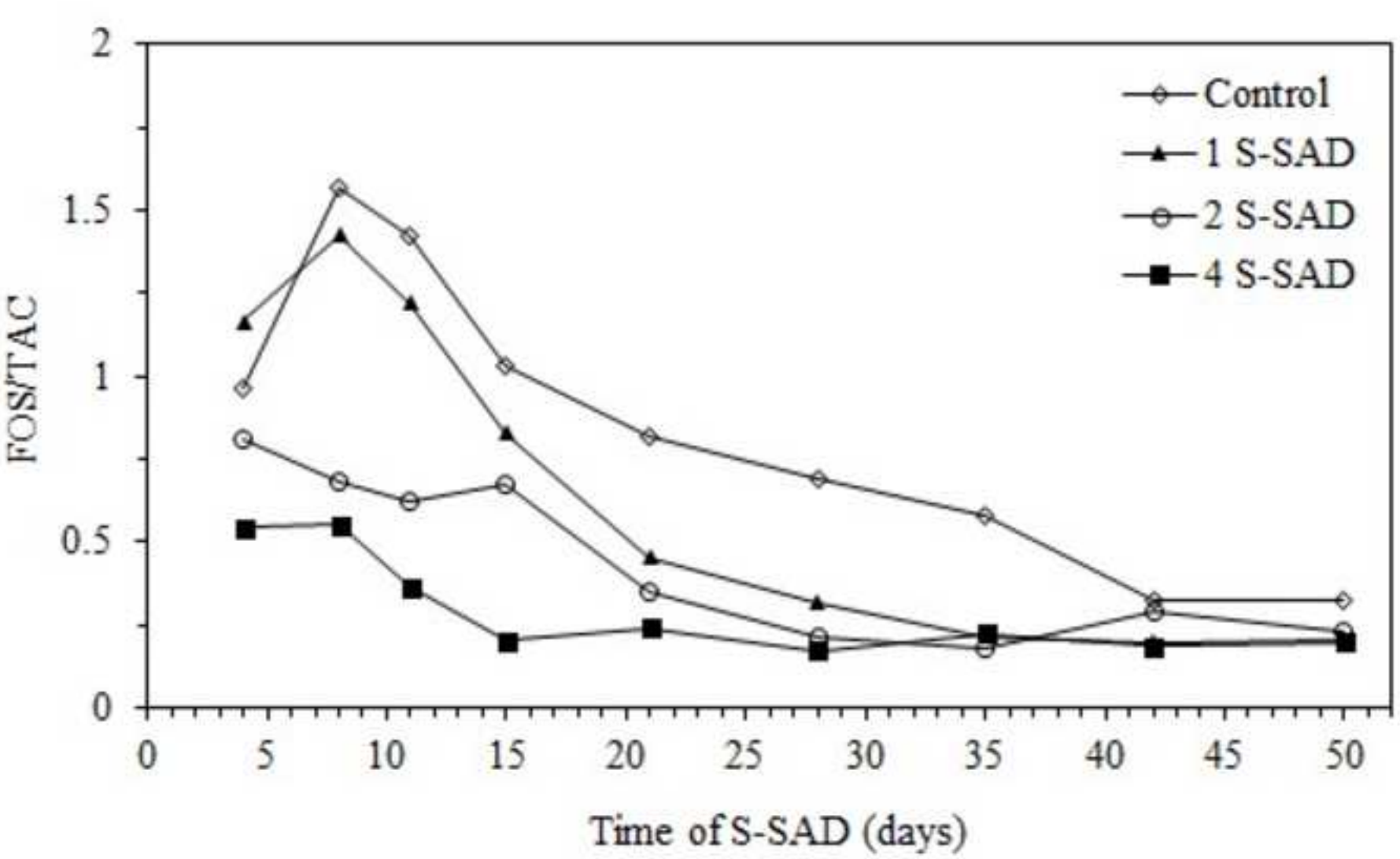

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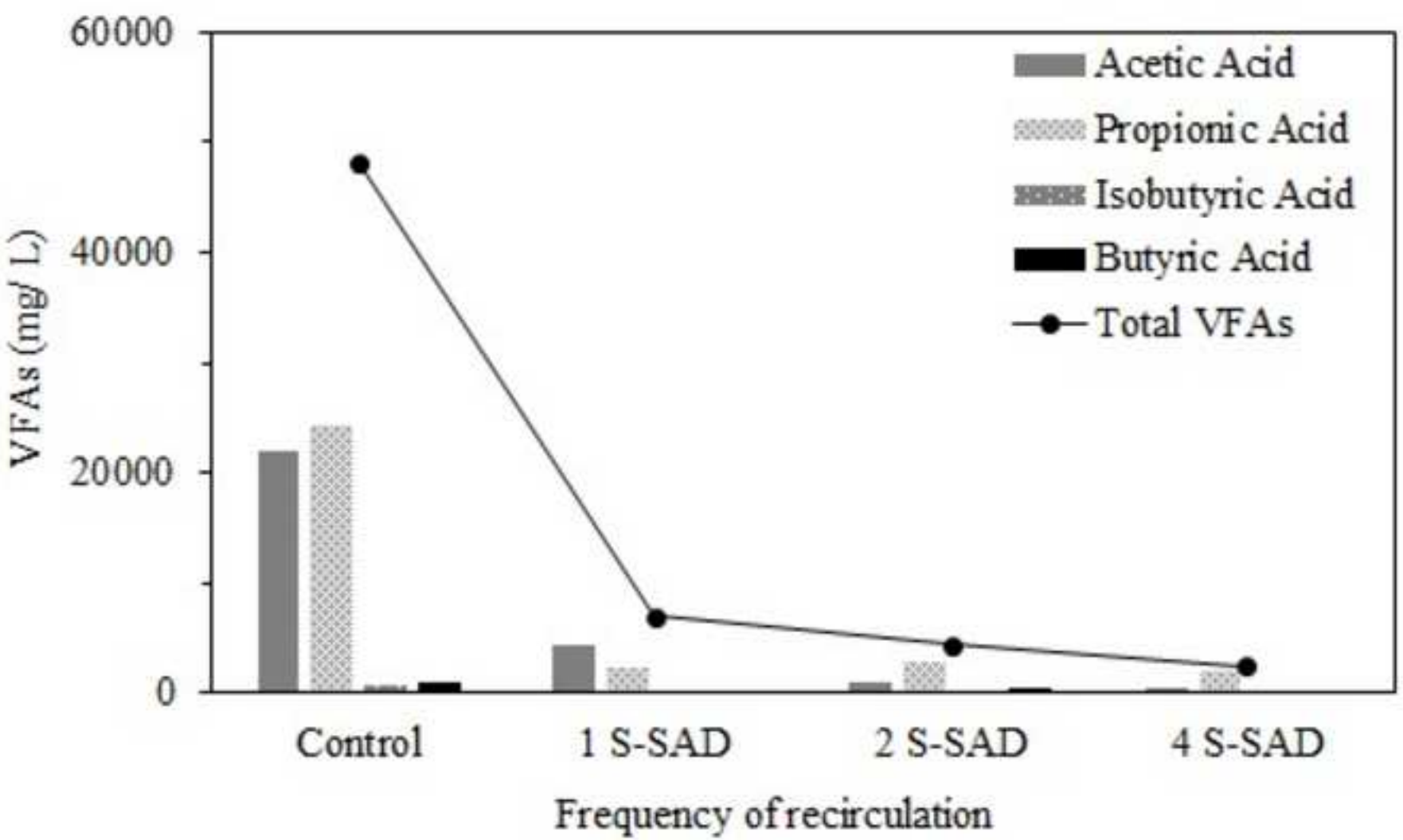

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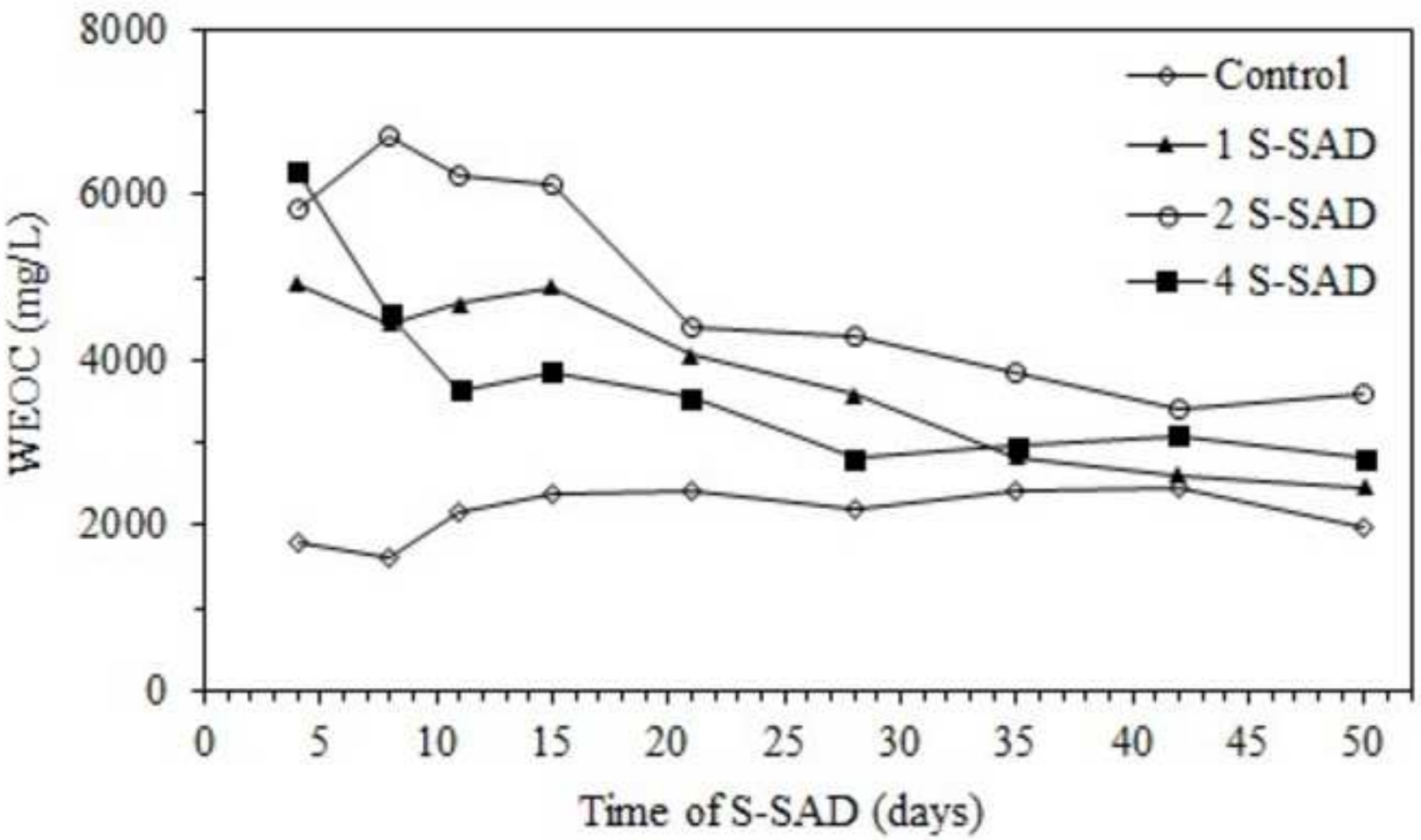

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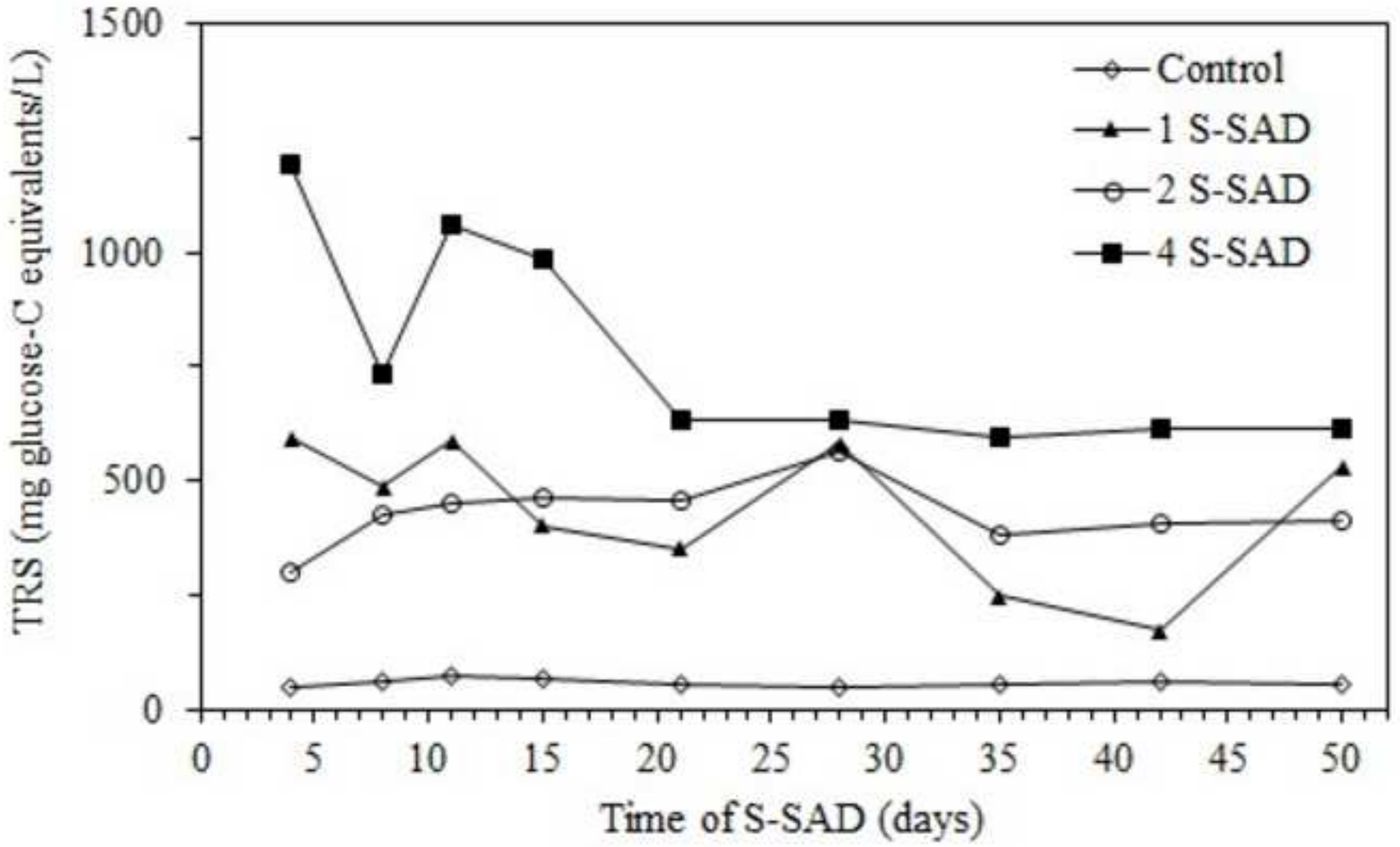

Figure 7

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