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Pre-treatment of sewage sludge to enhance methane production: optimal technology's evaluation through continuous reactor operation

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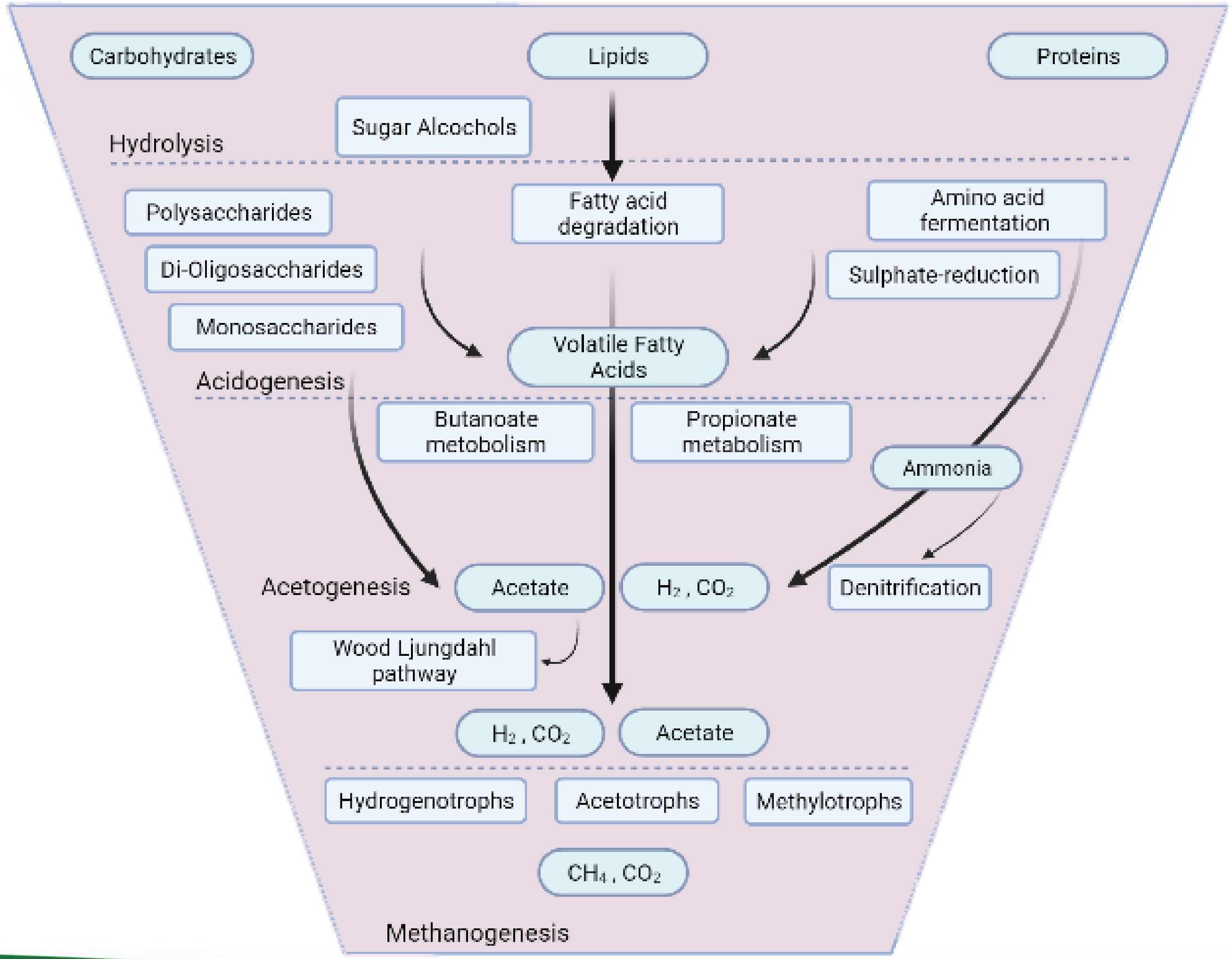
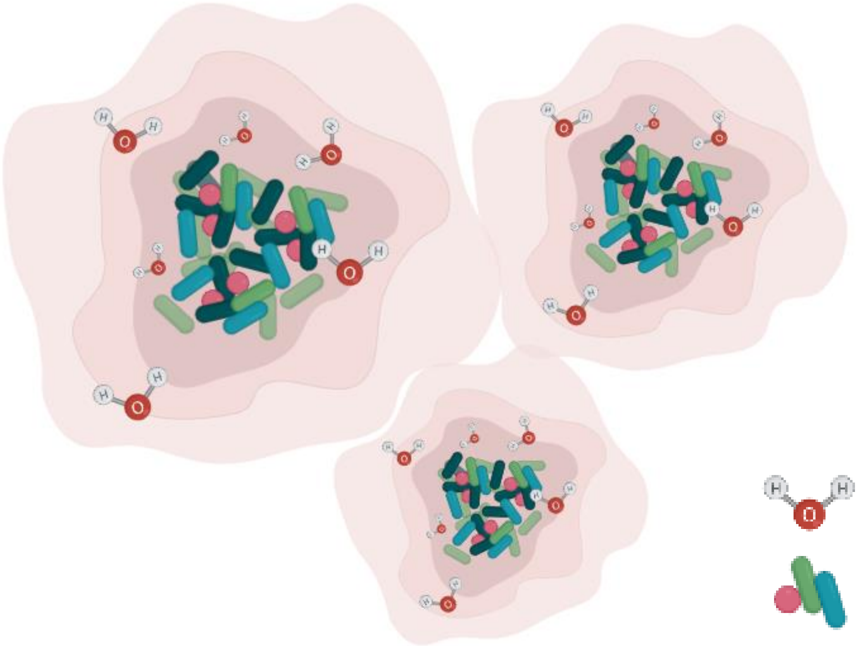
The Anaerobic Digestion



AD is a biological process through which complex organic matter is degraded with the aid of sequence of actions of mutually dependent microorganisms and converted into CH_4 and carbon dioxide (CO_2) in the absence of oxygen.

Sewage sludge's structural special features



Bound water

Microbial aggregates

Tightly Bound EPS

Loosely Bound EPS

Soluble EPS

Sewage sludge floc structure

- Microbial aggregates
- Organic substances
- Inorganic particles
- Bound water
- Refractory cell walls
- Extracellular Polymeric Substances (EPS)

Why is sludge's pre-treatment important?

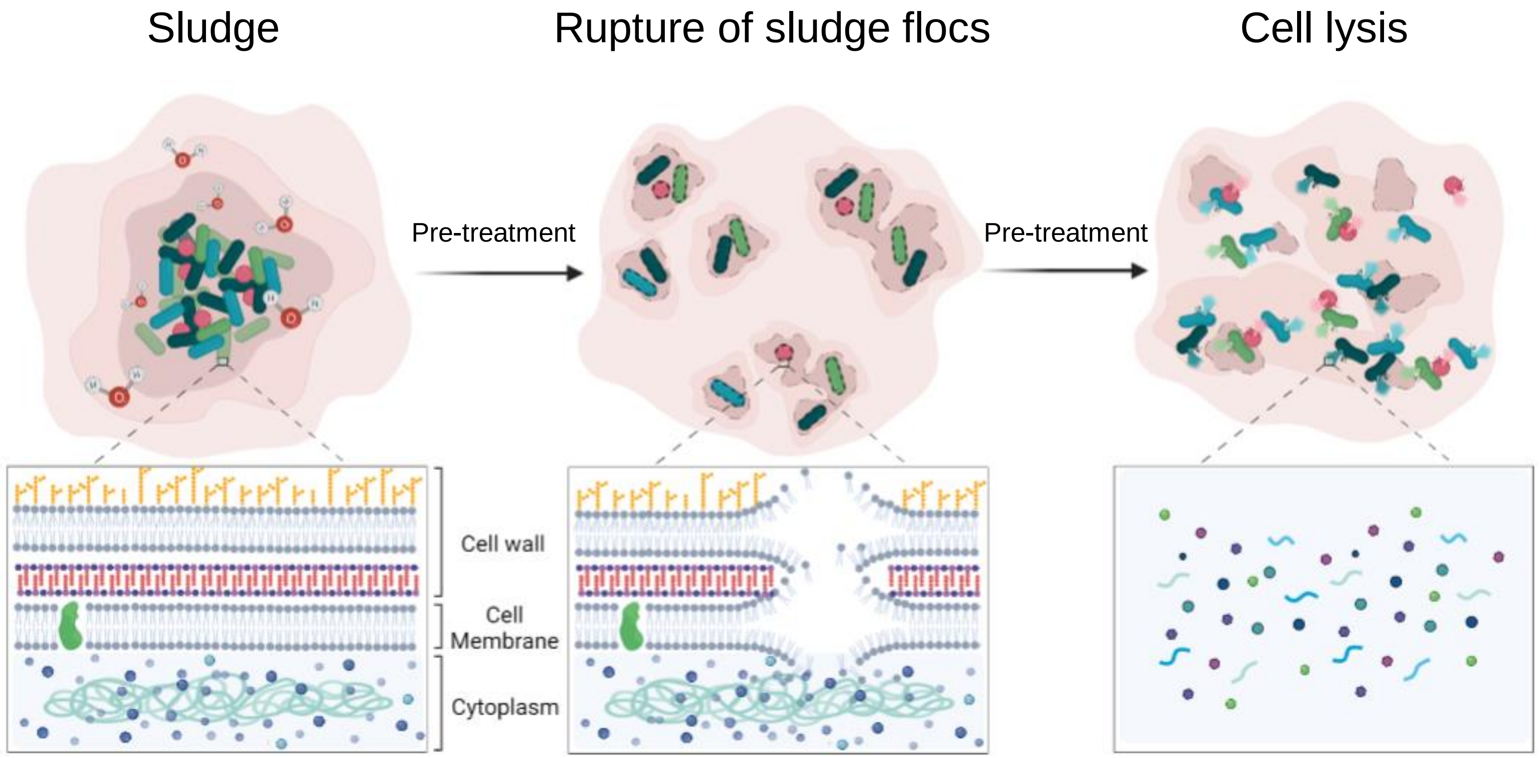
Pre-treatment's beneficial aspects

- Rupture of sludge flocs
  - Particle size reduction
  - Increased surface area
  - Enhanced hydrolysis
- Rupture of EPS and cell walls
  - Release of intracellular organic substances
  - Increased bioavailability

↓

✓ Enhanced AD efficiency

✓ Increased Biogas Production



Aim & Objectives

Development of A Green Method

Supercritical Carbon dioxide Explosion (SCE)

SCE Optimization

Optimum conditions determination

Conventional Pre-treatments

Combined with SCE or as standalone procedures

Continuous Stirred Reactors

Two optimal methods’ evaluation

Process Monitoring

Biochemical parameters evaluation

Supercritical CO_2 Explosion

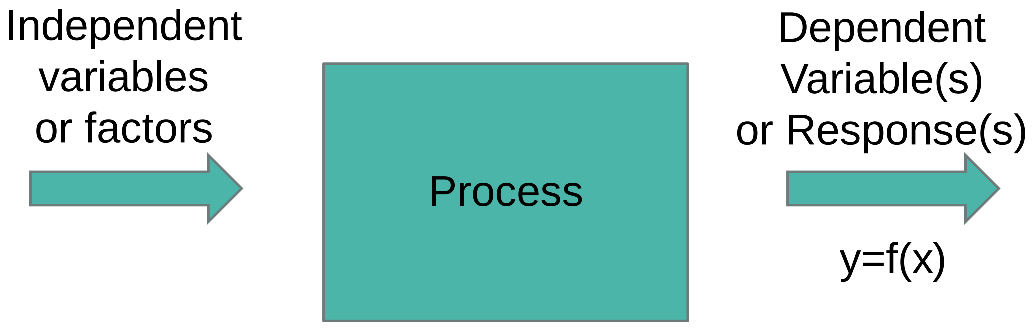
Principle of action

- Critical temperature (T_c=31,7 ^oC) and pressure (P_c=72,9 atm)
- Properties similar to that of liquid and gas
- Penetration of solvent in the micropores of sludge matrix and cell walls
- Reaction chamber decompression→ abrupt expansion of solid surface
- Increase of sludge’s floc structure accessibility
- Organic substances’ increased bioavailability

Design of Experiments and SCE Optimization

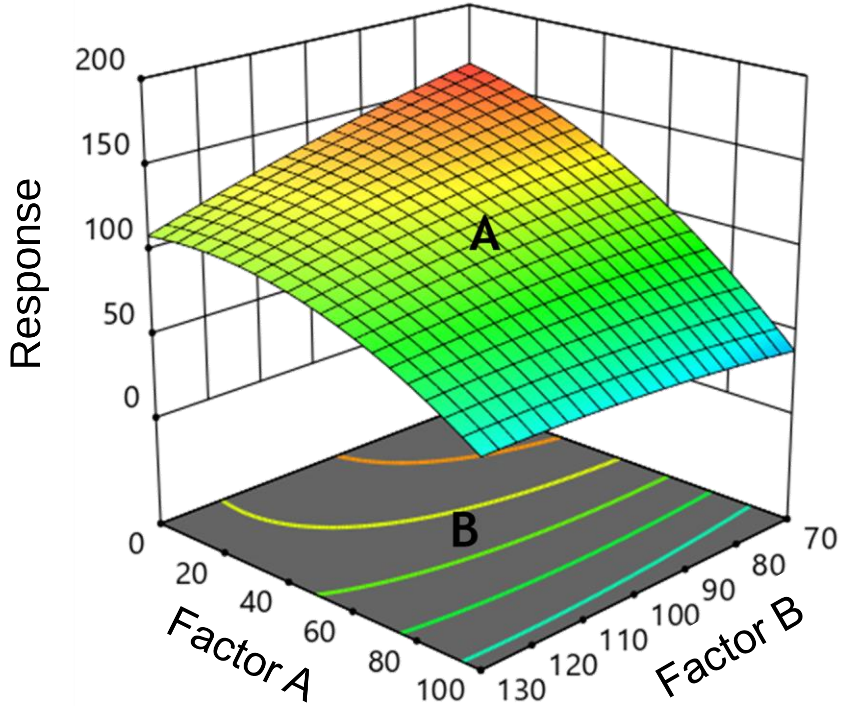
Aim: Optimum conditions determination for sludge pre-treatment with SCE → maximize methane production

DoE
Design of Experiments



- Experimental design
- Simultaneous alteration of all factors
- Use of statistical tools

Data modelling → A: Response Surface
B: Contour plot



Experimental Procedure for SCE optimization

Optimization based on a two-step procedure

1st set of experiments

Screening among the factors examined

2nd set of experiments

Optimization of significant factors

1^{st} set of experiments - Screening

1^{st} set of experiments → Screening

Factors

1. Temperature, X_A (35 & 125 ^oC)
2. Pressure, X_B (150 & 250 bar)
3. Time, X_C (10 & 120 min)
4. Decompression speed, X_D (fast & slow)

Response

1. Methane yield, Y_1

Run	Factors			
	X_A (^oC)	X_B (bar)	X_C (min)	X_D
1	35	150	10	Fast
2	125	150	10	Slow
3	35	250	10	Slow
4	35	250	10	Slow
5	35	150	120	Slow
6	125	150	10	Fast
7	35	150	120	Slow
8	35	150	120	Fast
9	35	250	10	Fast
10	35	150	10	Slow
11	35	150	10	Slow
12	125	250	120	Fast
13	125	150	120	Fast
14	35	150	10	Fast
15	125	250	10	Slow
16	125	250	10	Fast
17	35	250	120	Slow
18	35	250	10	Fast
19	125	250	120	Fast
20	125	150	120	Slow
21	125	150	10	Slow
22	125	250	120	Slow
23	35	250	120	Slow
24	125	250	120	Slow
25	35	250	120	Fast
26	125	150	10	Fast
27	35	150	120	Fast
28	125	150	120	Slow
29	125	250	10	Slow
30	125	250	10	Fast
31	125	150	120	Fast
32	35	250	120	Fast

Experimental Procedure for SCE optimization

1

Screening Experiments

1. A total of 32 pre-treatment tests

Run	Factors			
	X_A (ºC)	X_B (bar)	X_C (min)	X_D
1	35	150	10	Fast
2	125	150	10	Slow
3	35	250	10	Slow
4	35	250	10	Slow
5	35	150	120	Slow
6	125	150	10	Fast
7	35	150	120	Slow
8	35	150	120	Fast
9	35	250	10	Fast
10	35	150	10	Slow
11	35	150	10	Slow
12	125	250	120	Fast
13	125	150	120	Fast
14	35	150	10	Fast
15	125	250	10	Slow
16	125	250	10	Fast
17	35	250	120	Slow
18	35	250	10	Fast
19	125	250	120	Fast
20	125	150	120	Slow
21	125	150	10	Slow
22	125	250	120	Slow
23	35	250	120	Slow
24	125	250	120	Slow
25	35	250	120	Fast
26	125	150	10	Fast
27	35	150	120	Fast
28	125	150	120	Slow
29	125	250	10	Slow
30	125	250	10	Fast
31	125	150	120	Fast
32	35	250	120	Fast

2

BMP tests

1. Replicate batch vials/treatment
2. Working volume 100 mL
3. Mesophilic Conditions

3

Gas Chromatography

1. Methane produced x2/week

Design matrix – Obtained Response's values

Run	Factors				Response
	X_A (ºC)	X_B (bar)	X_C (min)	X_D	Methane yield (mL CH_4/gVS)
1	35	150	10	Fast	238
2	125	150	10	Slow	305
3	35	250	10	Slow	275
4	35	250	10	Slow	296
5	35	150	120	Slow	273
6	125	150	10	Fast	270
7	35	150	120	Slow	253
8	35	150	120	Fast	233
9	35	250	10	Fast	255
10	35	150	10	Slow	297
11	35	150	10	Slow	277
12	125	250	120	Fast	309
13	125	150	120	Fast	305
14	35	150	10	Fast	239
15	125	250	10	Slow	273
16	125	250	10	Fast	249
17	35	250	120	Slow	259
18	35	250	10	Fast	267
19	125	250	120	Fast	303
20	125	150	120	Slow	298
21	125	150	10	Slow	287
22	125	250	120	Slow	273
23	35	250	120	Slow	258
24	125	250	120	Slow	281
25	35	250	120	Fast	248
26	125	150	10	Fast	265
27	35	150	120	Fast	238
28	125	150	120	Slow	291
29	125	250	10	Slow	280
30	125	250	10	Fast	252
31	125	150	120	Fast	280
32	35	250	120	Fast	252

Screening among the factors examined

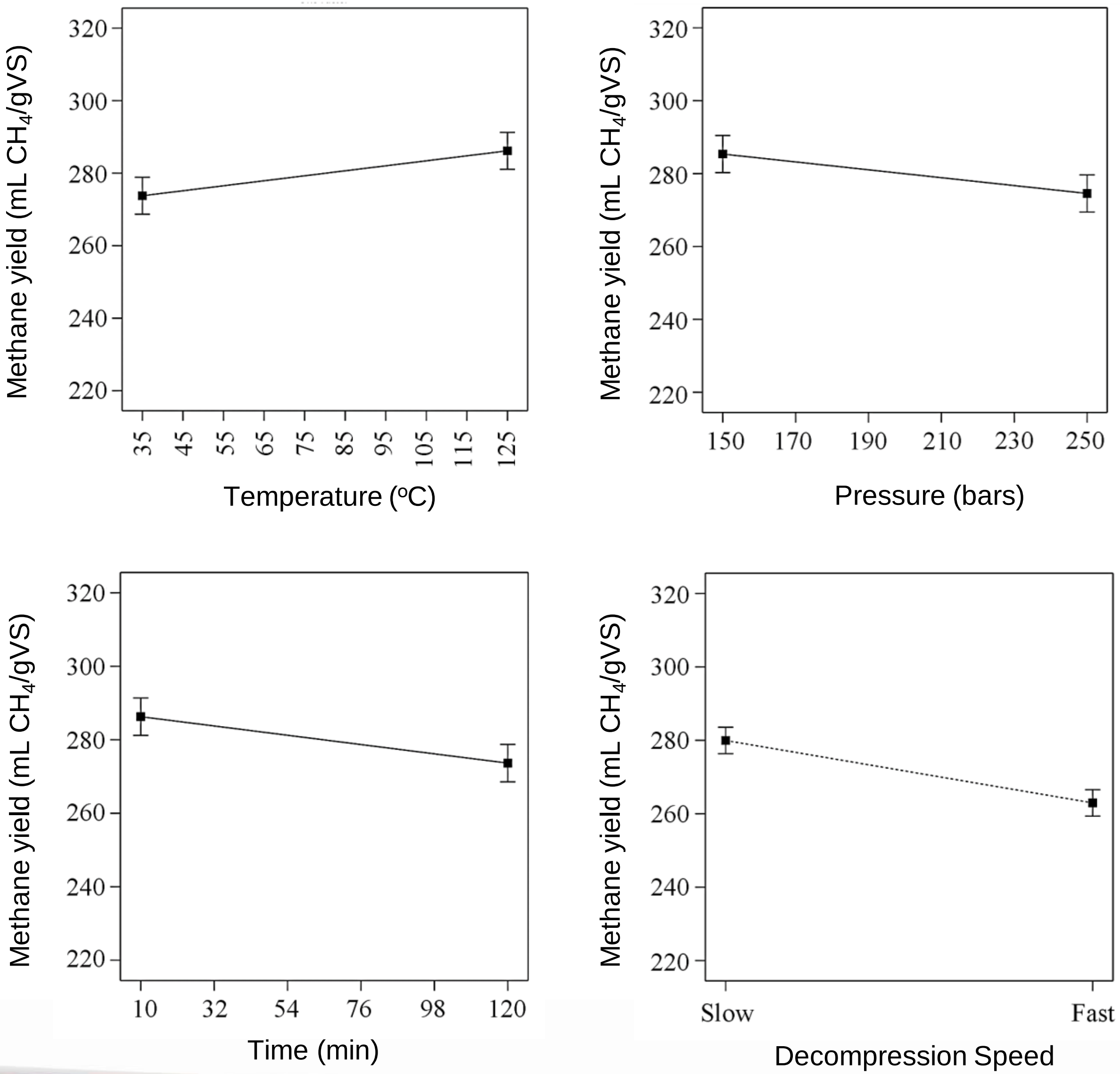
1st experimental set:
Screening among all the factors

ANOVA
Statistical significance evaluation

Temperature > Decompression speed > Time > Pressure

Statistically significant factors

Temperature & Time



Optimization of statistically significant factors

2nd experimental set:

Optimization of statistically significant factors

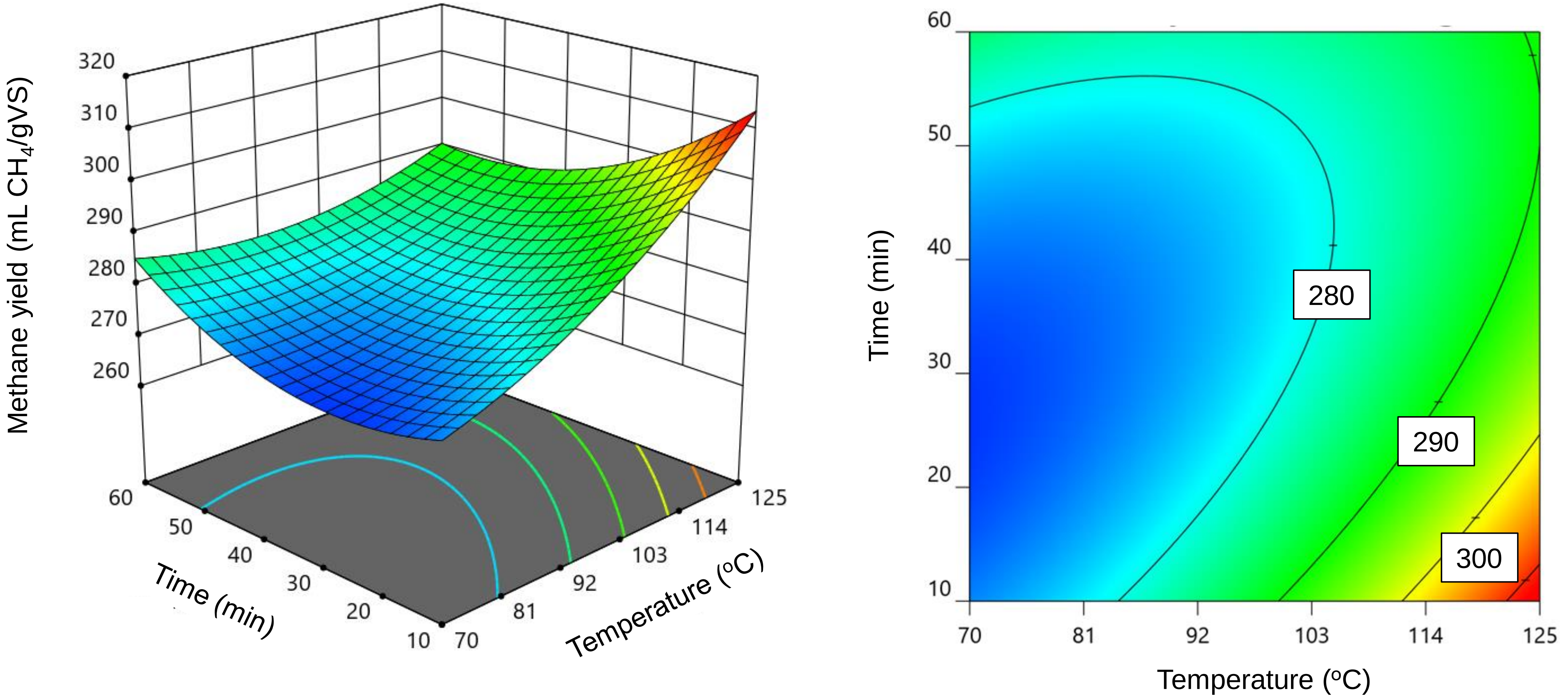
1. Temperature, X_A (70 - 125 ^oC)
2. Time, X_C (10 - 60 min)

- Pressure = 150 bar
- Slow decompression

Design matrix - Optimization

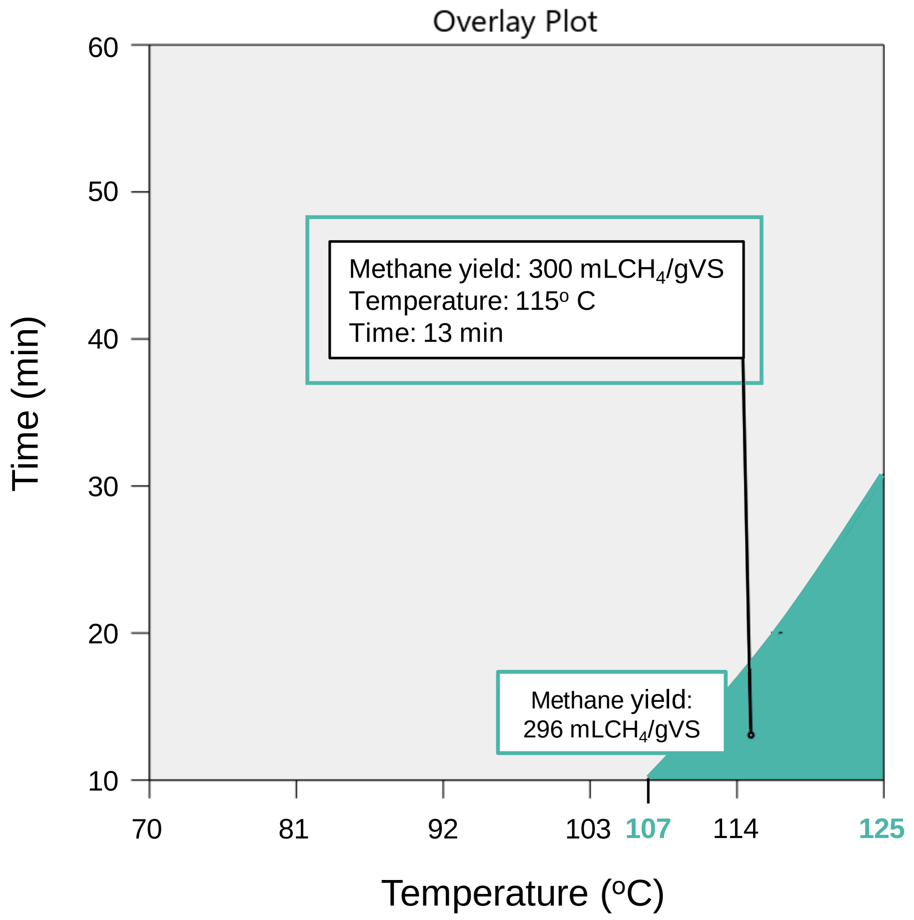
Run	Factors		Response
	X_A (^oC)	X_C (min)	Methane yield (mL CH_4/gVS)
1	70	60	292
2	97.5	10	296
3	125	35	299
4	125	60	291
5	125	60	297
6	70	10	272
7	70	35	268
8	97.5	35	274
9	97.5	35	279
10	70	10	270
11	97.5	60	270
12	97.5	35	282
13	125	35	290
14	70	35	268
15	125	10	305
16	70	60	290
17	125	10	311
18	97.5	10	295
19	97.5	60	276

Response Surface and Contour Plot



Effect of main factors (temperature, °C; and time, min) on methane yield

Desired Space and selected optimum conditions



- Untreated sludge → 274 mLCH$_4$/gVS
- Low-limit criterion → 296 mLCH$_4$/gVS

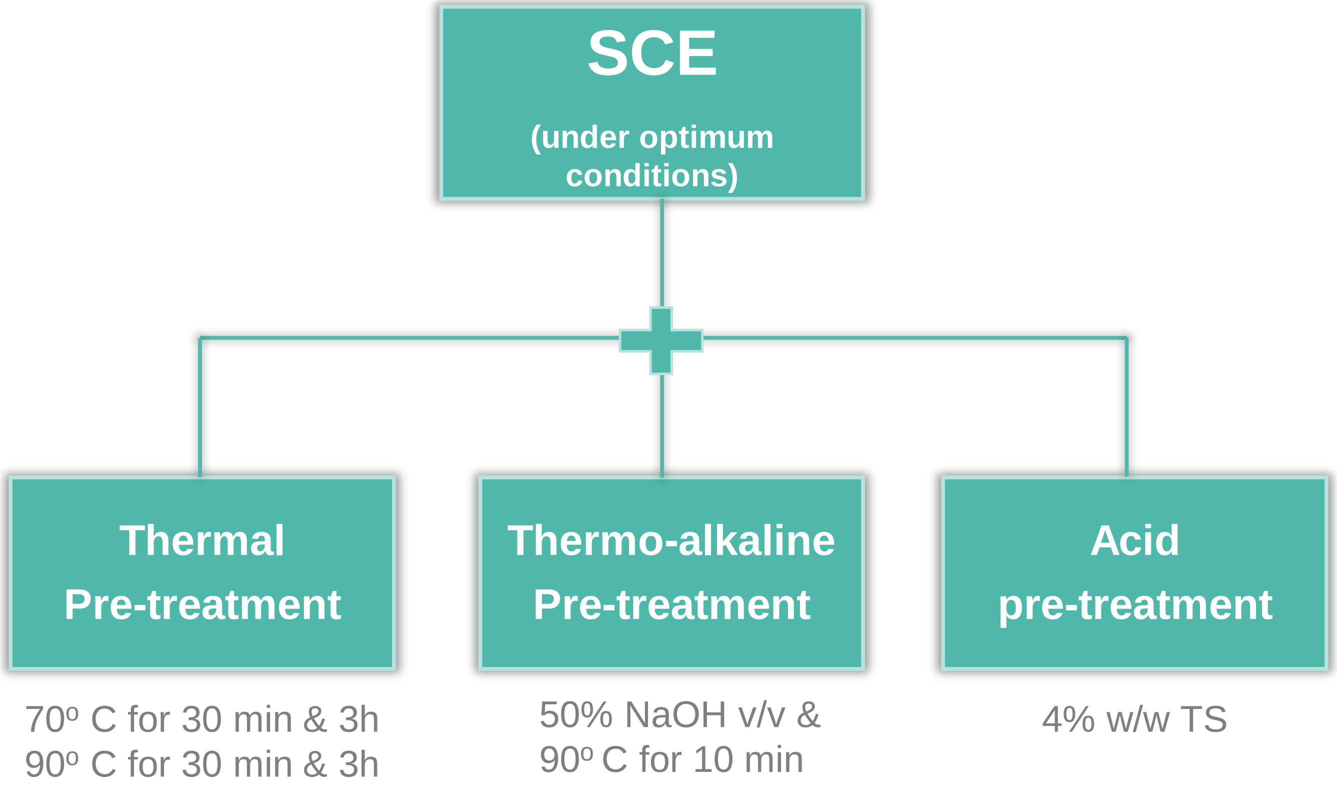
$p < 0.05$

- Chosen pre-treatment set of conditions

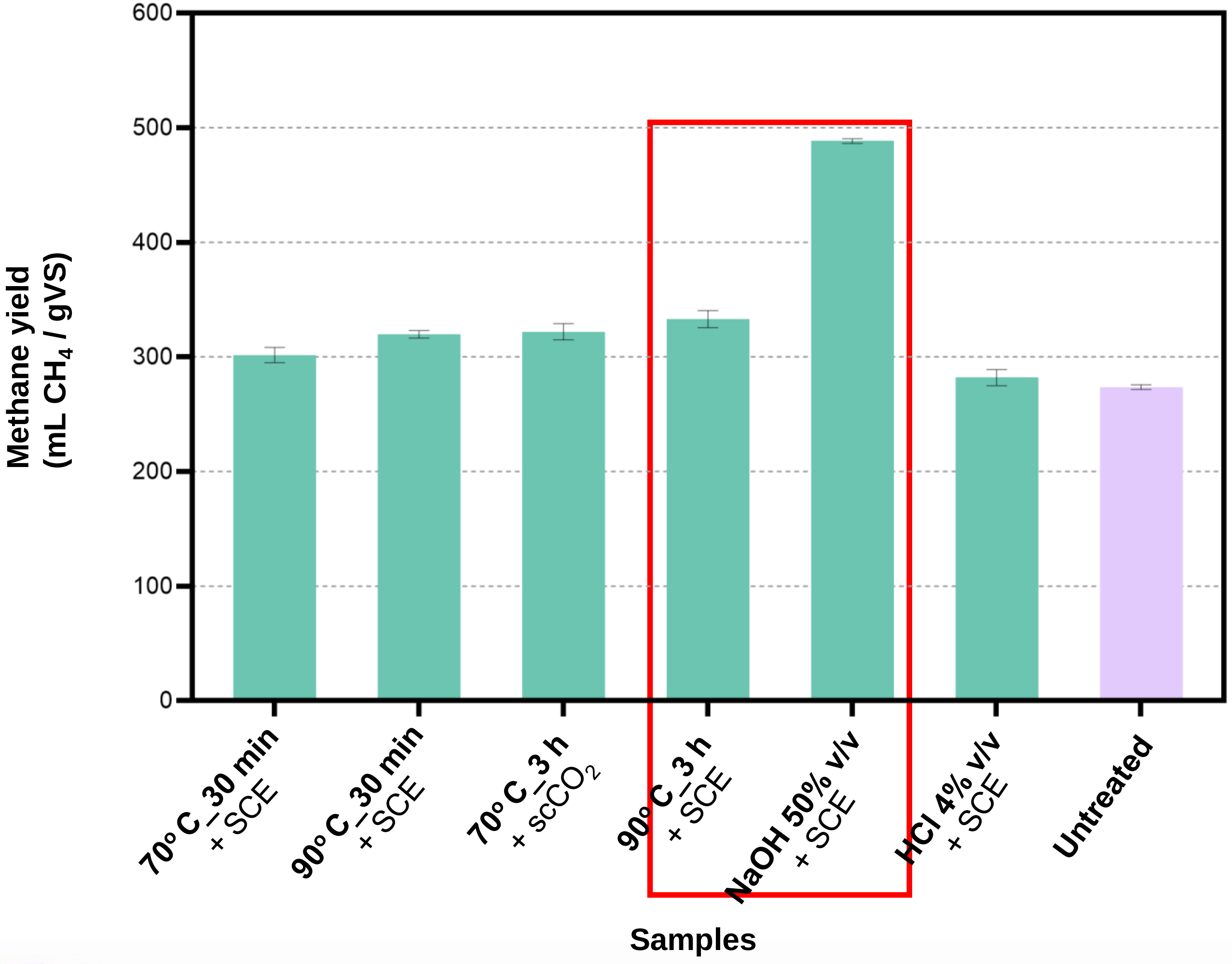
Validation Experiment

Correlation 99 %
between predicted and experimental value

SCE combined with thermal and chemical methods



Combined pre-treatments – Methane yield

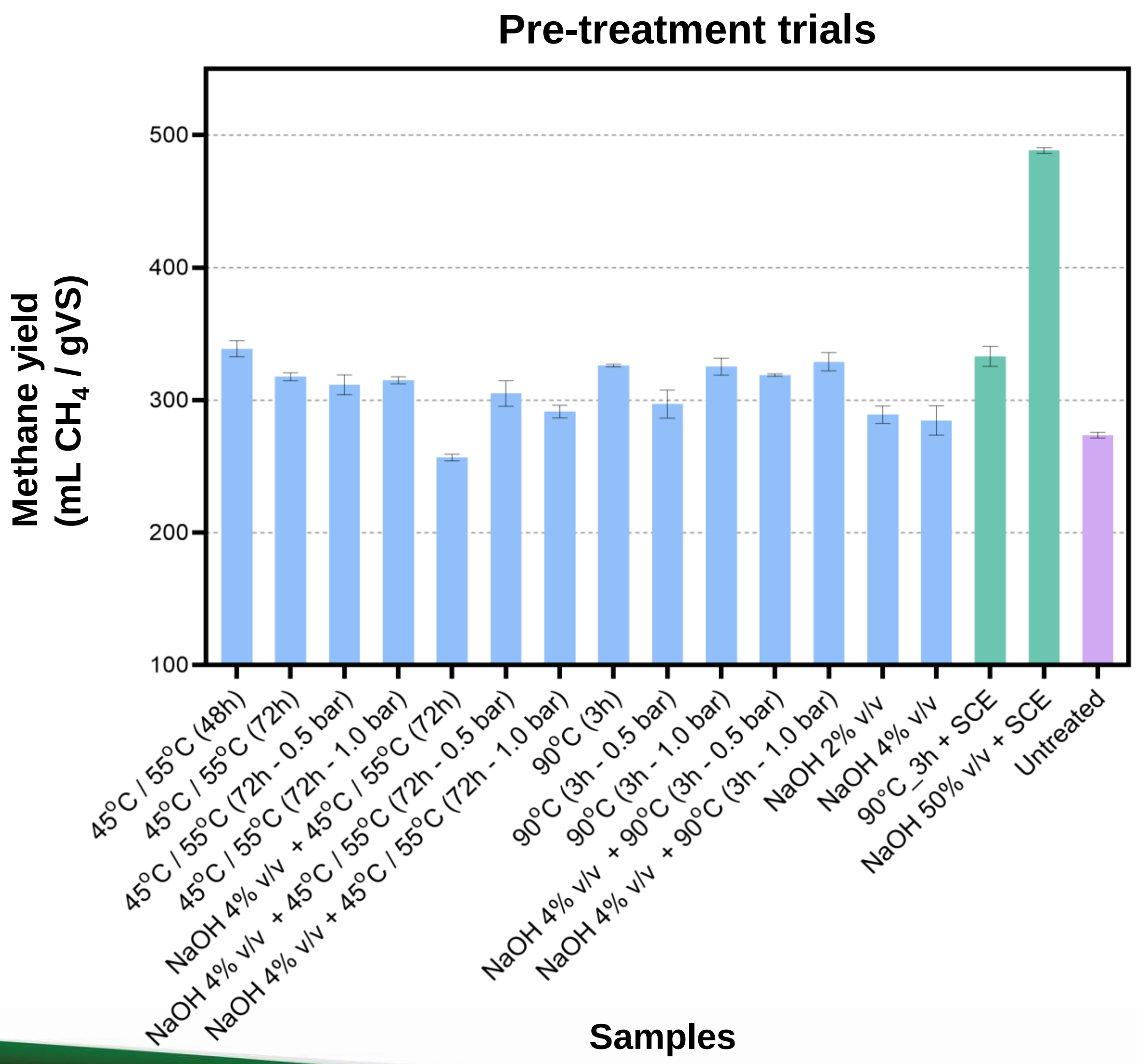


Methane yield enhancement for all the combinations

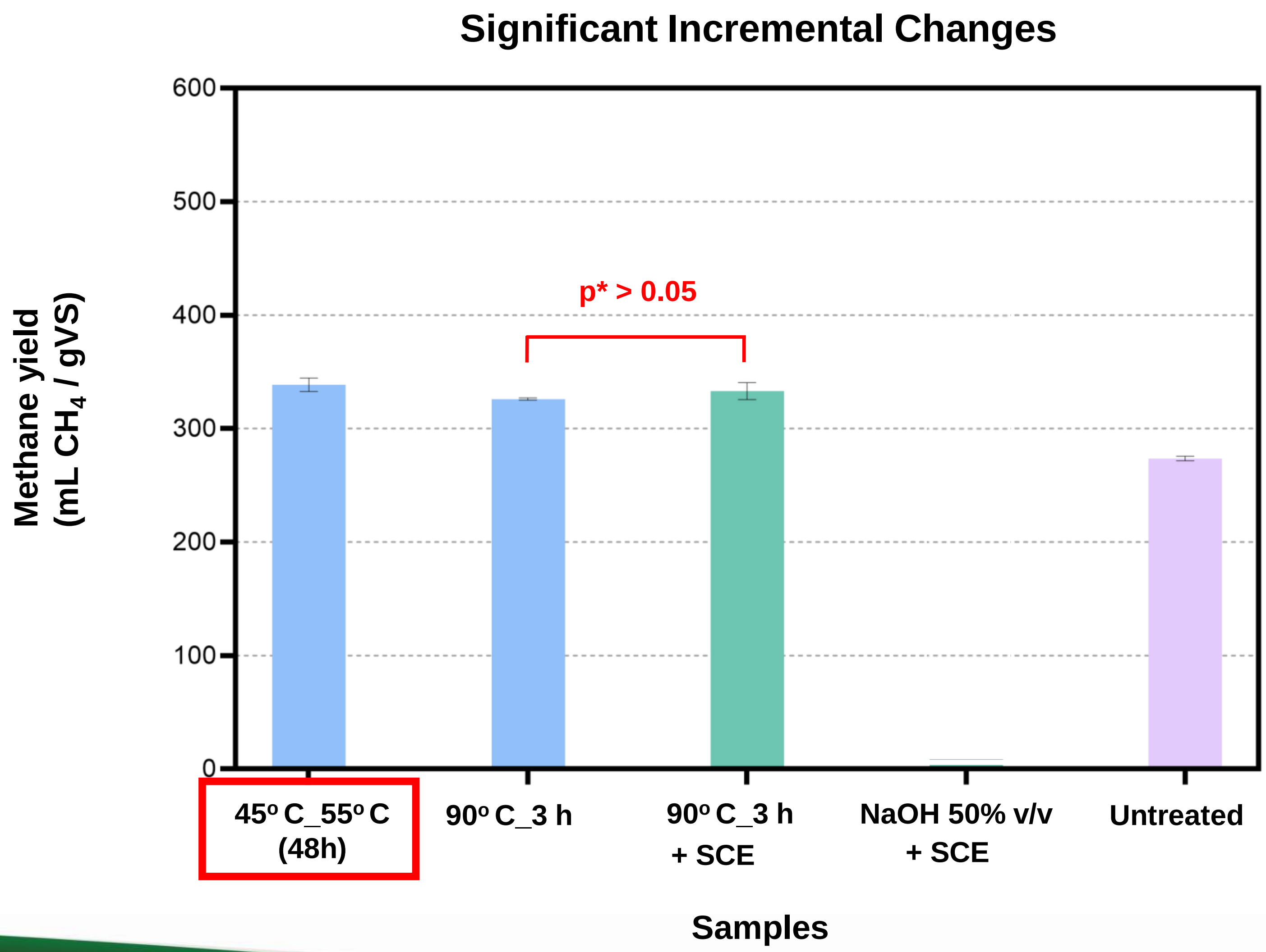
Additional individual pre-treatments

Thermal Hydrolysis	
1	45º C for 48 h and then 55º C for extra 48 h
2	45º C for 72 h and then 55º C for extra 72 h
3	45º C for 72 h and then 55º C for extra 72 h under 0.5 bar of CO_2 pressure
4	45º C for 72 h and then 55º C for extra 72 h under 1.0 bar of CO_2 pressure
5	90º C for 3 h
6	90º C for 3 h under 0.5 bar of CO_2 pressure
7	90º C for 3 h under 1 bar of CO_2 pressure
Alkaline Hydrolysis	
8	NaOH 2% v/v
9	NaOH 4% v/v
Thermochemical pre-treatments	
10	NaOH 4% v/v , 45º C for 72 h and then 55º C for extra 72 h
11	NaOH 4% v/v , 45º C for 72 h and then 55º C for extra 72 h, under 0.5 bar of CO_2 pressure
12	NaOH 4% v/v , 45º C for 72 h and then 55º C for extra 72 h, under 1 bar of CO_2 pressure
13	NaOH 4% v/v and 90º C for 3 h, under 0.5 bar of CO_2 pressure
14	NaOH 4% v/v and 90º C for 3 h, under 1 bar of CO_2 pressure

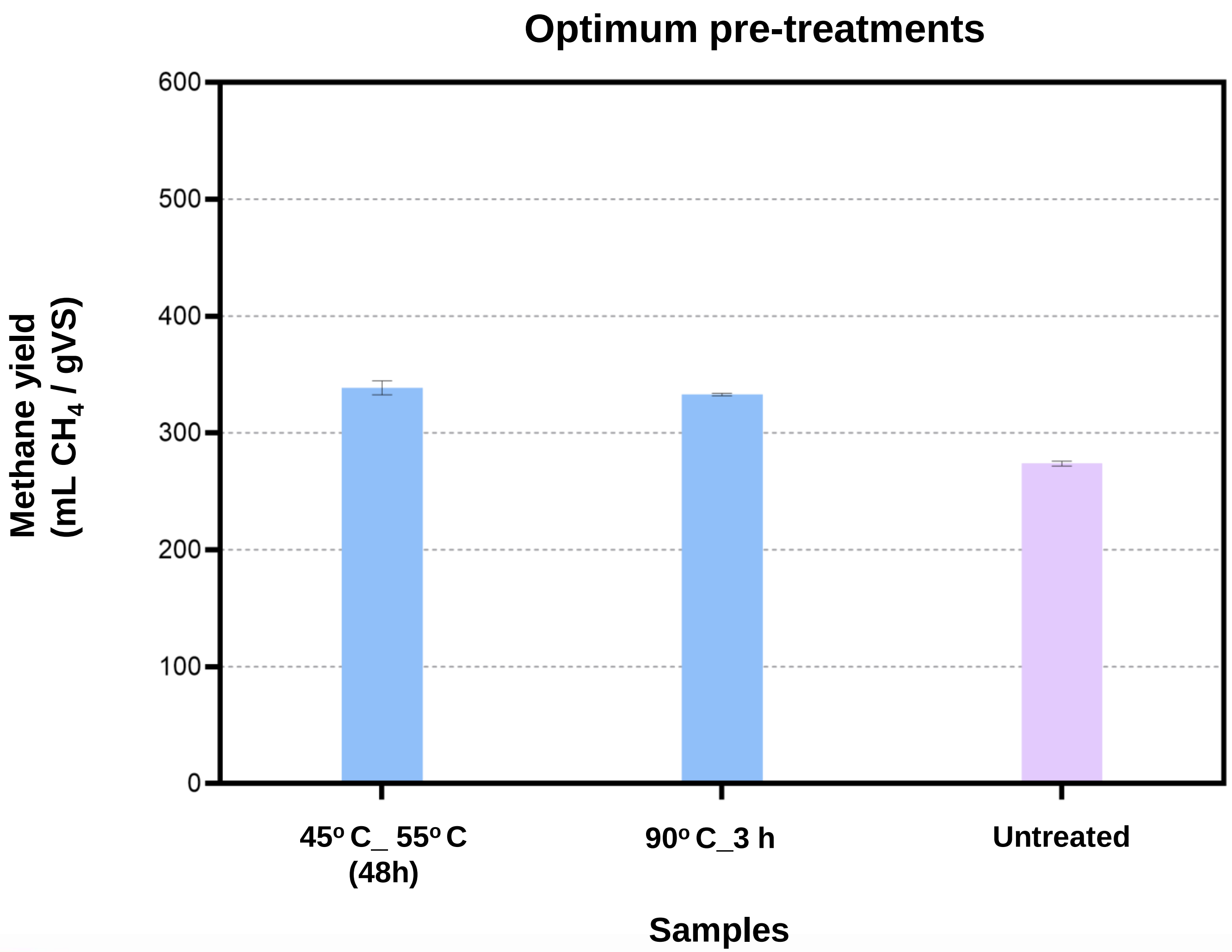
All pre-treatments – Statistically significant differences



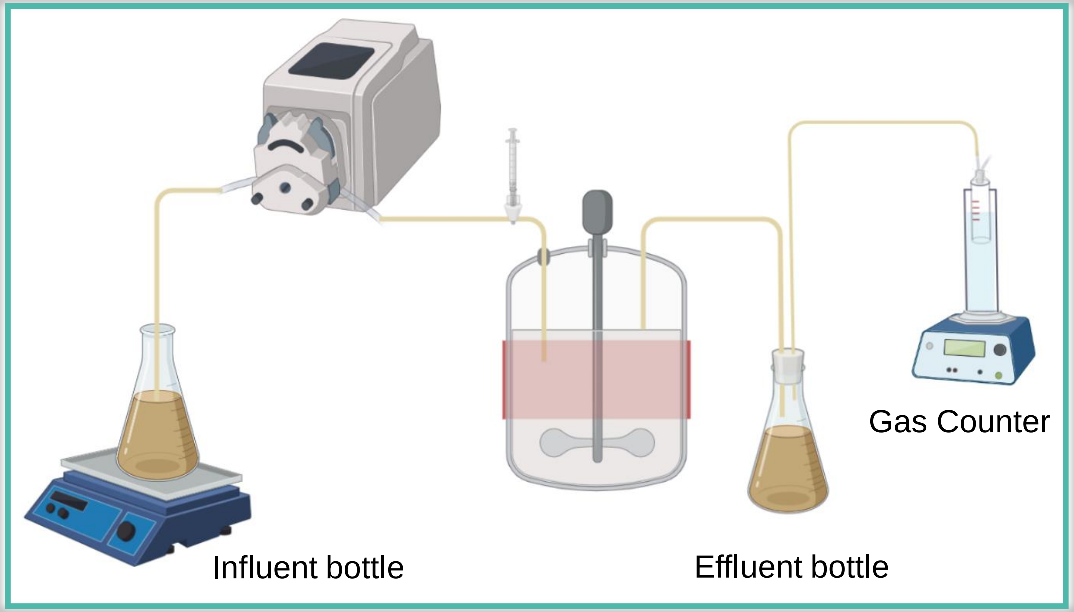
Significant incremental changes



Optimum pre-treatment methods



Ongoing …



- 3 CSTRs
  - raw sludge
  - Pre-treated sludge (2 optimal methods)
- Mesophilic Conditions (37 ± 2^{o} C)
- 3 periods → Increasing Organic Loading Rate (OLR)
- Biochemical parameters x2/week
- Microbial consortium monitoring

Conclusions

- ✓ The model developed was effective in predicting the response's value with good accuracy.
- ✓ Supercritical CO_2 Explosion is effective for sewage sludge pre-treatment.
- ✓ The use of supercritical CO_2 as an alternative green reactant/solvent for the pre-treatment of sludge is scientifically valid.
- ✓ **A significant increment of 8.7%** was observed in methane yield under optimum conditions.
- ✓ Among the additional methods examined, thermal pre-treatment at 45^{o} C for 48h and then at 55^{o}C for additional 48h led to the most significant increase in methane yield.

Acknowledgement

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Thank you for the attention!

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