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Sulfite pretreatment on the anaerobic sludge digester for improving methane production and volatile solid reduction

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This study presents the sulfite pretreatment in order to improve sludge biodegradability and methane production during anaerobic digestion. Different SO_3 concentrations (0-500 mg/L SO_3) have been used to investigate the sulfite pretreatment considering sludge disintegration. First, a 24 h period has been applied to determine the pre-treatment effects. At the end the period, 500 mg/L SO_3 achieved the highest performance in terms of volatile solid reduction and increase in soluble chemical oxygen demand concentration. 13.84 % of organic matter reduction, 18.9 % of increase in soluble chemical oxygen demand and 1.18 % of disintegration degree are obtained. After that, effects of sulfite pre-treatment on methane production have been investigated during anaerobic digestion. Similarly, the anaerobic digester which fed with pretreated sludge using 500 mg/L SO_3 showed the highest methane production with 96.5 mL CH_4/g VS. Besides, in first time for the sulfite pre-treatment of sludge, Monte Carlo simulation has been used to estimate the volatile solid reduction and methane production considering removed chemical oxygen concentration and changes of volatile solid concentrations As a result of simulation, maximum organic matter reduction is found as 33 % and while methane production was 26,83 % LEL.

Keywords: Anaerobic digestion, Disintegration, Methane production, Monte Carlo Simulation, Sulfite pre-treatment

Introduction

A large amount of waste activated sludge is produced from biological wastewater treatment plants. Sludge treatment and disposal requires high costs[1]. The increasing demand for sustainable sludge management leads to increased interest in both sludge volume reduction and resource and/or energy recovery from sludge[2]. Briefly, sludge ensures the recovery of resources/energy and eliminates the cost and difficulty of disposal[1]. Anaerobic digestion is an effective process not only for the stabilization of waste activated sludge but also for the recovery of bioenergy in the form of methane[1]. It converts sludge to valuable resources such as methane, volatile fatty acids and hydrogen providing less sludge disposal cost, making easer the operation of wastewater treatment plants and presents sustainable sludge management. However, the complex structure of sludge lead slow sludge biodegradability and required high retention times during anaerobic treatment. To overcome this limitation, different pretreatment techniques have been extensively investigated and significant efforts have been made to improve the biodegradability of sludge and the efficiency of anaerobic sludge treatment[2]. Various pretreatment techniques such as biological hydrolysis with enzymes, free nitrous acid, ultrasonication, ozone, chlorination, alkaline and thermal techniques have been extensively investigated to increase methane production[3,4,5,6,7,8]. However, most of the above-mentioned approaches are extremely costly due to high energy input or excessive chemical consumption. Therefore, it seems necessary to investigate a new low-cost pretreatment method[1].

Recently, sulfite pretreatment has been shown to be effective in causing sludge breakdown and dissolution of waste activated sludge[1,9]. Through evaluation of biogenic sulfide production tests, it has recently been confirmed that the biodegradability of waste activated sludge can be significantly increased after sulfite pretreatment[10]. The advantages of the sulfite pretreatment versus other treatment methods are summarized in Table 1 and a comparison table summarizing sulfite pretreatment performance versus other pretreatments (thermal, alkaline, ozone, etc.) (Table 2).

Monte Carlo methods and simulation in all of the sciences has increased in importance during the past several years. Monte Carlo experimentation is the use of simulated random numbers to estimate some functions of a probability distribution[21]. In this study, waste activated sludge was pre-treated with sulfite and the improvement in methane production after anaerobic digestion was observed. The effect of sulphite pretreatment on sludge degradability was determined considering disintegration degree. Monte Carlo Simulation was used to improve the reduction of volatile suspended solid and methane production.

Table 1 — Sludge characterization

Parameter	Value	
	Thickened Sludge	Anaerobic Inoculum Sludge
pH	6.72	6.71
Temperature (°C)	24	19.7
Conductivity (µS/cm)	917	6260
Alkalinity (mg/L)	17250	8500
ORP (mV)	-190	-202
Sludge Volume Index (mL/g)	53	29.47
Total Solids (TS) (mg/L)	18535	39120
Volatile Solids (VS) (mg/L)	10677.5	14230
Mixed Liquer Suspended Solids (MLSS) (mg/L)	17460	33760
Mixed Liquer Suspended Solid (MLVSS) (mg/L)	10090	13100
Chemical Oxygen Demand (COD) (mg/L)	33177.6	45465.6
Soluble Chemical Oxygen Demand (CODs) (mg/L)	752.64	2119.68

Experimental Section

Sludge Characterization

The thickened sludge and the inoculum used in the study were taken from the Şanlıurfa Central Wastewater Treatment Plant. The characterizations of both thickened and anaerobic sludge were carried out such as pH, conductivity, oxidation reduction potential (ORP), alkalinity, total solids (TS), organic matter (volatile solid) (VS), mixed liquid suspended solids (MLSS), mixed liquid volatile suspended solids (MLVSS), chemical oxygen demand (COD) and soluble chemical oxygen demand (COD_S). These analyzes were performed according to standard methods[22].

Sulfite pretreatment

Anaerobic digestion was conducted to investigate the effects of sulfite pretreatment on anaerobic

Table 2 — Sulfite pretreatment performance versus other pretreatments

Pretreatment Method	Typical Conditions	Solubilization / Delignification (%)	Sugar Yield Increase (%)	Energy Demand (MJ/kg TS)	Chemical Cost	Inhibitor Formation	Key Advantages	Key Limitations	References
Sulfite (e.g., SPORL, sulfite-assisted)	120–160 °C, pH 2–5, Na_2SO_3 / $MgSO_3$	40–70% lignin removal	60–90%	2–4	Medium	Low–Moderate	High delignification, improved enzyme accessibility, reduced non-productive binding	Sulfur handling, recovery required	Zhu *et al*,[14] Mosier *et al.*[12]
Thermal (Hot water / Steam)	160–220 °C, no chemicals	10–30%	20–50%	4–8	Low	Moderate	Simple operation, no chemicals	High energy use, limited lignin removal	Sun & Cheng[15]
Alkaline (NaOH, $Ca(OH)_2$)	Ambient–120 °C, pH > 10	30–60%	50–80%	3–6	High	Low	Effective lignin solubilization, low sugar degradation	Chemical recovery, salt accumulation	Kumar, *et al.*[16] Alvira, *et al.*[17]
Ozonation	Ambient, O_3 dosage 0.05–0.2 g/g TS	40–65%	50–85%	8–15	Very High	Very Low	Highly selective lignin attack, minimal inhibitors	Extremely energy-intensive, costly	Taherzadeh& Karimi[18] Mosier *et al.*[12]
Acid (Dilute H_2SO_4)	120–190 °C, pH < 2	10–25%	40–70%	3–6	Medium	High	Hemicellulose solubilization, fast kinetics	Corrosion, inhibitor generation	Sun & Cheng[15] Alvira *et al.*[17]
Biological (Fungal)	Days–weeks, ambient	15–35%	20–45%	<1	Low	Very Low	Low energy, environmentally friendly	Slow, difficult to control	Isroi *et al.*[19] Taherzadeh& Karimi[18]
Mechanical (Milling)	Ambient, high shear	<10%	10–30%	10–25	Low	None	No chemicals, immediate effect	Very high energy consumption	Zhu & Pan[20] Kumar *et al.*[16]

digestion and methane production. 250 mL of thickened sludge was added to each 300 mL of bottle as an anaerobic digester for sulfite pretreatment. The pH was adjusted to 6 ± 0.1 with HCl (3 M). After that, different doses of sulfite (0-800 mg/L SO_3) were added to the bottles. Before the anaerobic digestion samples were taken from each bottle to determine the concentration of TS, VS, MLSS, MLVSS, COD, COD_S, sulfate and sulfite. Nitrogen gas was used in all digesters to provide anaerobic condition and closed tightly. The shaker was arranged to 100 rpm and kept to incubator at 20°C for 24 h-for the disintegration process. At the end of the period, the samples were taken to determine disintegration degrees. This is represented by DD_{COD} as given in Eq. (1)[23].

$$DD_{COD} \frac{(SCODpreated - SCODo)}{(TCOD - SCODo)} \quad \ldots (1)$$

Where, $SCOD_{pretreated}$ is the supernatant COD of the sulfite pretreatment (mg/L). $SCOD_o$ is the supernatant COD of raw sludge (mg/L) and TCOD is the total COD of raw sludge (mg/L)[24].

Anaerobic digestion studies

After the disintegration process, anaerobic digesters were established by adding 110 mL of disintegrated sludge and 50 mL of inoculum to 5 digesters. The temperatures of the digesters shaking at 100 rpm were ensured at 37°C using incubator. Biogas production was observed during a week observing biogas accumulation and methane contents of the biogas presented with % LEL was measured daily with the Drager X-am 5000 multi gas meter and then converted to mL CH_4/g VS considering following way[25].

LEL = 5% v/v CH_4 in air

$C_{CH4} = \frac{\%LEL}{100} \times 0.05$ C_{CH4} = methane volume fraction (v/v)

$$Y_{CH4} \frac{\frac{\%LEL}{100} X 0.5. Vgas}{MVS}$$

Y_{CH4} = methane yield (mL) CH_4/g VS)

Vgas = gas volume (mL)

mVS = mass of volatile solids (g)

The digesters were conducted during a week. During the operation, the reactors were not fed with sludge containing organic matter. Therefore, at the end of this period the biogas production of the digesters was decreased in depend of organic matter consumption. Thus, the further operation would have been redundant.

Monte Carlo simulation

Monte Carlo simulation was selected in order to analyze systems affected by significant uncertainty and variability in input parameters. Monte Carlo simulation allows inputs to vary across plausible ranges and quantifies how this uncertainty propagates to the outputs differ from deterministic models, which rely on single-point estimates. Input distributions were chosen to accurately reflect the best available knowledge about each uncertain variable while balancing realism and data availability. Sensitivity analysis was used to verify that results were not unduly dependent on any single distributional assumption[26,27].Monte Carlo Simulation was used to estimate the VS reduction (%) and methane production (% LEL) considering multiple parameters and ranges involving several conditions[28]. Several variables were considered, such as VS, COD, methane production.

Results and Discussion

Sludge Characterization and disintegration degree studies

The Sludge characterization are given in Table 3. TS, organic matter concentration and organic matter

Table 3 — Advantages of the sulfite pretreatment versus other treatment methods

Feature	Sulfite Pretreatment Advantage vs Other Methods	Reference
Lignin handling	Sulfonates lignin → more hydrophilic & less inhibitory, improving enzyme accessibility	Yang, B., & Wyman, C. E. (2010)
Fermentation inhibitors	Fewer sugar degradation products than dilute acid pretreatment, reducing detoxification needs	Mosier, N., *et al*. (2005).
Enzymatic digestibility	Higher saccharification yields due to lignin sulfonation and increased cellulose accessibility	Yang, B., & Wyman, C. E. (2010)
Biodegradability	Improves solute release and fermentation efficiency compared to some physical/biological pretreatments	Zan*et al*., (2021)
Energy demand	Often lower than high-energy physical methods like steam explosion or ultrasonication	Chen, L., *et al*. (2016)

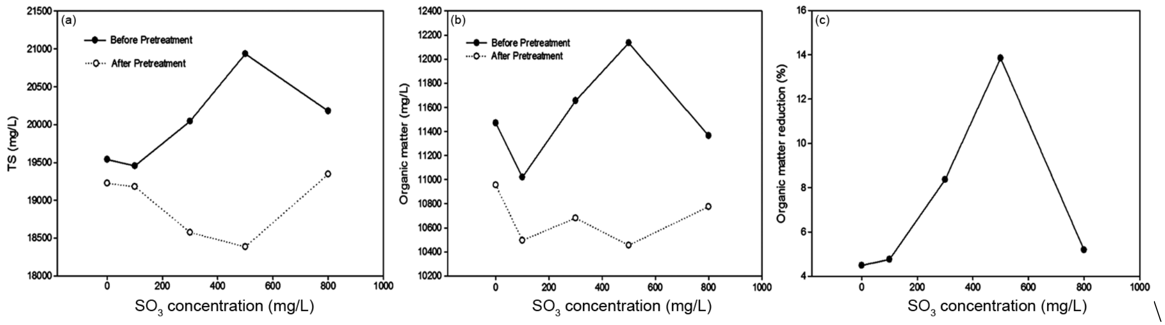

Fig. 1 — (a) TS change, (b) Organic matter (VS) changes and (c) Organic matter (VS) reduction

reduction with 24 h sulfite pretreatment with different SO_3 concentration are given in Figs 1a, 1b, 1c, respectively.

As shown in Fig. 1a, TS contents of the sludge were gradually decreased after the sulfite pretreatment concentration up to the 500 mg/L SO_3. It can be attributed to the cell lysis leading to the release of cell contents. After the 500 mg/L SO_3, TS contents was increased due to the mineralization. It can be concluded from Fig. 1(b), the changes of organic matter contents leading to TS decrease. Especially, it can be easily realized from Fig. 1 (c) that at 500 mg/L SO_3 concentration, the organic matter reduction was reached to 13.84 %. In the study by Zan *et al.*[9] in the later stage of the long-term anaerobic digestion, the VS reduction was 38.17±2.41 % in the experimental reactor, while it was 30.64±1.91 in the control reactor leading to an improvement of about 24.57 %. From the view of this comparison, it can be said that VS reduction can be enhanced by sulfite pretreatment in long term operation[9].

MLSS and MLVSS variation before and after sulfite pretreatment were illustrated in Fig. 2. It can be concluded that MLSS and MLVSS contents of the sludge were decreased after the sulfite pretreatment for all SO_3 concentrations. It can be referred that the most effective SO_3 concentration considering significant decrease in MLSS or MLVSS was at 100 mg/L SO_3.

The change in total COD (COD_T) and dissolved COD (CODs) after the 24 h disintegration process are presented by Fig. 3. COD_T was decreased gradually after sulfite pretreatment while CODs was increased. It can be understood that the sulfite pretreatment lead to soluble COD increasing due to the increasing of organic matter contents. Li *et al.*[29] demonstrated that, the electron transfer efficiency and COD flows from the substrate to products were enhanced by up to 25% due to the sulfite pretreatment, which supports the enhanced waste activated sludge degradation[29].

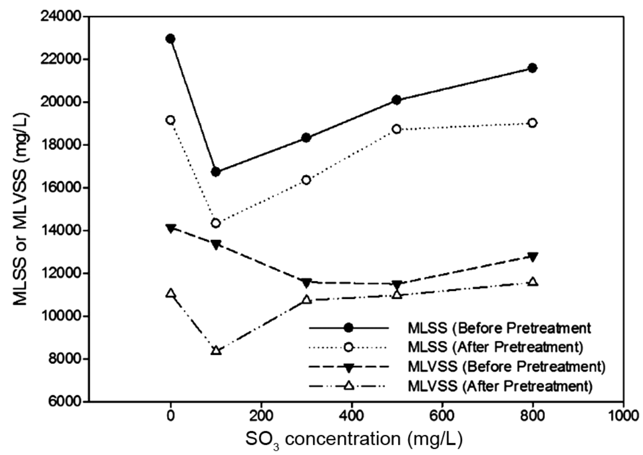

Fig. 2 — MLSS and MLVSS change

The results of disintegration degree are given in Fig. 4. It can realized that when SO_3 concentration was increased, disintegration degree was also increased. Meanwhile, it can be said that, SO_3 pretreatment above 800 mg/L, higher disintegration degree would be expected.

Sulfate change is given in Fig. 5. Normally, after the sulfite pretreatment, increase in SO_4 concentration was expected. This is verified with Fig. 5. The highest SO_4 concentration was obtained at 500 mg/L SO_3. Li *et al.*[29] suggested that the sulfite pretreatment also enhanced the waste activated sludge degradation from 25 ± 2 % in the control to a maximum of 39 ± 2 % under 500 mg S/L sulfite pretreatment[29].

Anaerobic digestion studies

Li *et al.*[18] presented that, sulfite pretreatment also promoted the solubilization, hydrolysis, and acidification processes during the anaerobic fermentation by up to 200%, 60%, and 45%, respectively[18]. According to the anaerobic digestion studies, anaerobic digester fed with 500 mg/L SO_3 pretreated sludge was achieved the highest CH_4 was

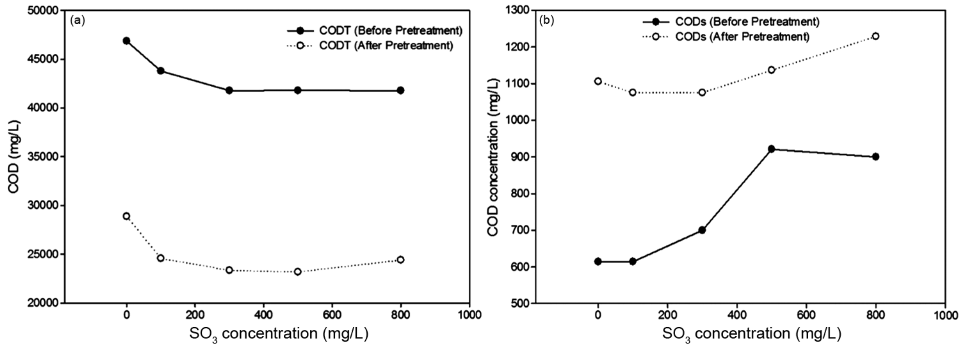

Fig. 3 — COD change (a) total COD (COD_T) and (b) Soluble COD (CODs)

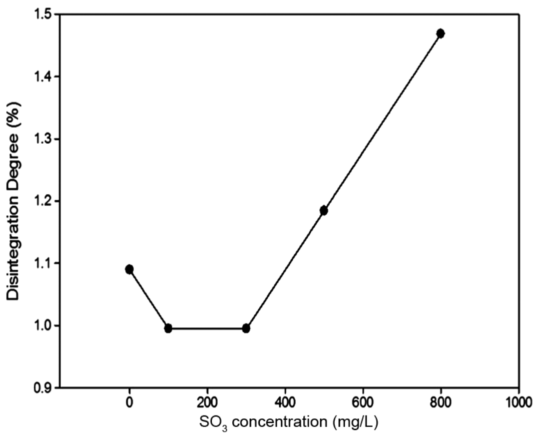

Fig. 4 — Disintegration degree (DD) (%)

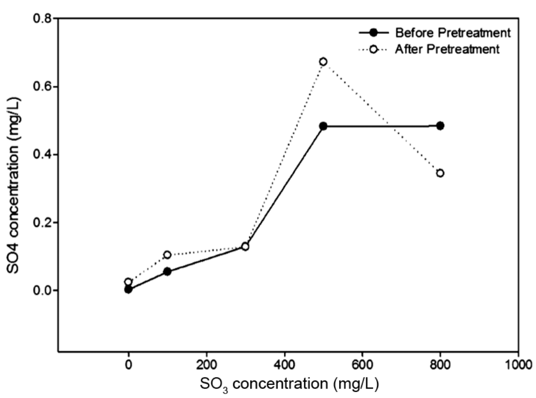

Fig. 5 — Sulfate change

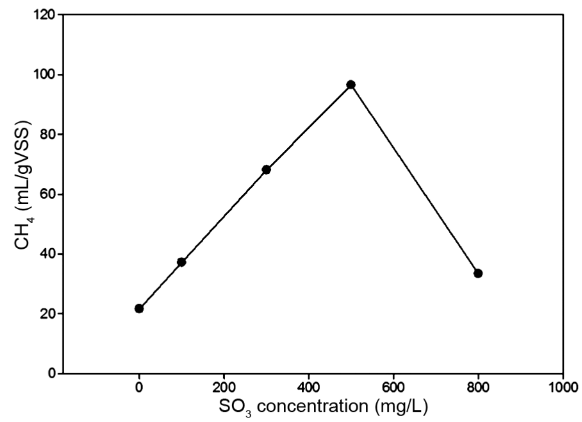

Fig. 6 — Methane production from anaerobic digestion process

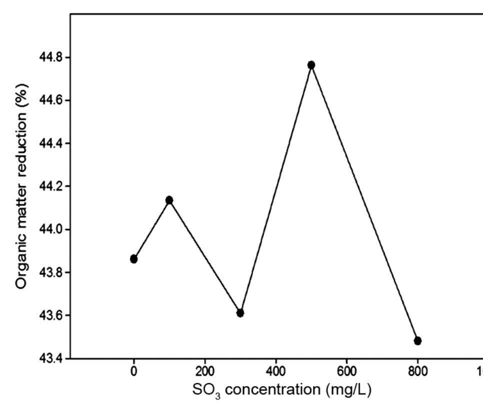

Fig. 7 — Organic matter reduction in anaerobic digestion

obtained with 100 mL CH_4/g VS (Fig. 6). Related to this the highest organic matter reduction with 44.76 % was achieved in the same digester (Fig. 7). Considering the results, it can be concluded that the methane production were significantly improved by 33 % with pretreatment of 500 mg/L SO_3 for 24 h. Similarly, the methane production and volatile solid reduction of sulfite-pretreated were improved by 25 % with pretreatment at sulfite of 100 mg S/L pH of 6 for 24 h[9]. In the other study, the methane production from the primary sludge, pretreated with 500 mg SO_3^{2-}-S/L of sulfite, was reduced by up to 37%[30].

Monte Carlo simulation

In order to optimization of VS reduction and CH_4 contents of biogas, the effects the operational conditions of anaerobic digestion were examined using Monte Carlo Simulation. Fig.8 demonstrates the simulation results.

According to the simulation results, it is possible to maximize the VS reduction if the digester is operated

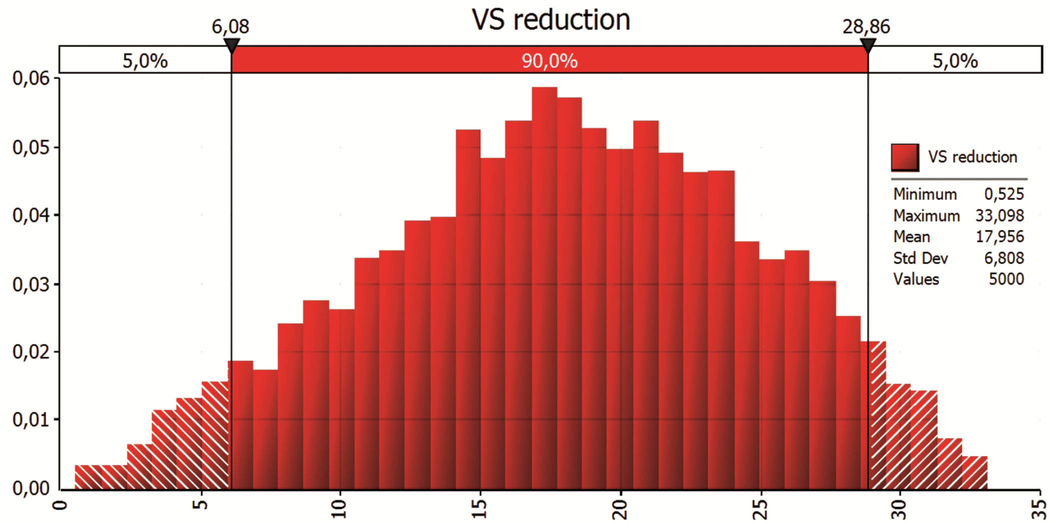

Fig. 8 — Monte Carlo simulation results for volatile solid (VS) reduction

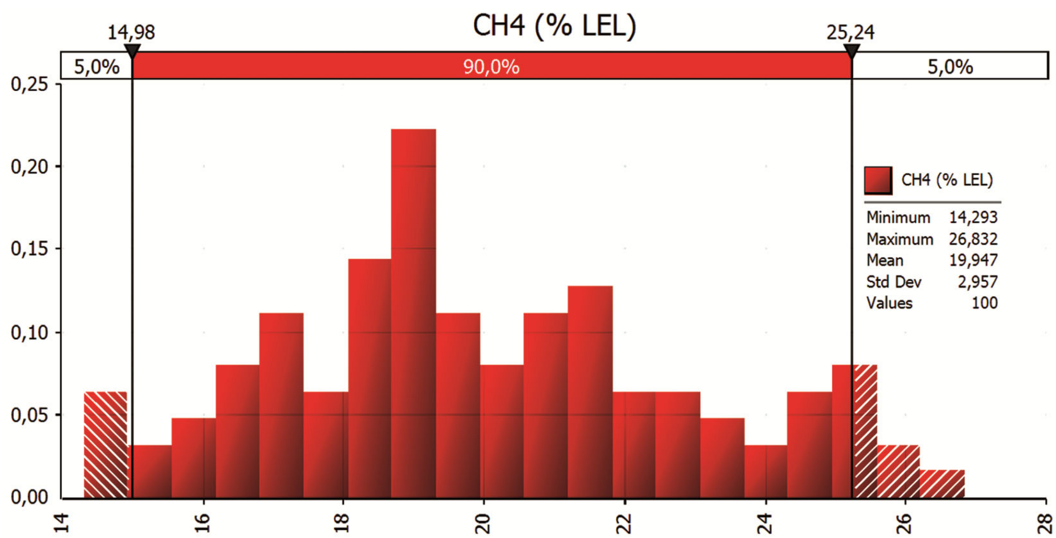

Fig. 9 — Monte Carlo Simulation results for CH_4

under the conditions of pH=7 and 37 °C of temperature. The maximum VS reduction would be 33 % if the digester was fed with sludge had 15000 mg/L VS content (Fig. 8). Each bar represents how often a certain VS-reduction value occurred across those 5000 runs. The simulation reflects uncertainty/variability in the process. The bell-shaped histogram indicates an approximately normal distribution. Most outcomes cluster around the center, meaning VS reduction is most likely to fall near the mean. The system is most likely to achieve ~18% VS reduction. Performance is variable, but not chaotic which results cluster strongly around the mean[16,17].

In the same condition of the digester mentioned above, maximum 26.83 % LEL of CH_4 was achieved in case of 50000 mg/L COD was referred according to the Monte Carlo Simulation Method (Fig. 9). Most measurements fall well inside the acceptable range (15–25% LEL). A small number of values fall below ~15 % LEL and above ~25% LEL (hatched bars), indicating occasional excursions. The distribution is roughly bell-shaped, centered near 20% LEL → this suggests a stable process, not random chaos. The upper tail (near 25–27% LEL) is slightly more concerning than the lower tail because it moves closer to hazardous conditions.

Conclusion

In this study, the stabilization efficiency and methane production of anaerobic digestion was improved using sulfite pretreatment. Organic matter reduction represents the degradation of complex organic substrates during treatment, such as proteins, carbohydrates, and fats. As these insoluble organics are broken down through hydrolysis and acidogenesis, they are converted into soluble compounds, leading to an increase in soluble chemical oxygen demand (sCOD). This rise in sCOD reflects the formation of bioavailable intermediates, including sugars, amino acids, and volatile fatty acids, which can then be metabolized by methanogenic microbes. During methanogenesis, these soluble compounds are further converted into CH_4 and CO_2, linking the extent of organic matter reduction to methane production. This metabolism was proved with 13.84% of organic matter reduction, 18.9% of soluble COD increasing and 1.18% of sludge disintegration were achieved at 500 mg/L SO_3. In the period of anaerobic digestion, 96.5 mL CH_4/g VS methane production was also obtained at 500 mg/L SO_3. According to the Monte Carlo Simulation the reduction of maximum organic matter was obtained as 33% while methane production was 26.84 of % LEL.

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Conflict of Interest

The authors declare that they have no conflict of interest.

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