Continuous Algae-based Carbon Capture and Utilization (CACCU) to Transform Economics and Environmental Impacts: DE FE 0032108

Texas A&M University
Washington University in St Louis
NCCC at Southern Company

U.S. Department of Energy
National Energy Technology Laboratory
Carbon Management Project Review Meeting

Project managed by Dr. Lei Hong

Susie Dai
Texas A&M University

August 08, 2024

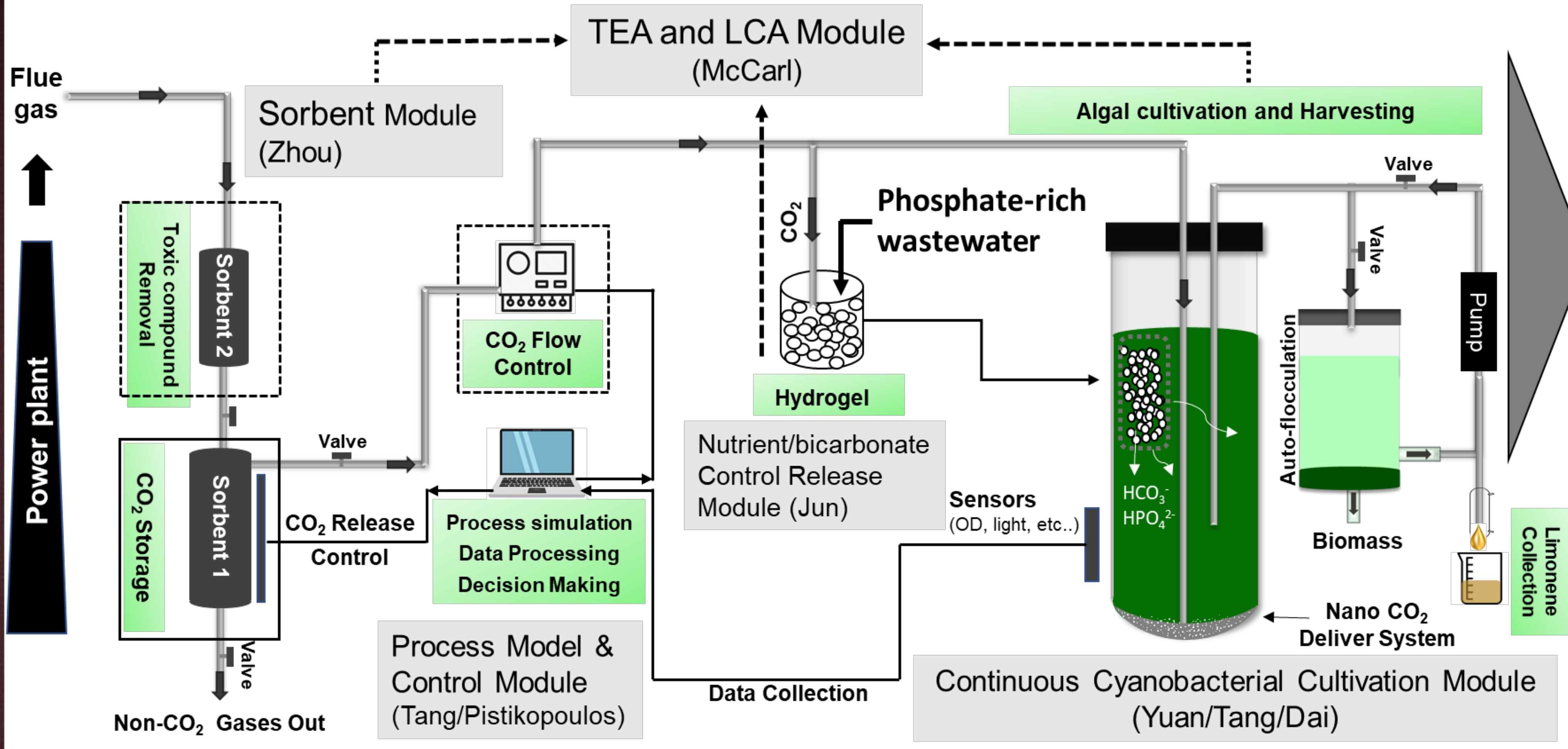
Project Overview

- Funding
  - DOE $2,000,000; Cost Share $510,583
- Overall Project Performance Dates
  - Original 10/01/2021-09/30/2024, three BPs
  - Currently: with 12-month extension to Sep 2025, in BP3
- Project Participants
  - TAMU: Drs. Susie Dai, Joe Zhou, Bruce McCarl, Stratos Pistikopoulos, Chengcheng Fei
  - WUSTL: Drs. Young-shin Jun, Yinjie Tang, Joshua Yuan, Benjamen Kumfer
  - NCCC at Southern Company: Frank Morten, Tony Wu

Overall Project Objectives

- The project integrates novel CO_2 capture/controlled release sorbent with a breakthrough continuous algal cultivation system, assisted by hydrogel technology to reduce media cost, fertilize the algae with controlled nutrient delivery.
- Objective 1: Project management.
- Objective 2: Integrates CO_2, bicarbonate, and nutrient capture and delivery to the low-cost harvest-empowered continuous algal cultivation system with ultra-high productivity and CO_2 uptake plus valuable chemical bioproduct production. We also advance algal strain, sorbent, and hydrogel technologies to enhance carbon capture and yields of limonene, biomass, and glycogen.
- Objective 3: Scale up the sorbent technology and integrate it with algal cultivation.
- Objective 4: Test the prototype CACCU system with flue-gas coupled 100 L photobioreactor (PBRs).

Technology Background



Outcomes

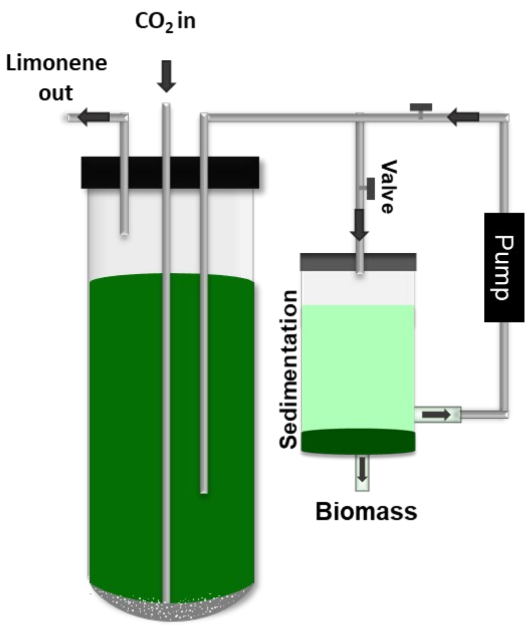
- Sorbent CO2 capture
- Gel nutrient release
- Fast algal growth
- Easy Biomass harvest
- Process integration
- Optimal Design
- Process control
- Capital Cost
- Operating Cost
- Biomass profit
- Environmental benefits

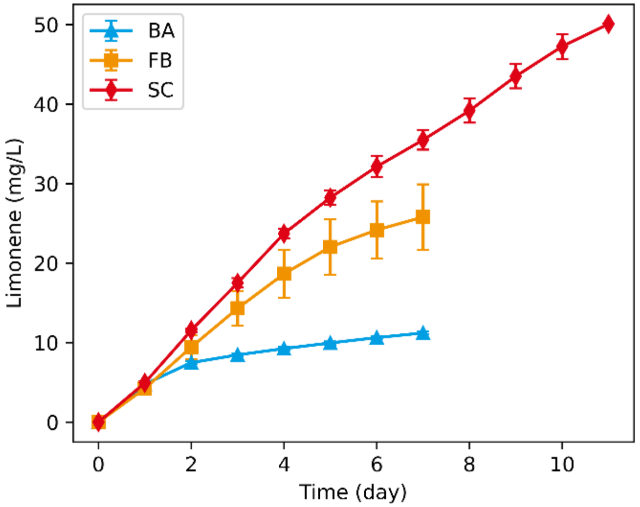
Milestones

Year 1: Small scale lab tests (bio and abiotic studies)
Year 2: 20~100 L PBR test
Year 3: Outdoor tests and TEA/LCA (>100 L)

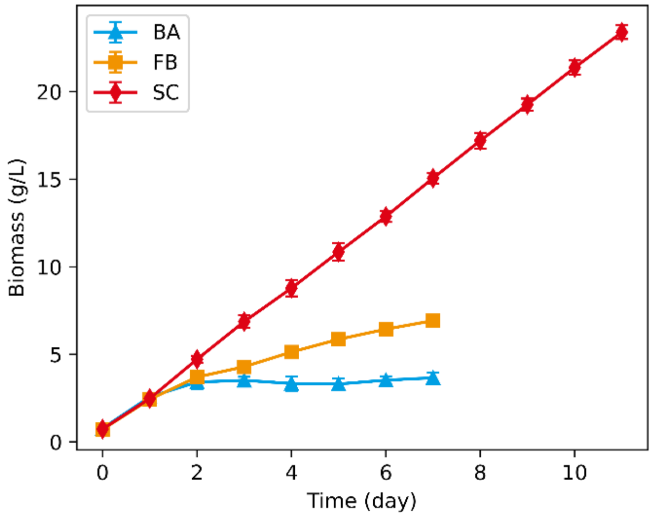
The integrated CACCU system

Sustainable co-production of limonene and biomass by semi-continuous cultivation





~5 mg/L/day



~2.2 g/L/day

Record productivities and yields in limonene productivity

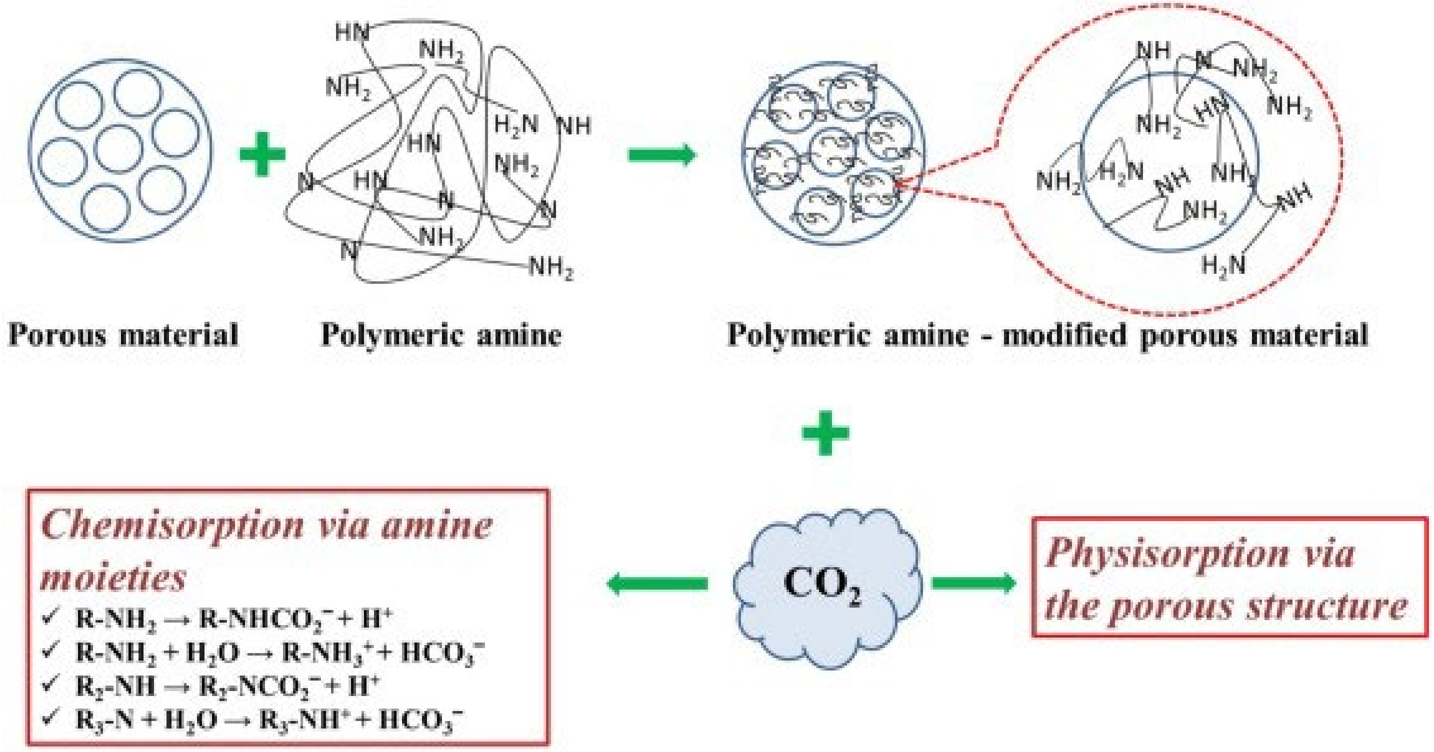
Sustainable biomass accumulation at about 1-2g/L/Day for a long period of time.

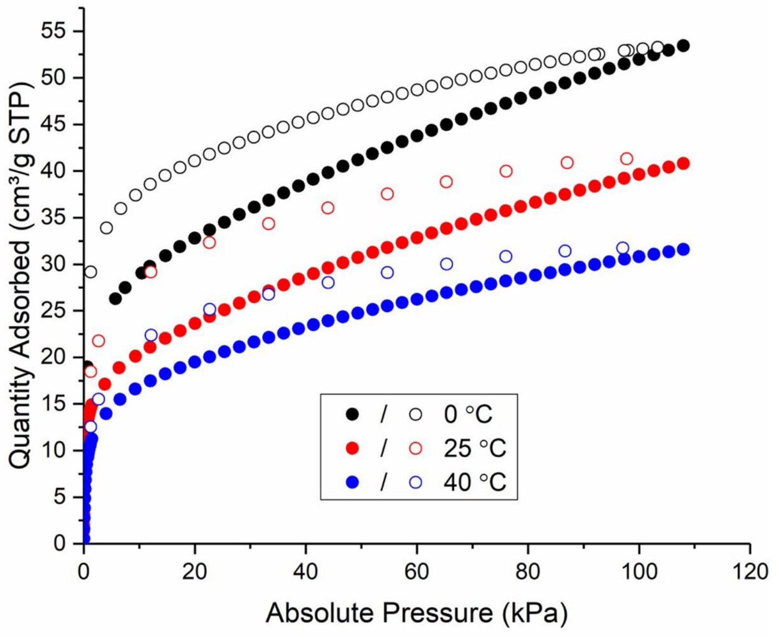
Machine learning informed semi- continuous cultivation.

Long et al., Nature Communications, 2022, 13:541

Dai and Yuan's groups@TAMU

Amine Grafted Porous Polymer Network





CO_2 adsorption of PPN-151-DETA

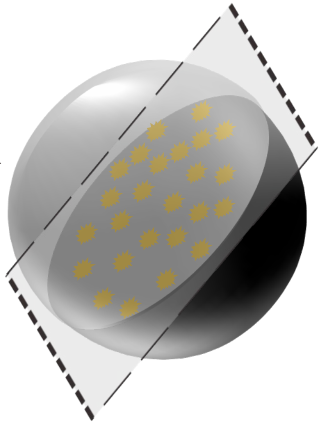
Zhou's group@TAMU

Mineral-seeded mineral hydrogel composites for nutrient delivery and pH control

Adding salts or P and P-rich wastewater → Ca^{2+}, HPO_4^{2-}

Struvite ($NH_4MgPO_4 \cdot 6H_2O$) → NH_4^+

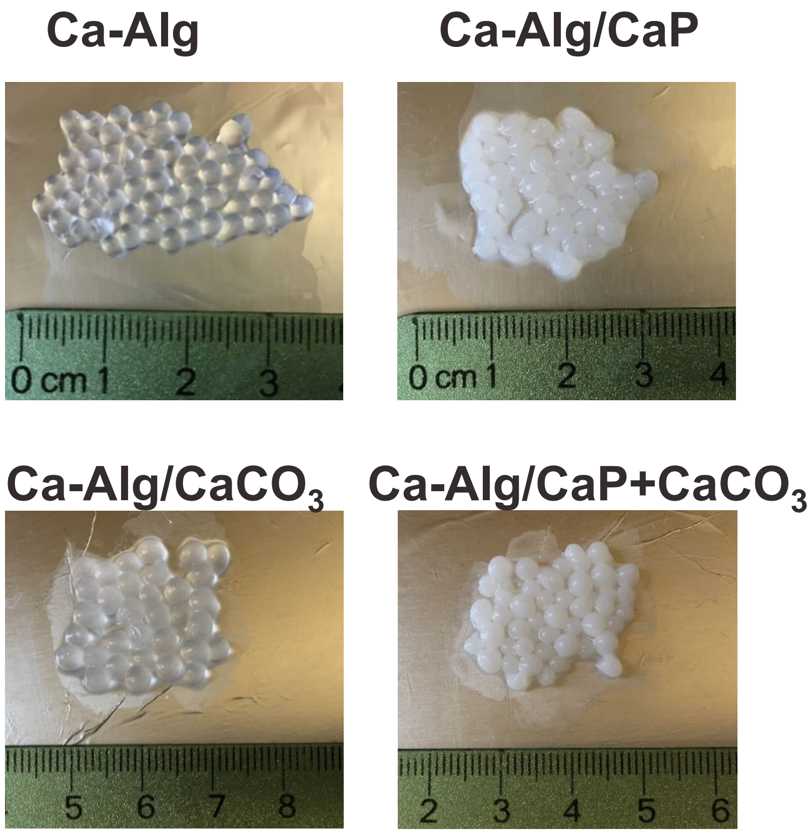
CO_2 capture/dissolution → HCO_3^-



Calcium-Alginate Hydrogel (Ca-Alg)

Mineral seed

Jun and Tang's groups@WUSTL



Kim, D and Jun, Y.-S., *Green Chemistry* **2018,** *20* (2), 534-543.

- Calcium phosphate, calcium carbonate, or ammonia-containing mineral seeds formed during alginate crosslinking.
- When placed into calcium phosphate/carbonate supersaturated solution, mineral seeds grow, collecting and incorporating phosphate, bicarbonate, and ammonia-containing minerals.

Translating process models into a process systems engineering framework at scale involves some critical steps

1) Accurate modeling of process dynamics

2) Reduced order approximation of nonlinear dynamics

Surrogate linear models can tame computational complexity

Linear programs can provide *certificates of optimality*

3) Design of control scheme

4) Formulation of a network design as a mixed integer program (MIP)

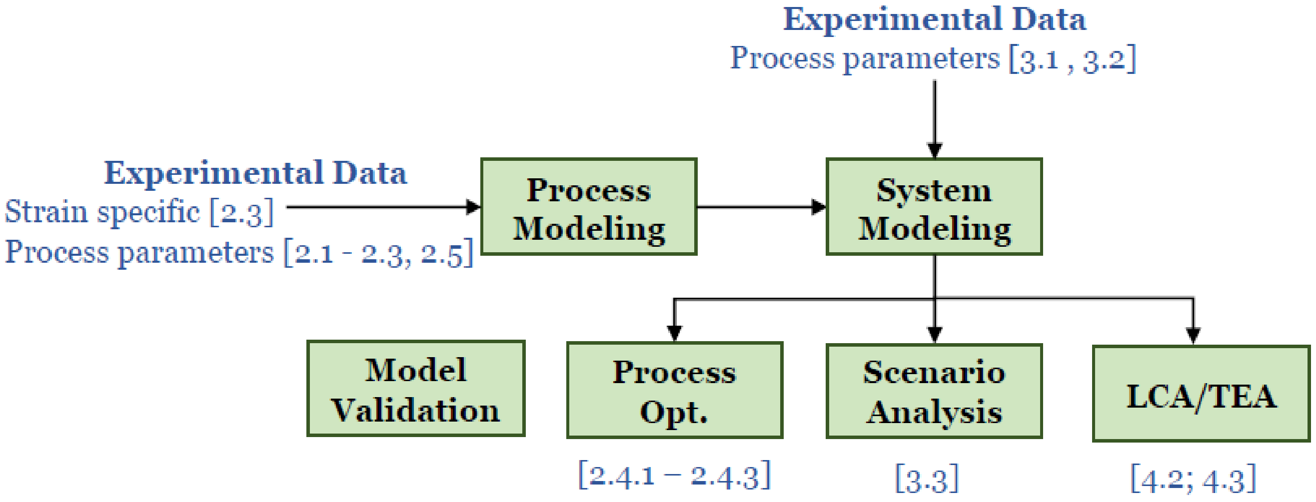
MIPs can be optimized to multiple objectives

Network decisions can be modeled as binary variables

Scheduling can be integrated (multiscale approach)

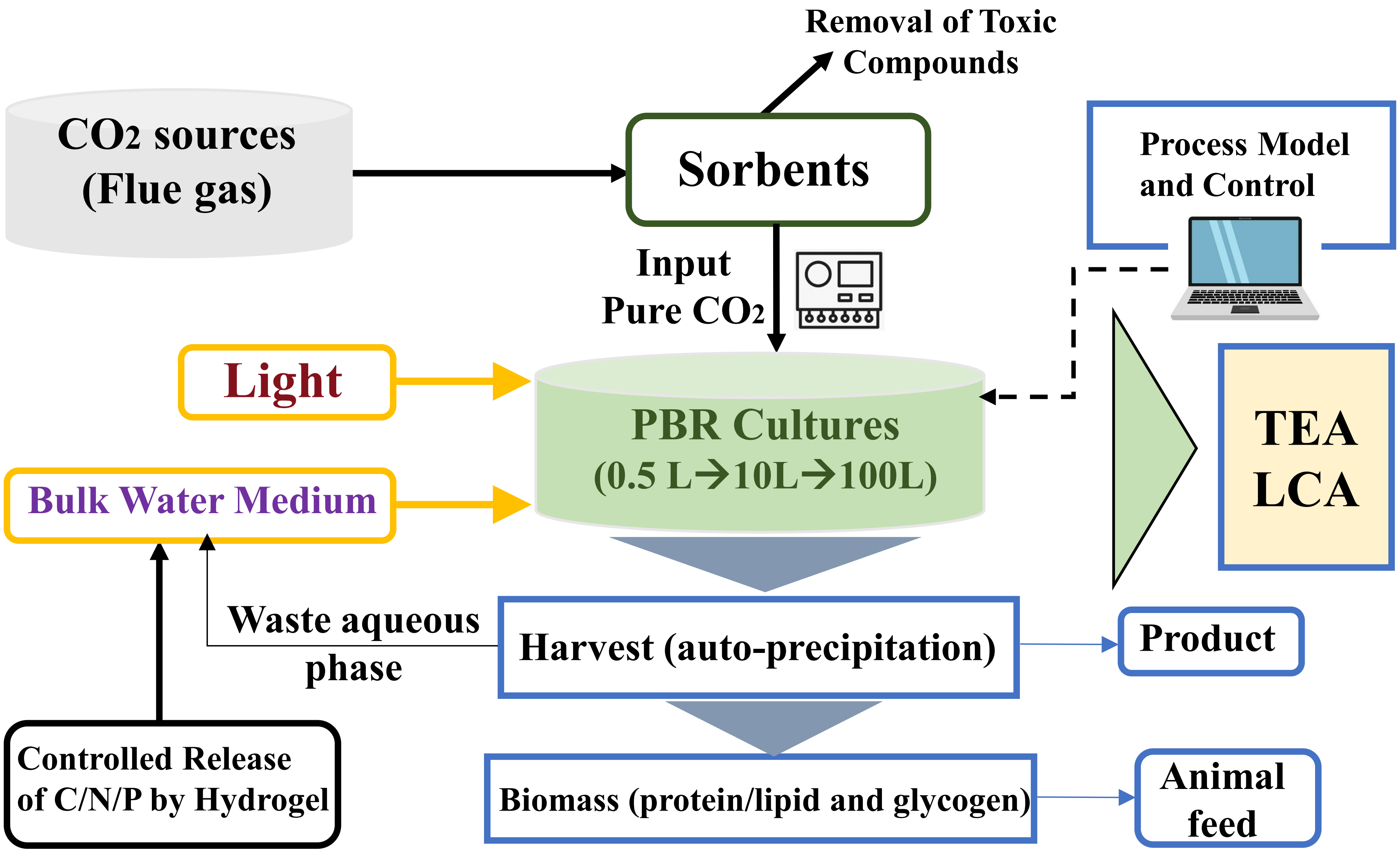
5) Integration of lifecycle tools

OpenLCA data integration with MIP framework (MIP)



Tang, Pistikopoulos and McCarl's groups@TAMU&WUSTL

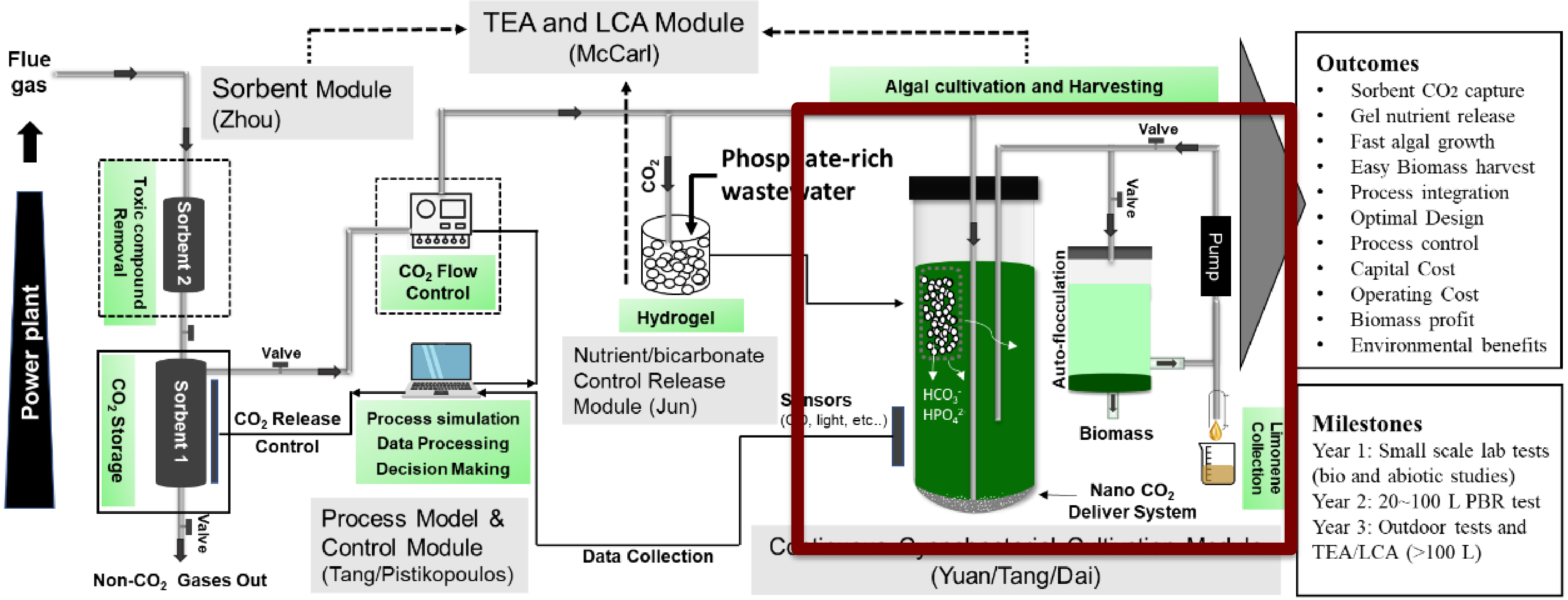
Technical Approach/Project Scope

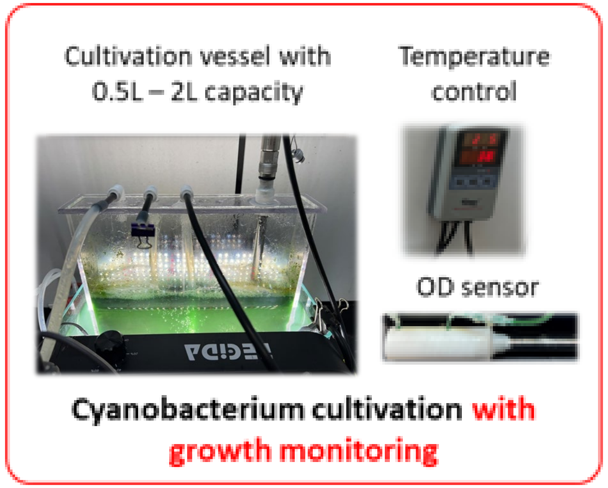


Progress

Tasks to be finished in BP2

Task	Milestone Title	Complete Date	Status
2.4.2	Compare the process control model and machine learning model and decide the strength and applicability of each model.	Q10(03/31/2024)	**Completed** Build the MAGMA model and plan to submit the manuscript in 2024.
2.5	Scale up to bench-scale at 2 Liter with algae biomass yield >1.8 g/L/D using engineered strains and sorbent-released CO_2	Q10(03/31/2024)	**Completed** Maximum biomass productivity of 2g/L/D and median productivity of 1.84 g/L/D
3.1	Re-design the sorbent to achieve the carbon capture capacity at 0.25 g CO_2/g Sorbent.	Q10(03/31/2024)	**Completed** The new sorbent reached 0.7g CO_2 /g sorbent adsorption capacity, and reached the milestone.



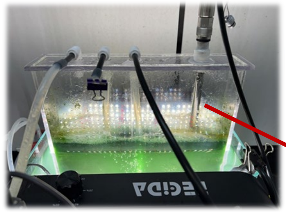


Dai’s group @TAMU
Yuan’s group @WashU

Evolution of The Integration System –Version 5 _ 2L

- ❑ Customized a 2L flat panel PBR
- ❑ Real-time growth monitoring
- ❑ Enhanced peristaltic pump for gas supply (higher flow rate)

Cultivation vessel with 2L capacity



Temperature control

Turbidity sensor

Cyanobacterium cultivation
with growth monitoring

CO_2 controller

Sorbent

Oil bath

Heating pad

Automatic CO_2 releasing

Maximum biomass productivity of 2g/L/D and median productivity of 1.84 g/L/D

Gas pump system

1% H_2SO_4 to remove amine while minimizing CO_2 dissolving

Amine removal

Data logging

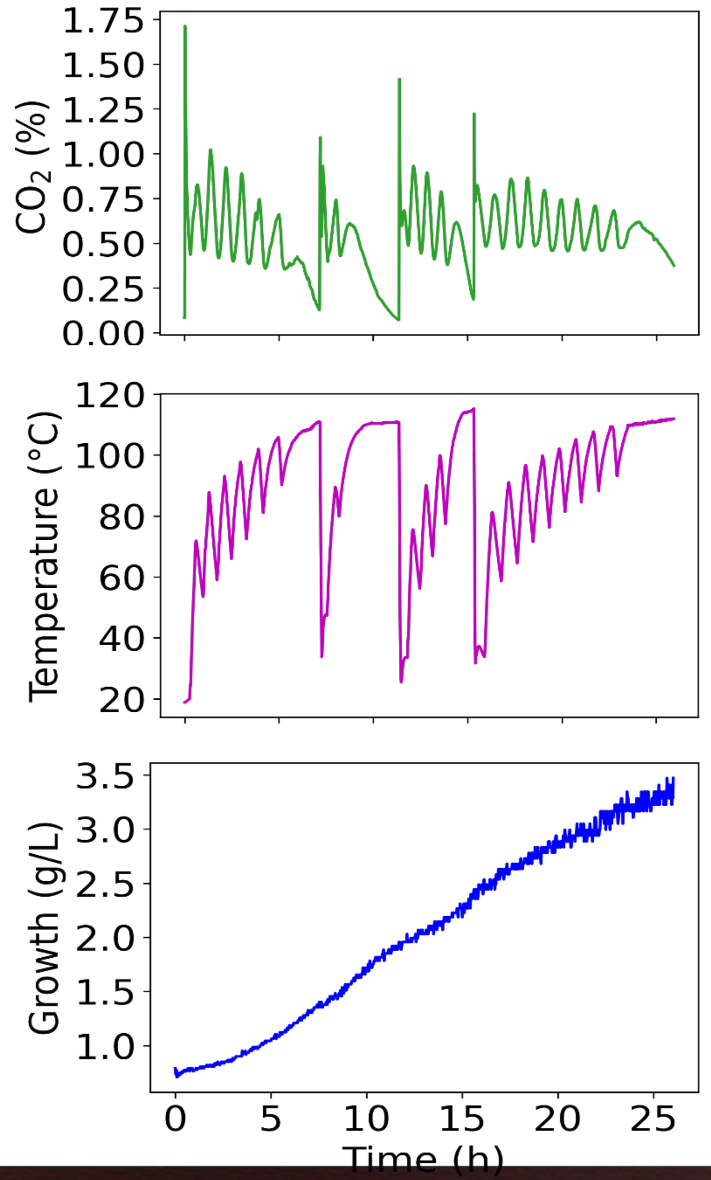
CO_2 sensor

CO_2 monitor

Logged data:

- CO_2 concentration
- Sorbent temperature
- Growth curve

Evolution of The Integration System –Version 5_2L



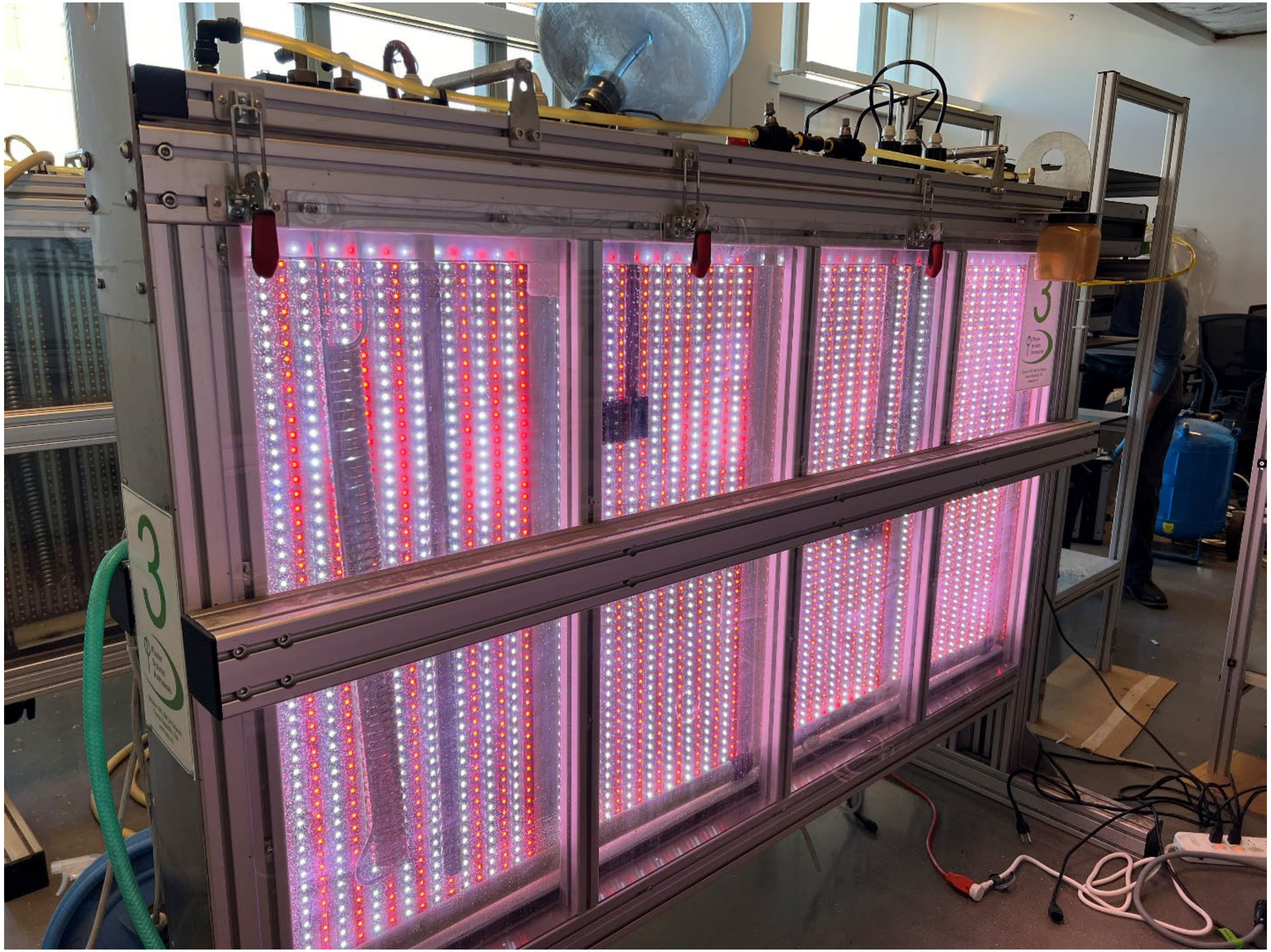
- ❑ Trigger threshold set to 0.8%
- ❑ Growth over 16h: median at 1.84 g/L and peak at 2.00 g/L, surpassing the Q10 milestone (1.8 g/L)

To be tested/optimized:

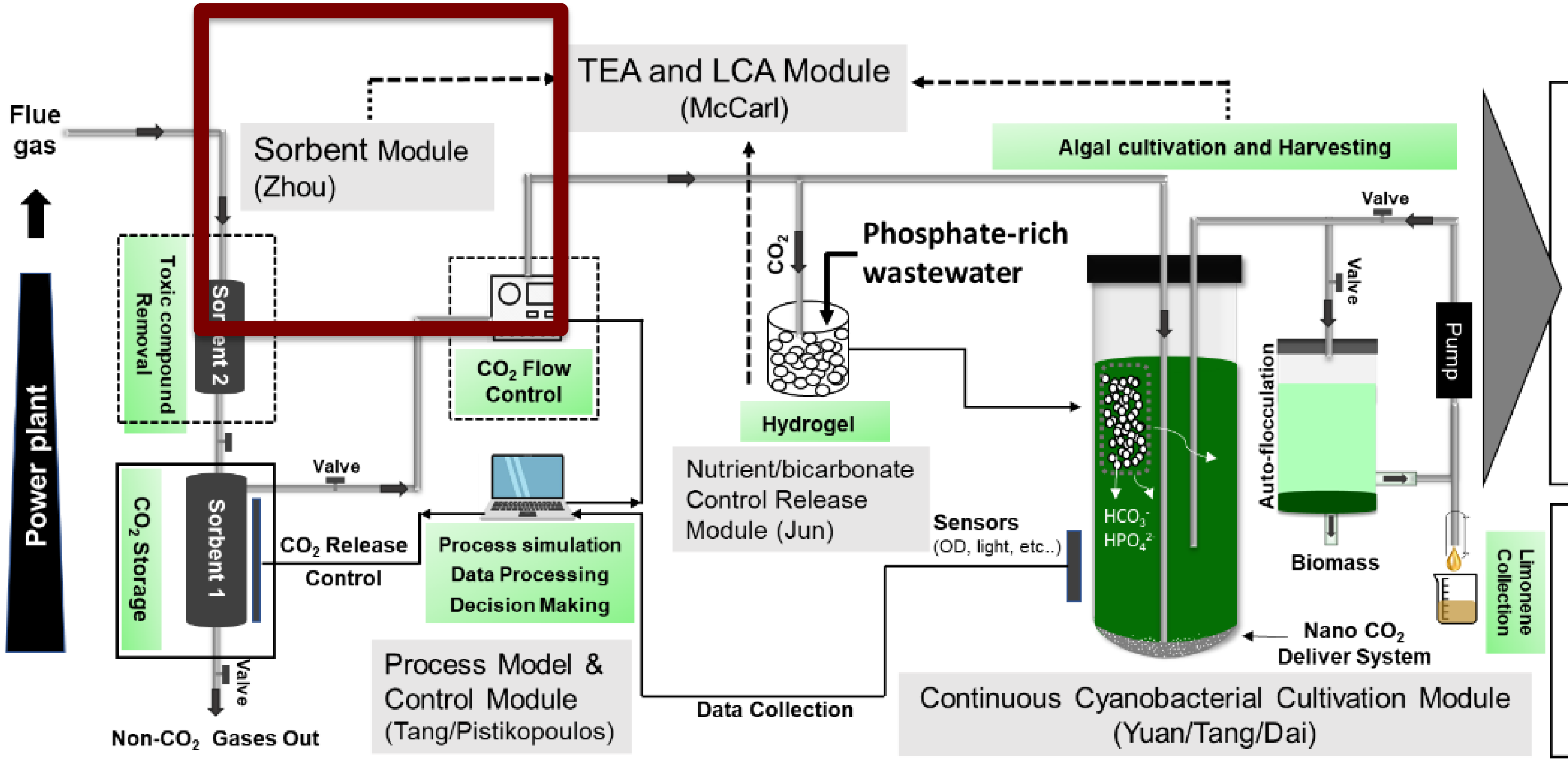
- ❑ Optimize the with CO_2 controlling system with capacity to maintain CO_2 at higher concentration

20 Liter PBR

100 Liter PBR



100 Liter PBR



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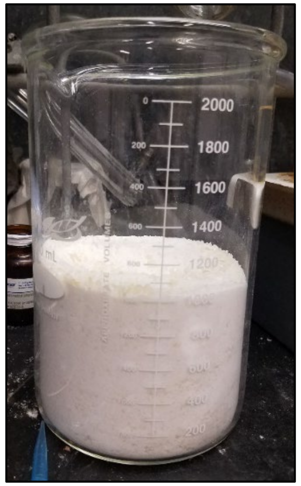
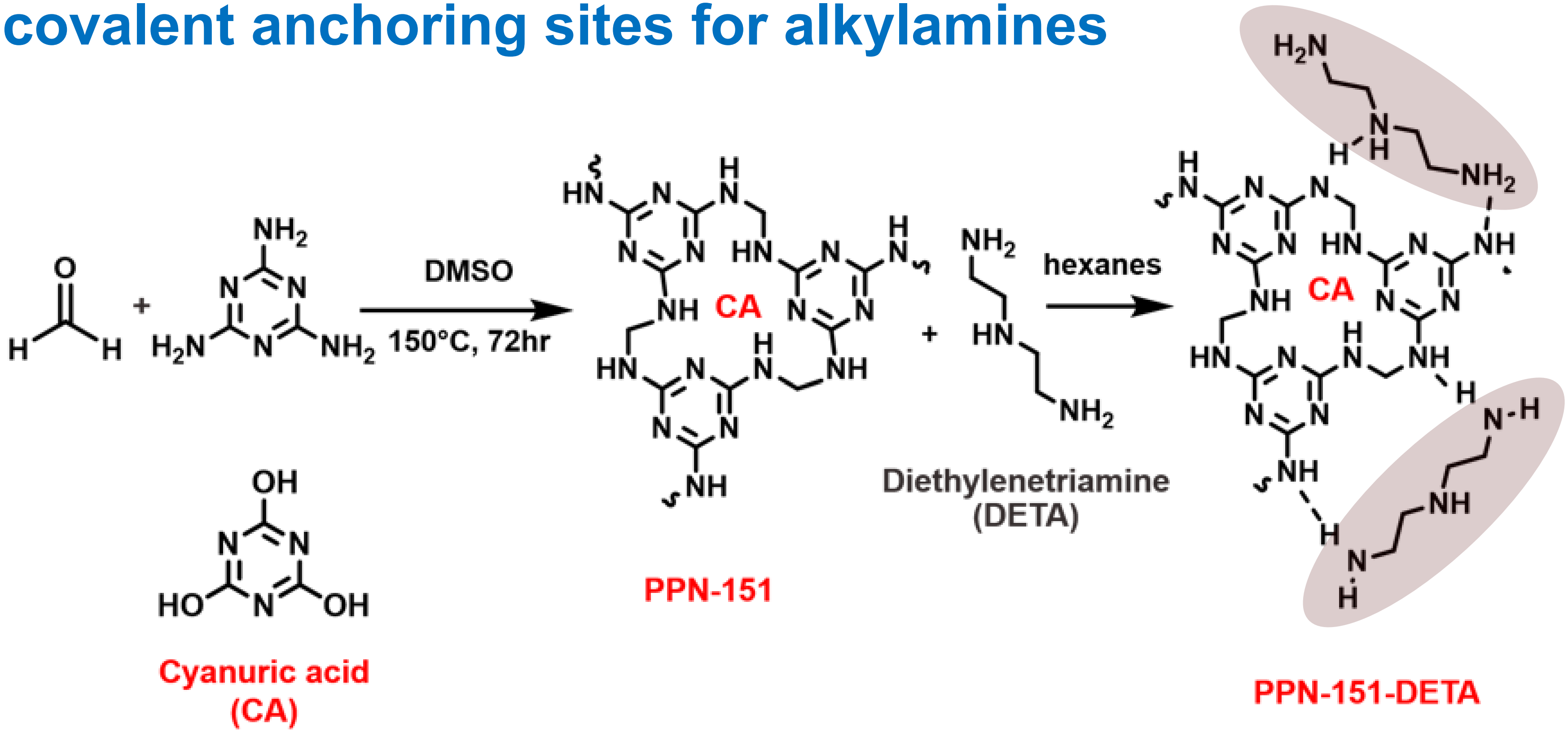


Zhou’s group@TAMU

Physically Attached Amines in PPN-151-DETA

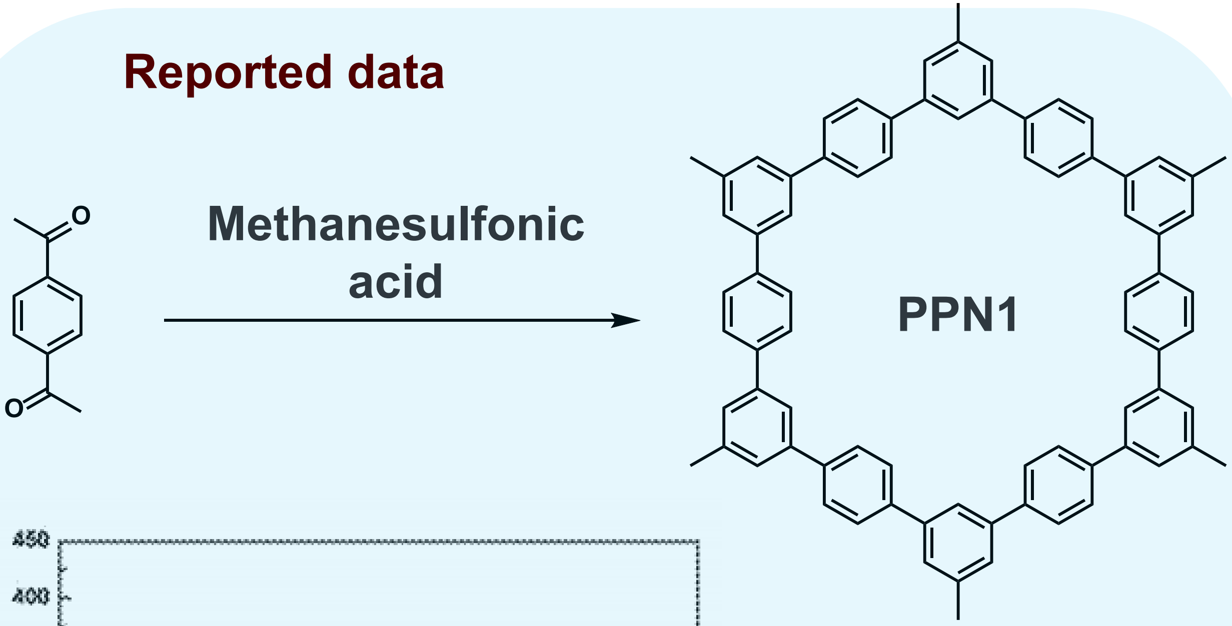
- Physically impregnated amines
- CA - noncovalent anchoring sites for alkylamines

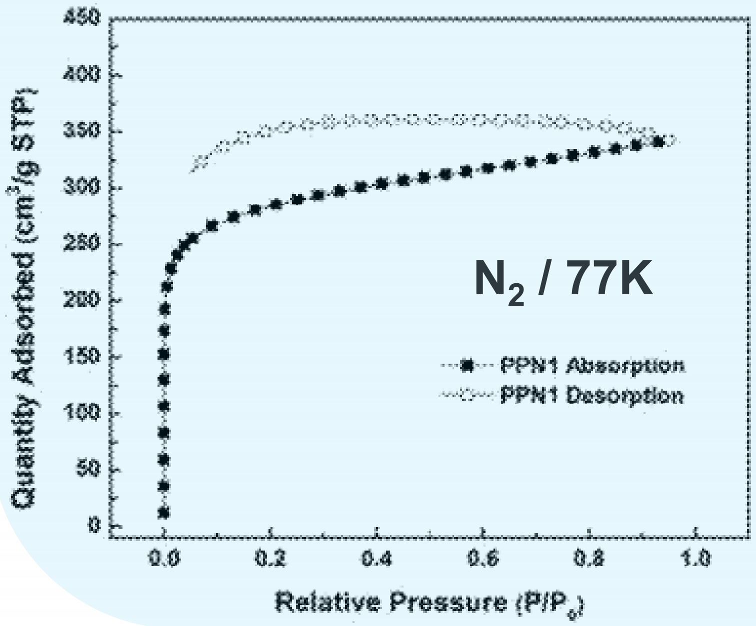


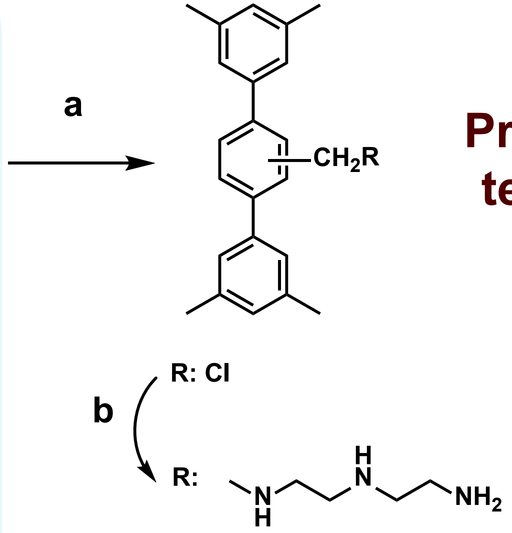
Advantage: Easy recycle of PPN-151 backbone;
Disadvantage: Potential amine loss during application.

All Carbon PPN Scaffold

Reported data







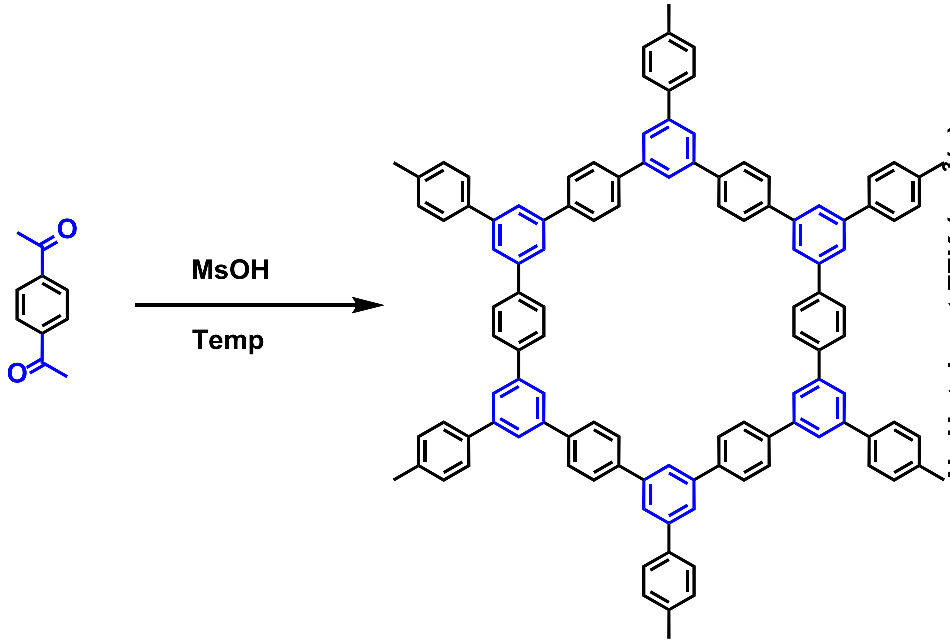
Proposed amine tethering route

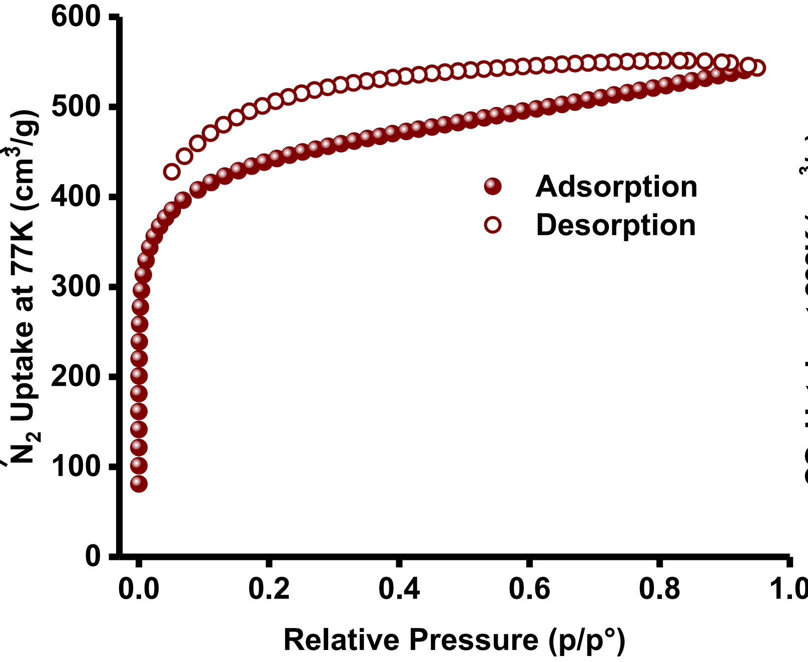
PPN1-DETA

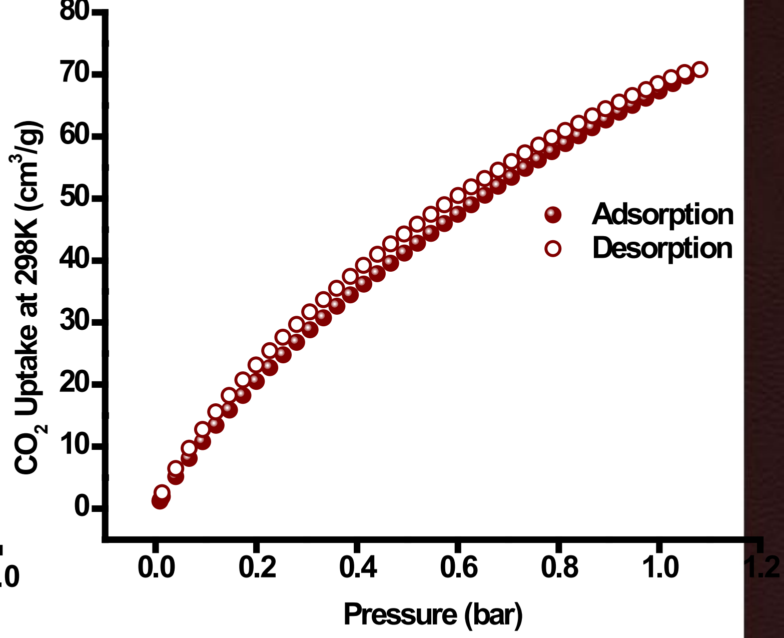
Fang, L. Zhou, H.-C. et al., Pub. No. US 20210230359A1

Porosity Optimization

PPN-KF3D







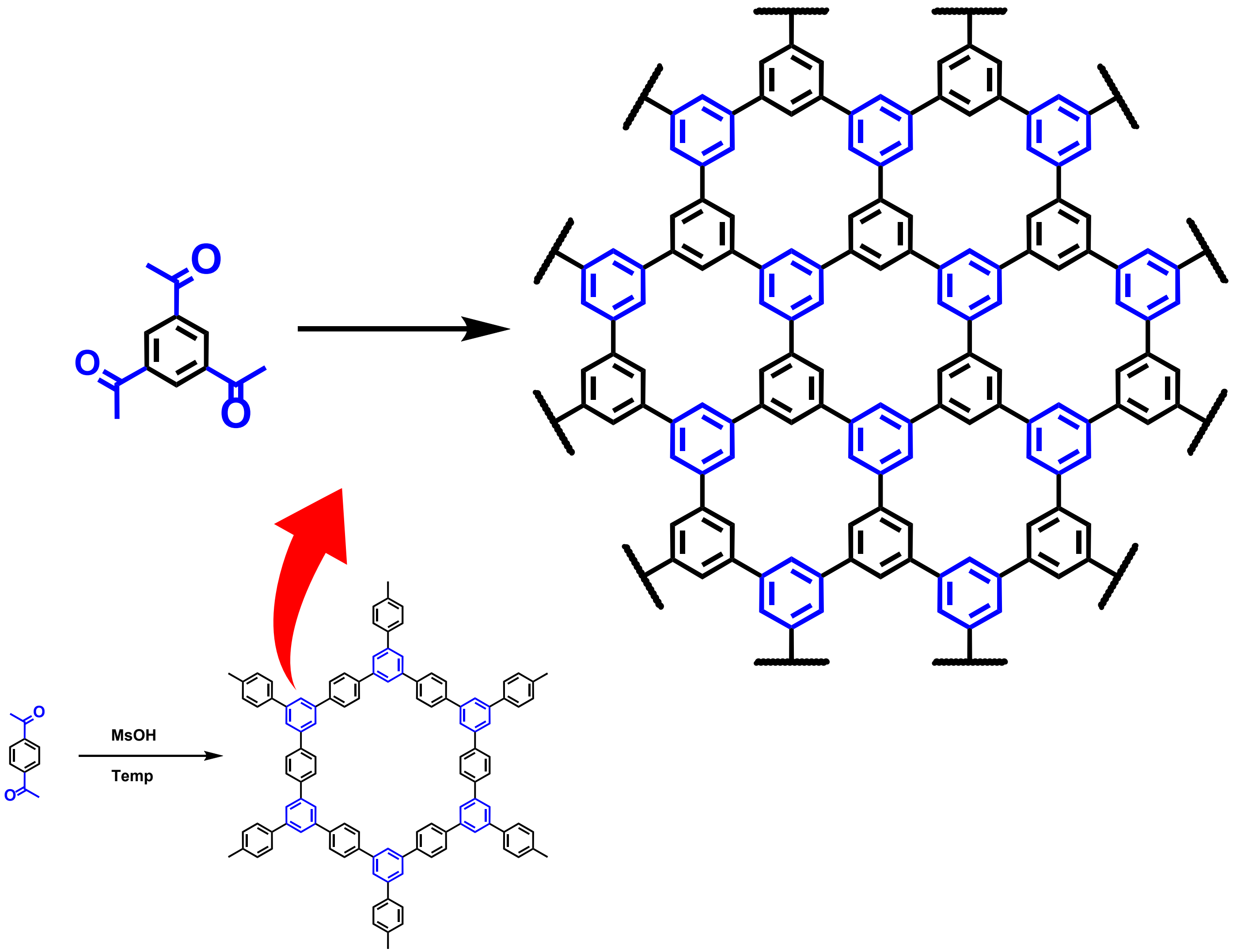
OPTIMIZED REACTION

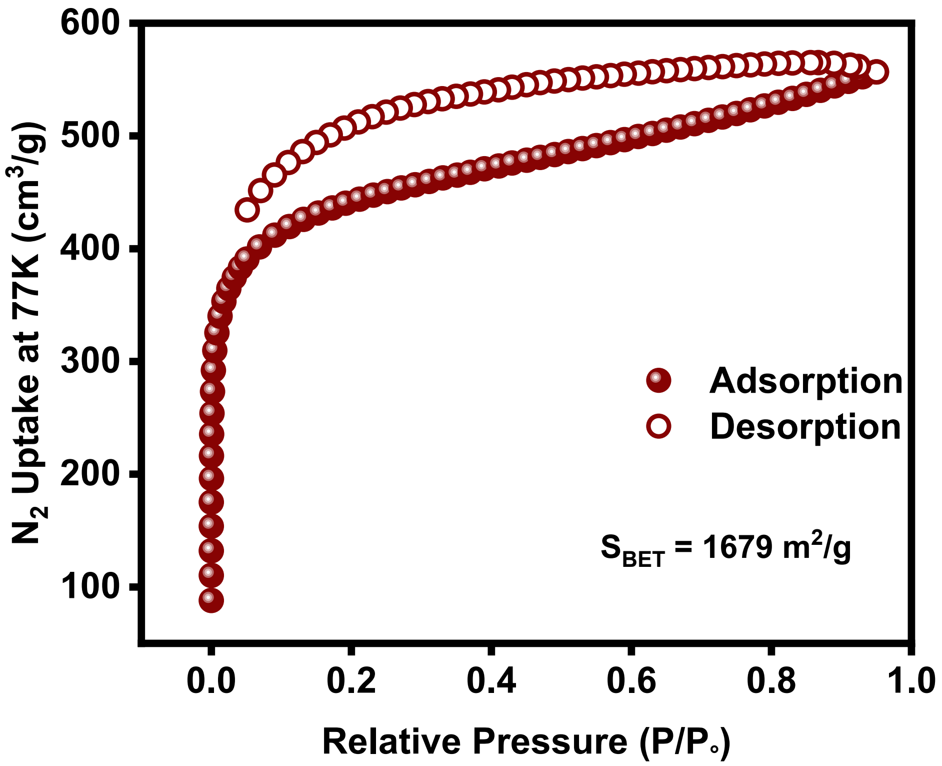
- ✓ High BET surface area
- ✓ Cheap starting materials
- ✓ Easy reaction

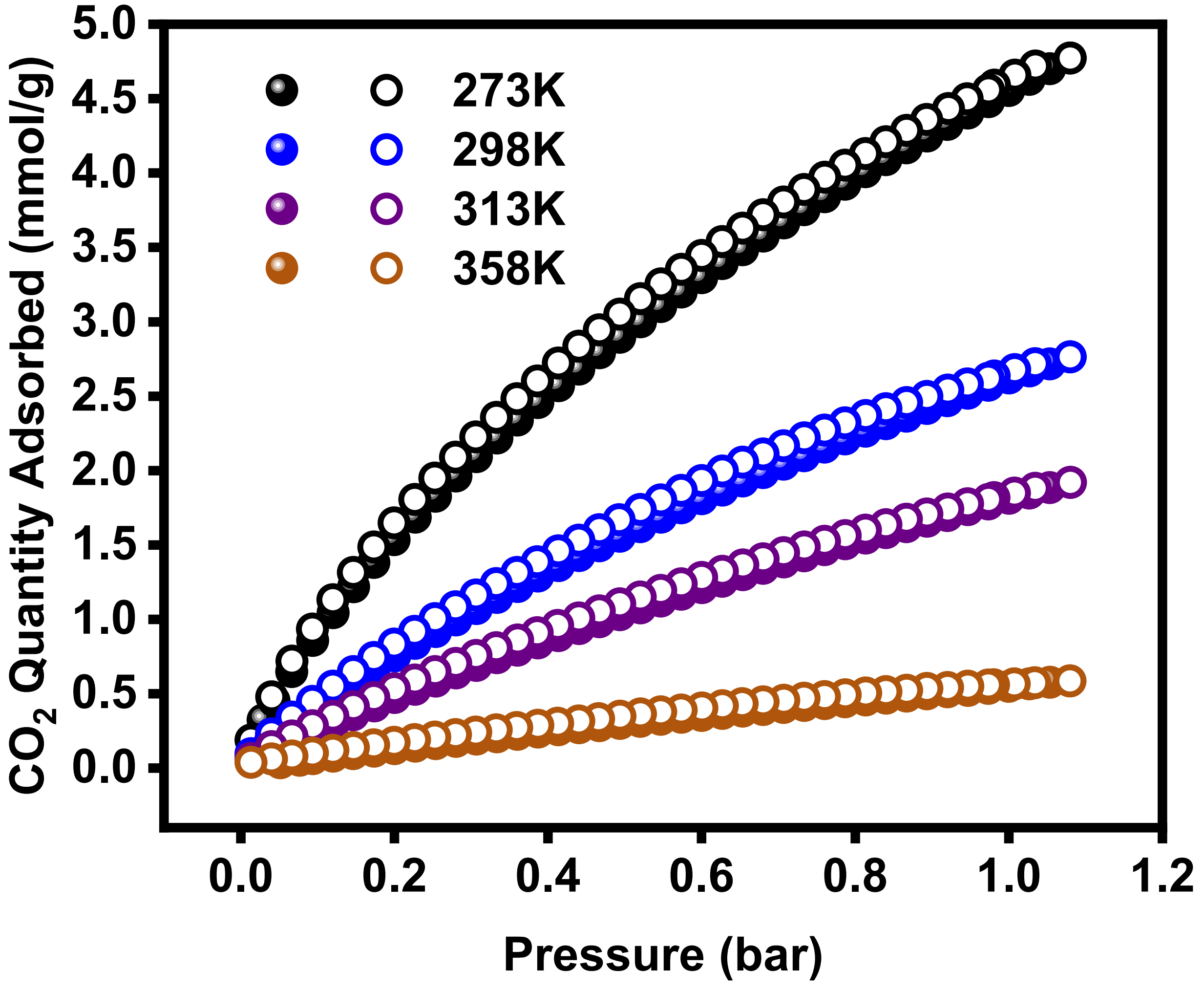
BET surface area 1600 m^2/g

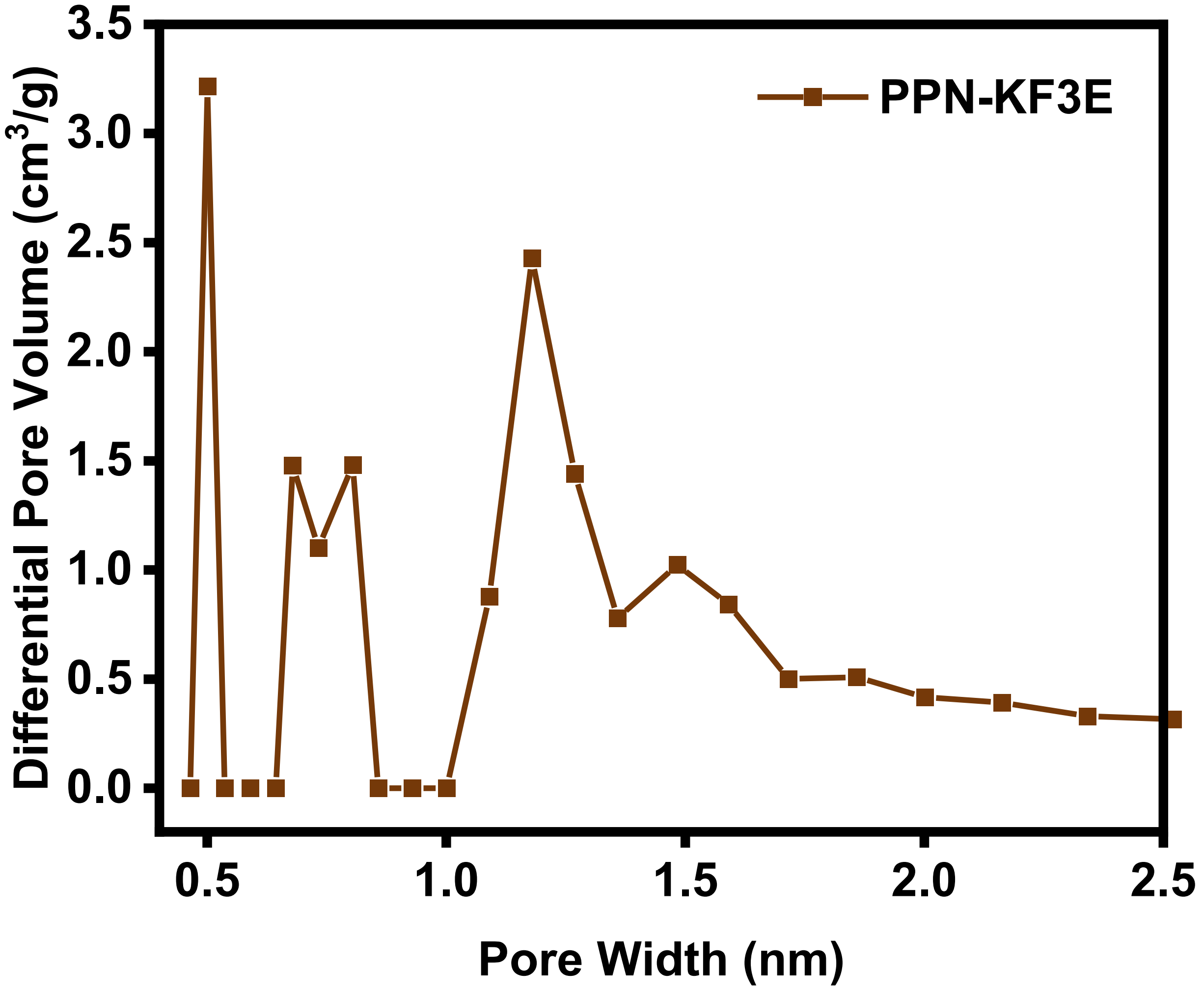
Maximum CO_2 uptake at room temperature 71 cm^3/g

New progress

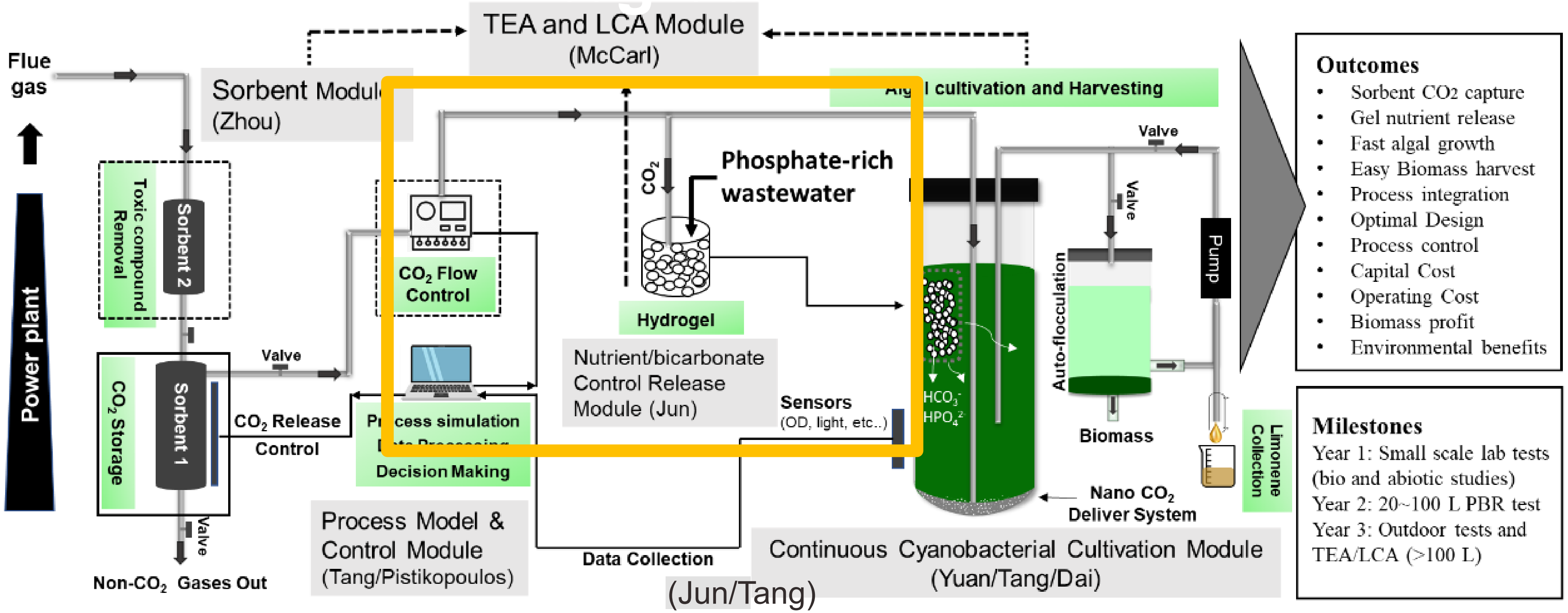




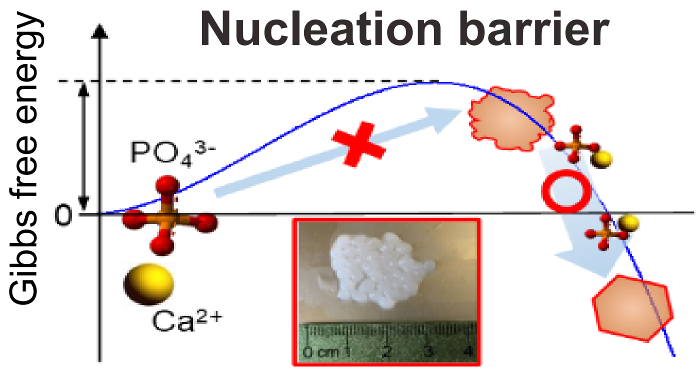


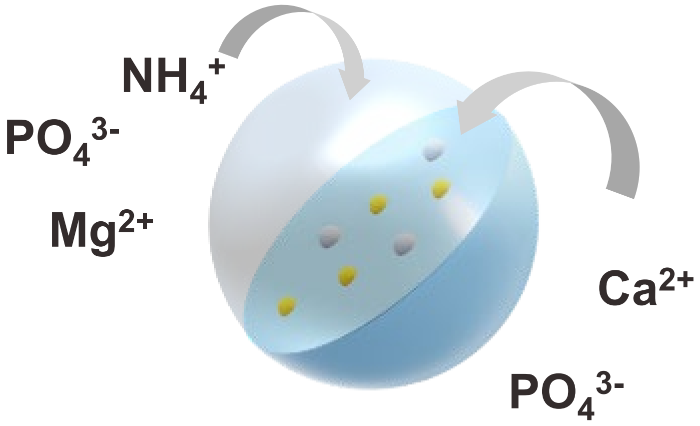


The new sorbent reached 0.7g CO_2 /g sorbent adsorption capacity



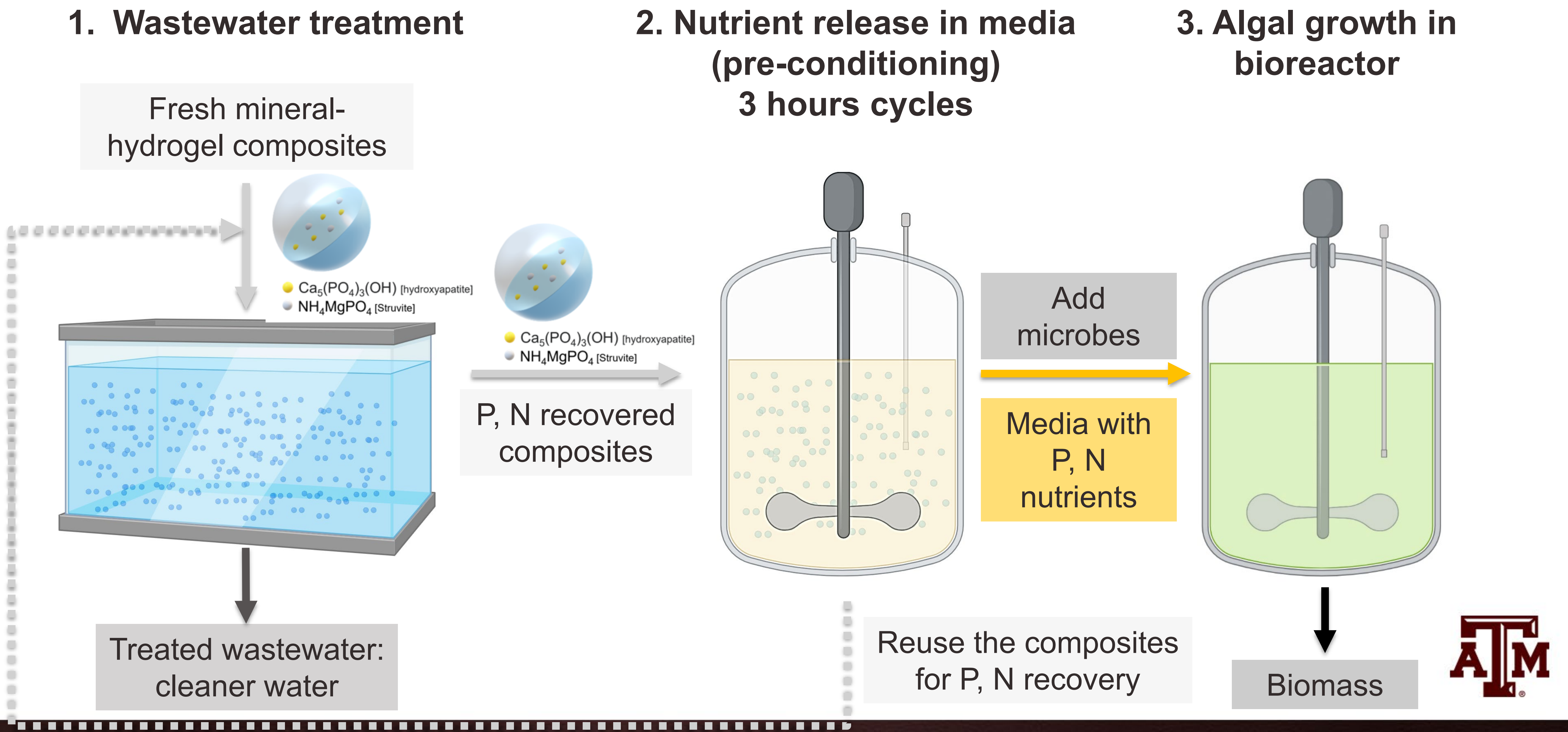
Jun's group @WashU





Nutrient delivery system
from mineral-hydrogel composites to bioreactor

Created with BioRender.com



Release rates of mineral-hydrogel composites
Ca-Alg/CaP+Wollastonite

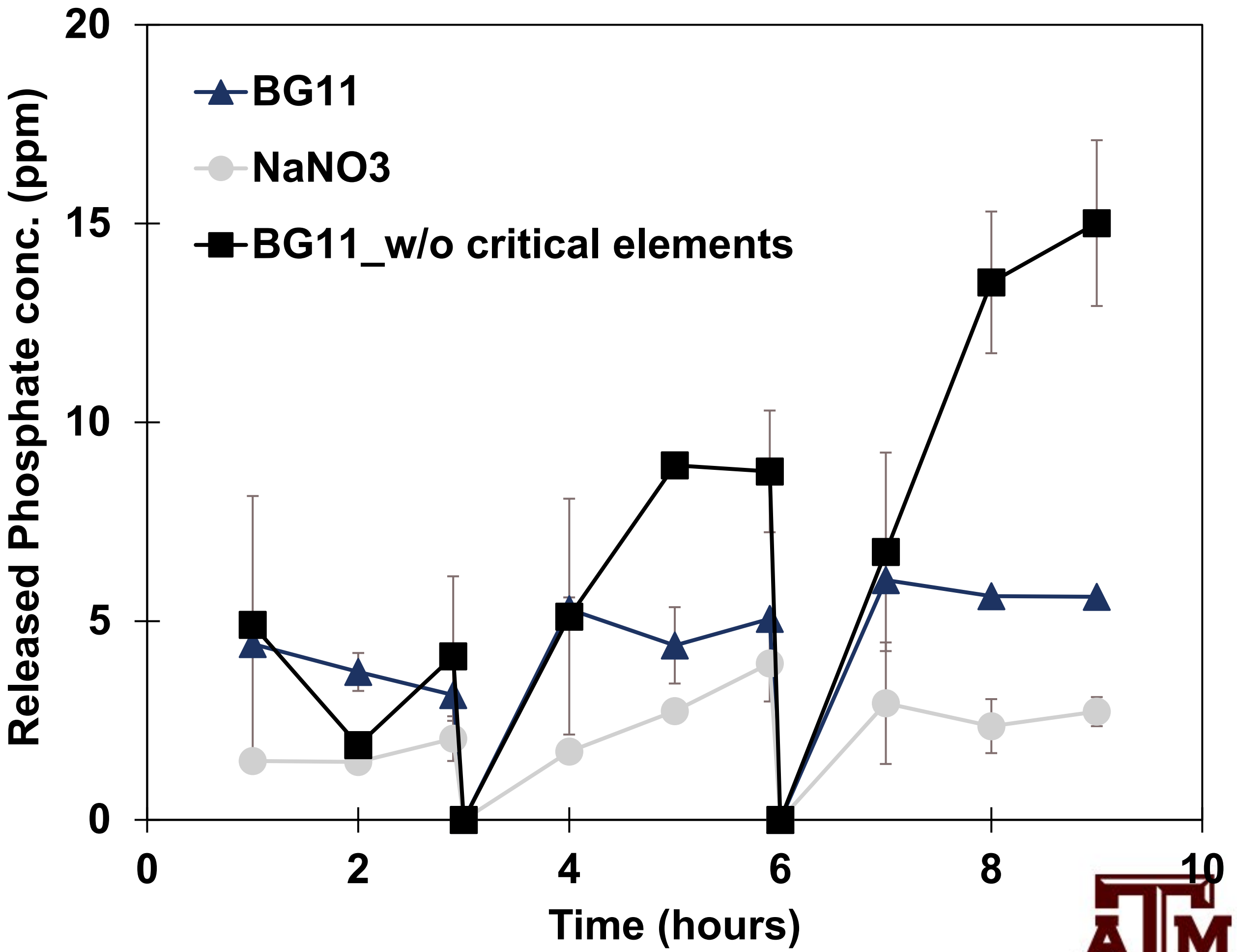
- Media
1. BG11 Media
2. 22 mM $NaNO_3$ (same ionic strength as BG11)
3. BG11 Media without critical elements (i.e., Ca, Mg, NH_4, PO_4)

Media was replaced by every 3 hours

- Dose - 10 % (v of hydrogel precursor/v of media)

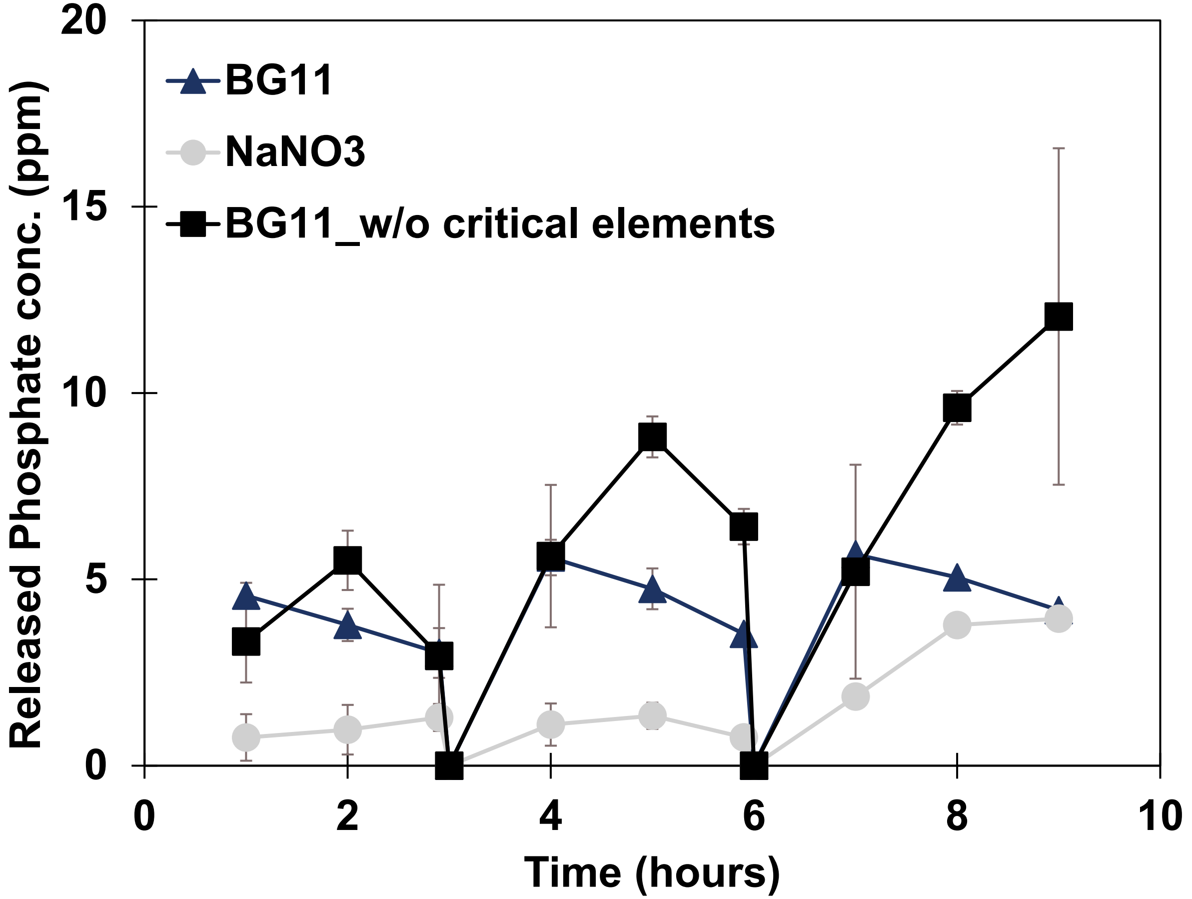
In each cycle, the composites released around 5.0 ppm, 8.9 ppm, 15.1 ppm of P from Ca-Alg/CaP+Wollastonite

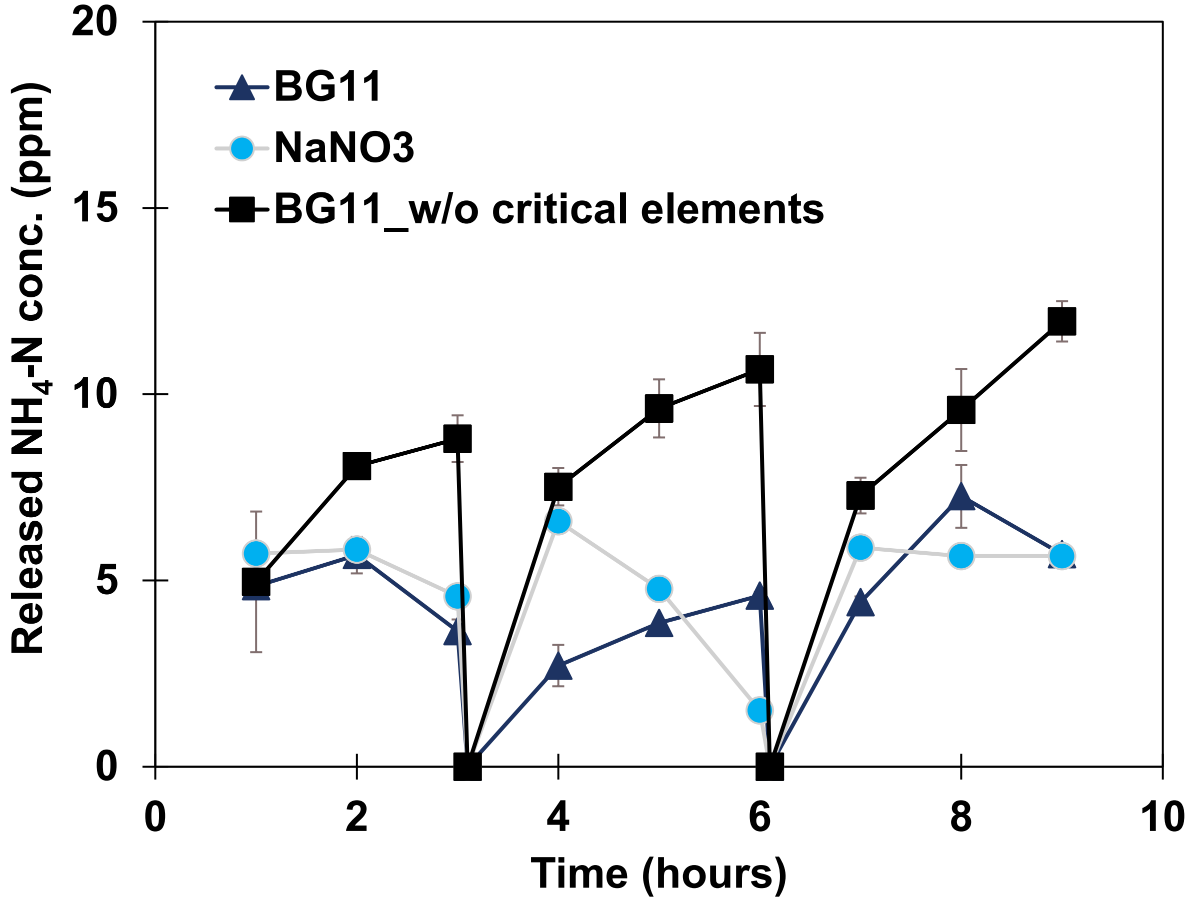
P release in each cycle is equivalent to P in BG11 media (5 ppm) or significantly over it.



Release rates of mineral-hydrogel composites

Ca-Alg/CaP+Struvite





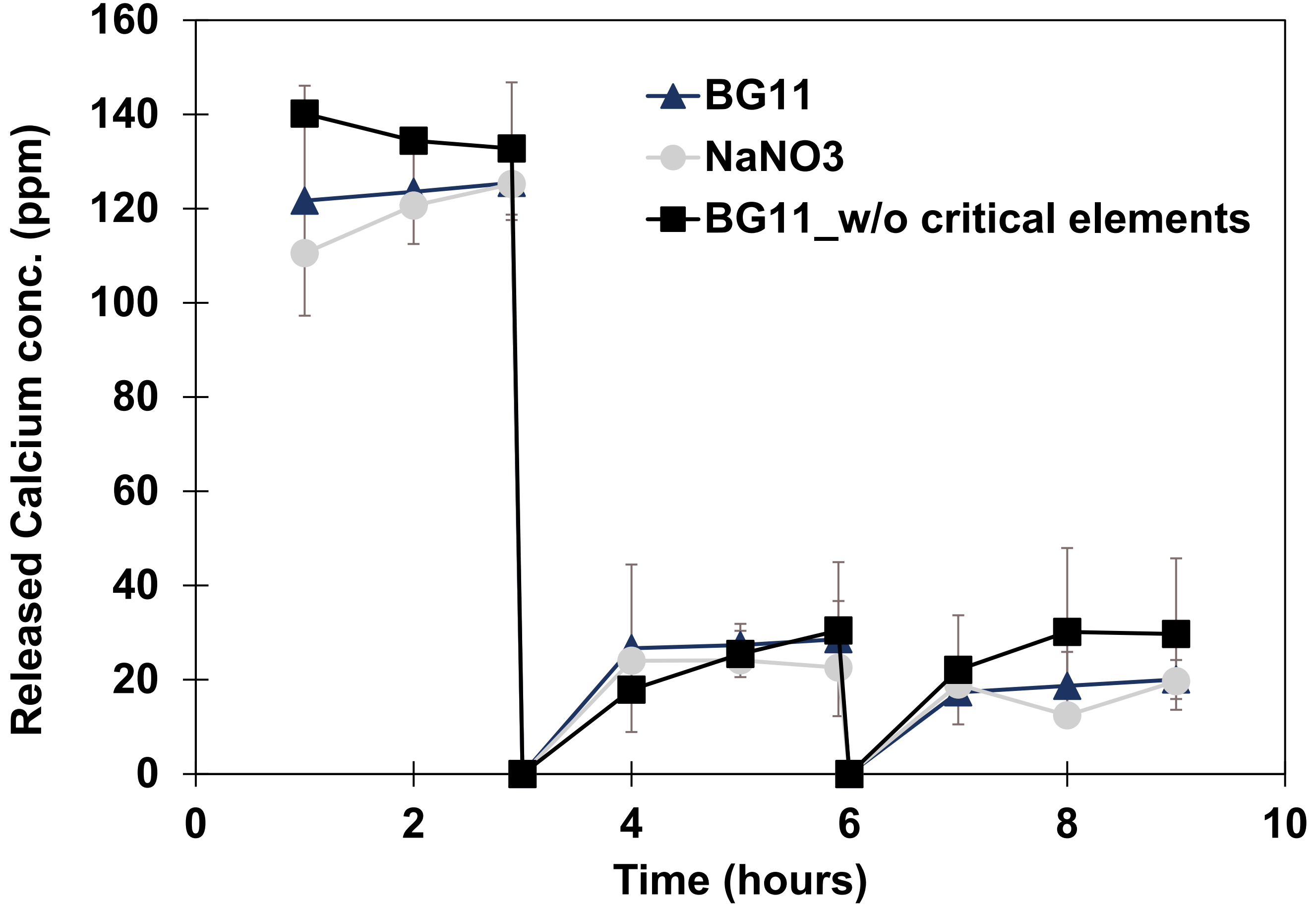
In each cycle, the composites released around 5 ppm, 9 ppm, and 13 ppm of P and 8.8 ppm, 10.7 ppm, and 12.0 ppm of NH_4-N.

P release in each cycle is equivalent to P (5 ppm) in BG11 media or higher.

We can utilize Ca-Alg/CaP+Struvite with sufficient nitrogen delivery for algal species preferring ammonium sources

Release rates of mineral-hydrogel composites

$Ca\text{-}Alg/CaCO_3$



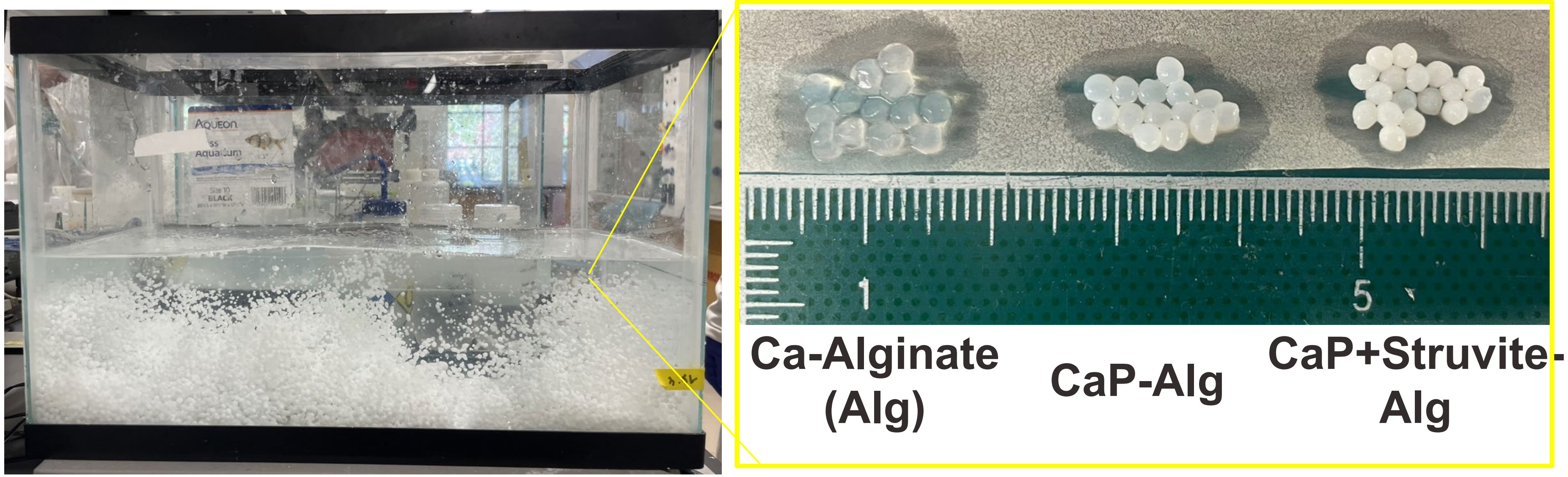
- Calcium carbonate dissolution kinetic is relatively faster than struvite and calcium phosphate.
- Thus, the first cycle with 3 hours released the highest calcium and gradually decreased.
- Total Ca released amount is around 200 ppm in BG 11 without critical elements. It is equivalent to 305 ppm of bicarbonate release.

Fabrication of mineral-hydrogel composites
at 250 g scale

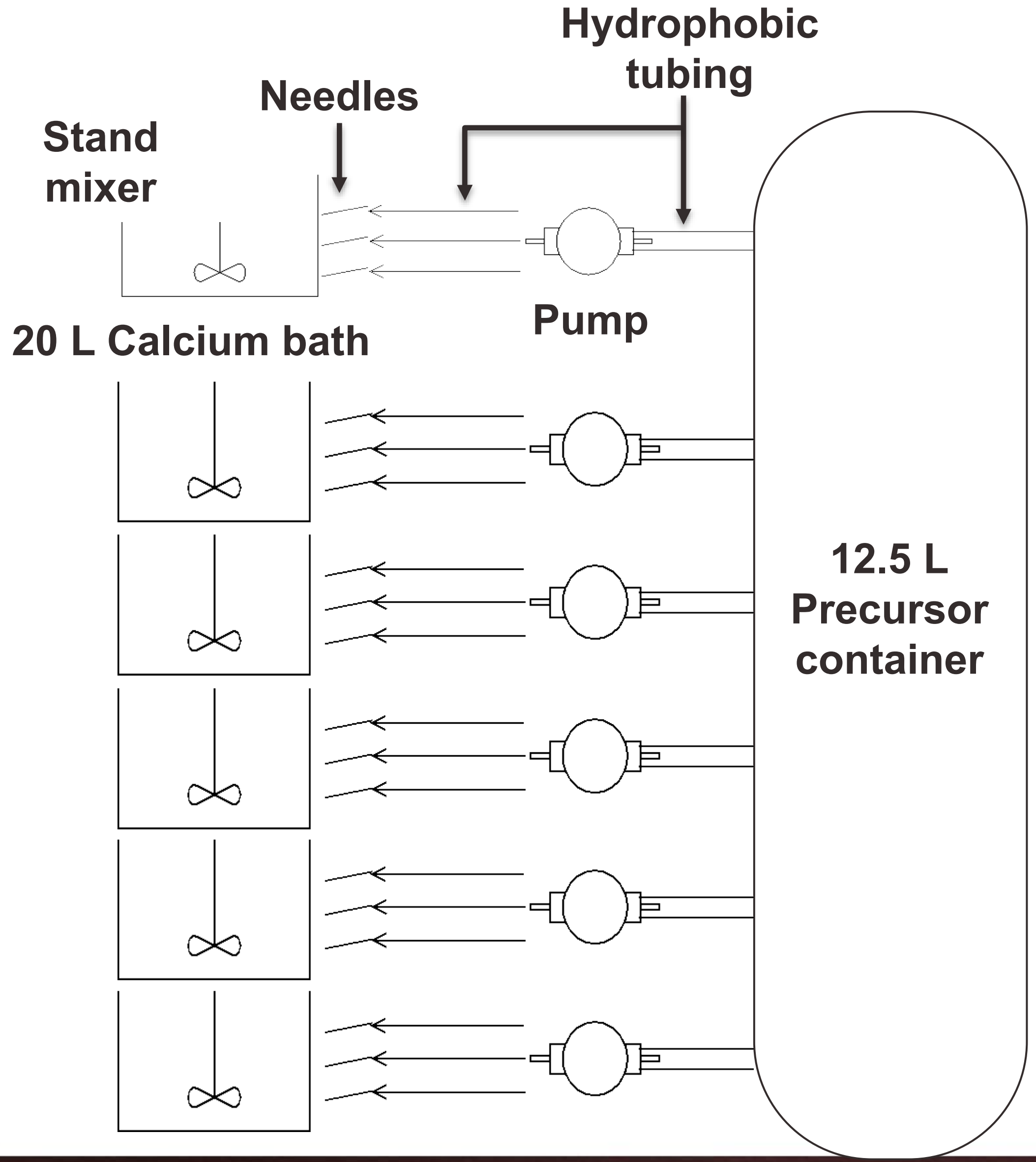
- **Task 2.2 Hydrogel advancement and cultivation integration**

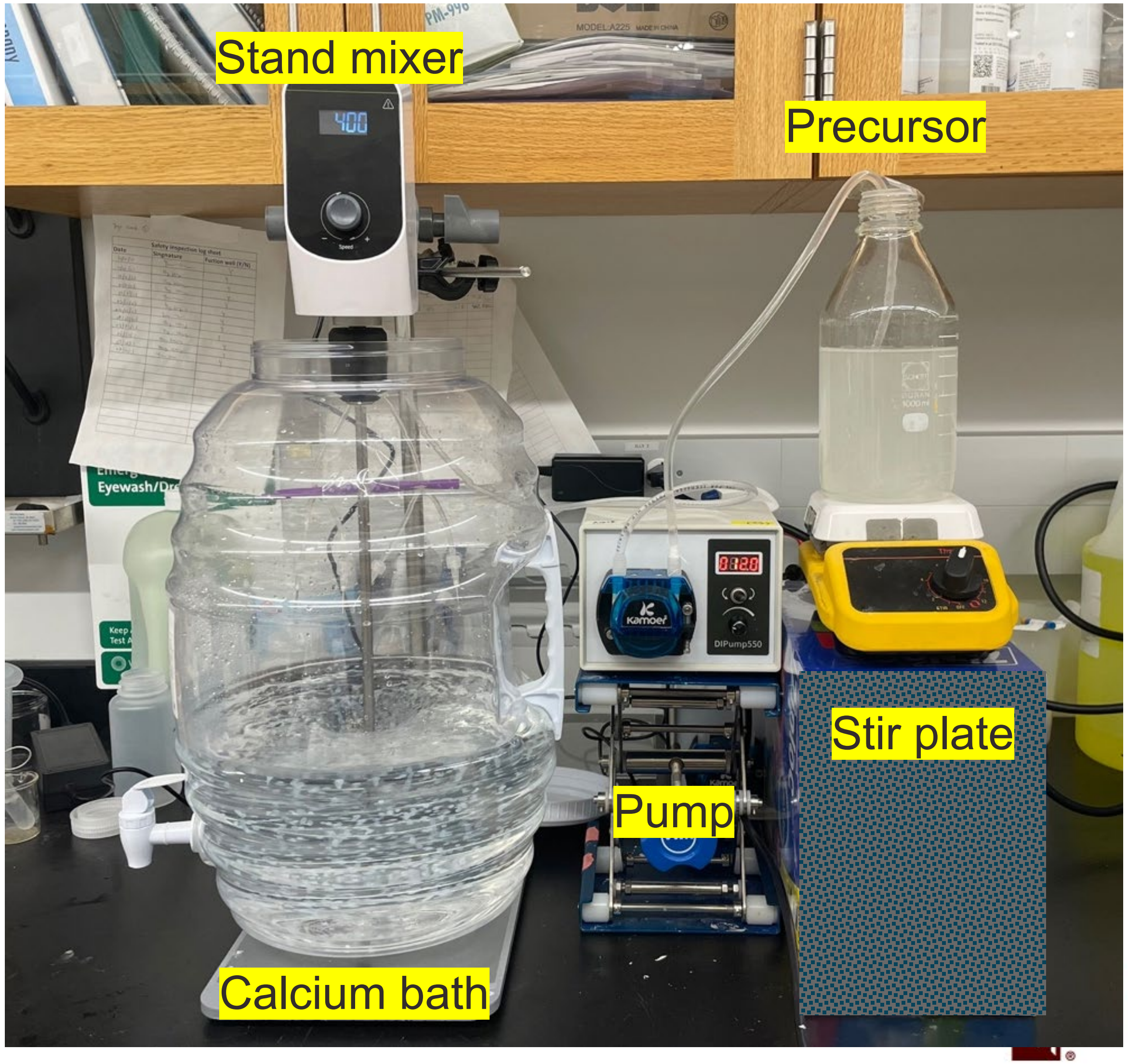
Milestone	Achieve average dry weight percent of carbonate/ P/ N-containing minerals -- mineral 40 wt.% at 50g scale by 6/30/2023→ Achieved
	Achieve average dry weight percent of carbonate/ P/ N-containing minerals -- mineral 50 wt.% at 250g scale by 9/30/2024→ In Progress (80% completion)

Mineral-hydrogel composite synthesis



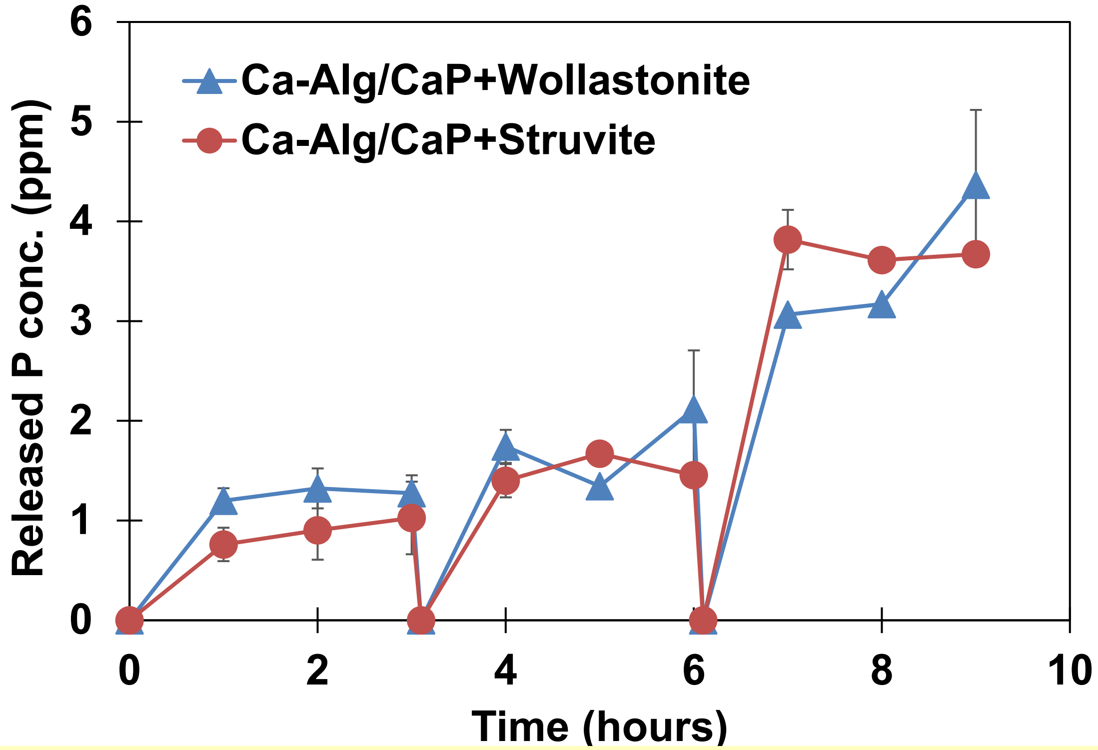
Fabrication of mineral-hydrogel composites at 250 g scale

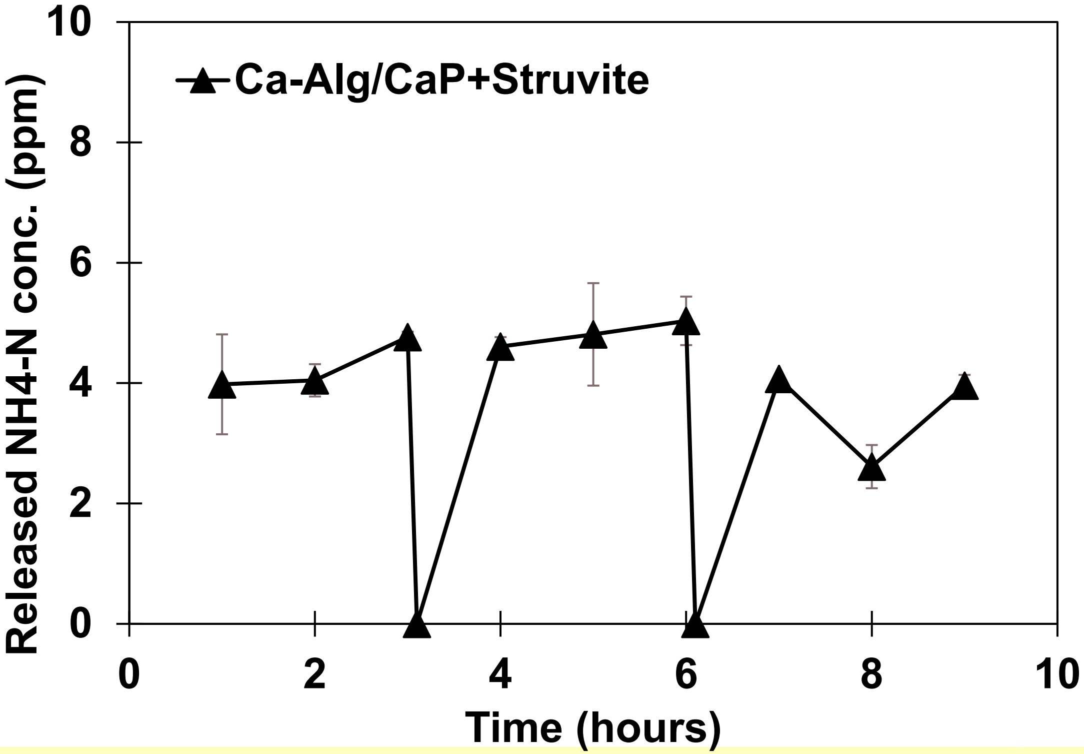




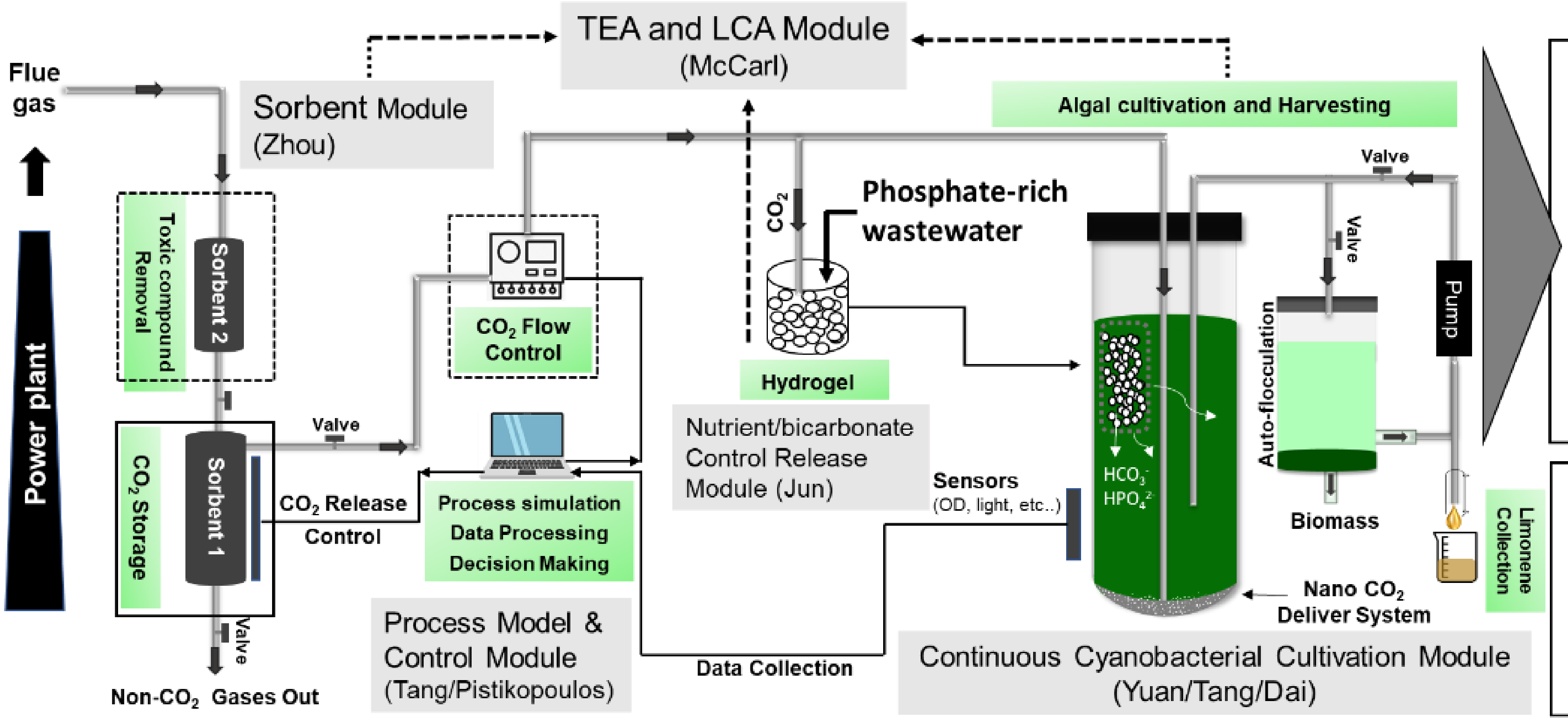
Release rates of mineral-hydrogel composites : Large scale dissolution

- Media - BG11 Media without critical elements (Ca, Mg, NH_4, PO_4)
- **Media was replaced by every 3 hours.**
- Dose - 10 % (v of hydrogel precursor/v of media)
- Total volume of media: **7.5 L (150 times increase than bench scale)**





- The P and N released concentrations lower than those at the bench scale. Thus, they required more extended time dissolution to reach a similar level of P and N in BG11.
- It can be improved by changing the hydrogel fixation system to enhance the nutrient transformation.



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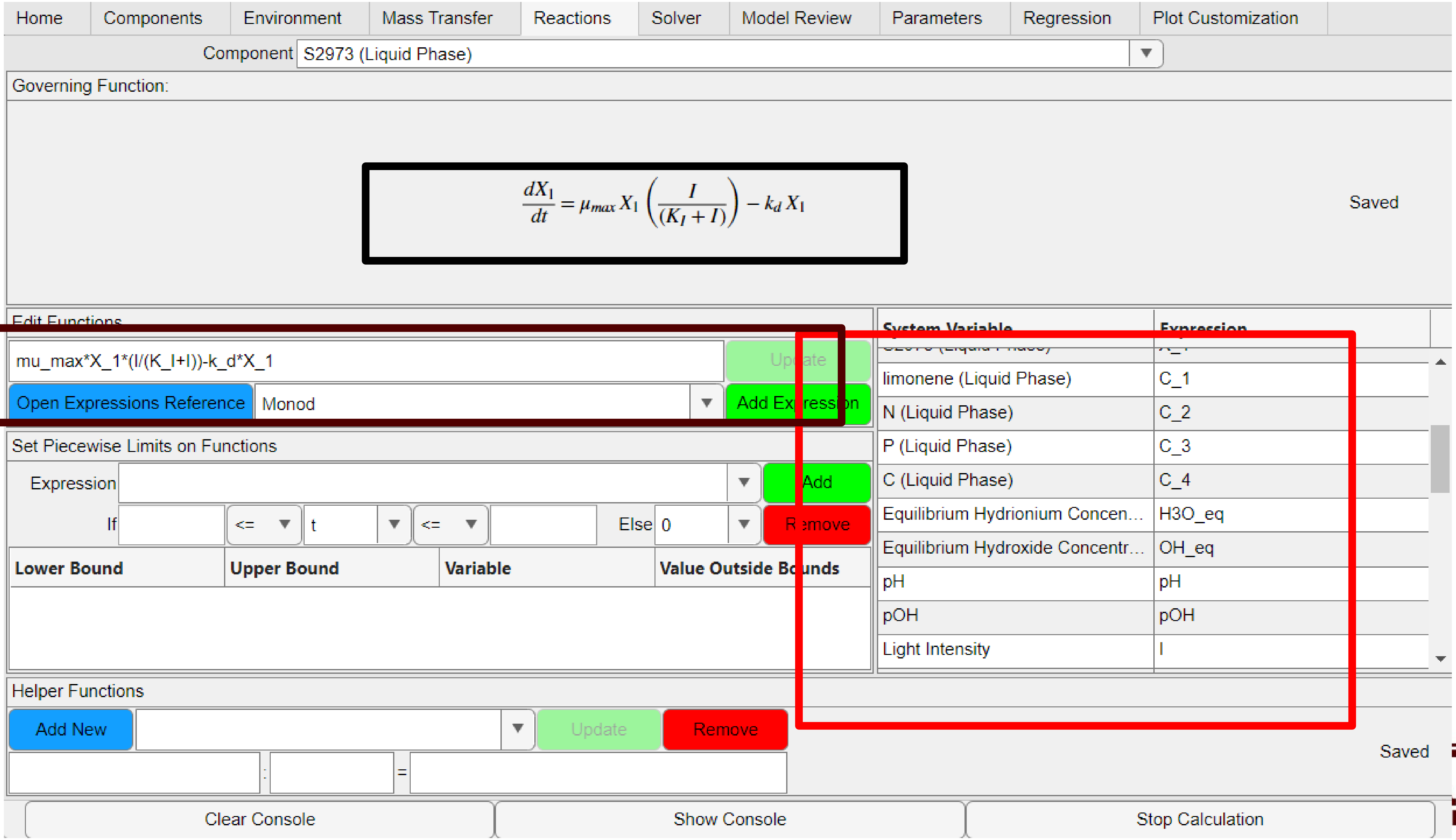
Modeling

Microbe Action and Growth Modeling Application (MAGMA)

Built with MATLAB

Simulation of bioreactors represented by ordinary differential equation (ODE) systems

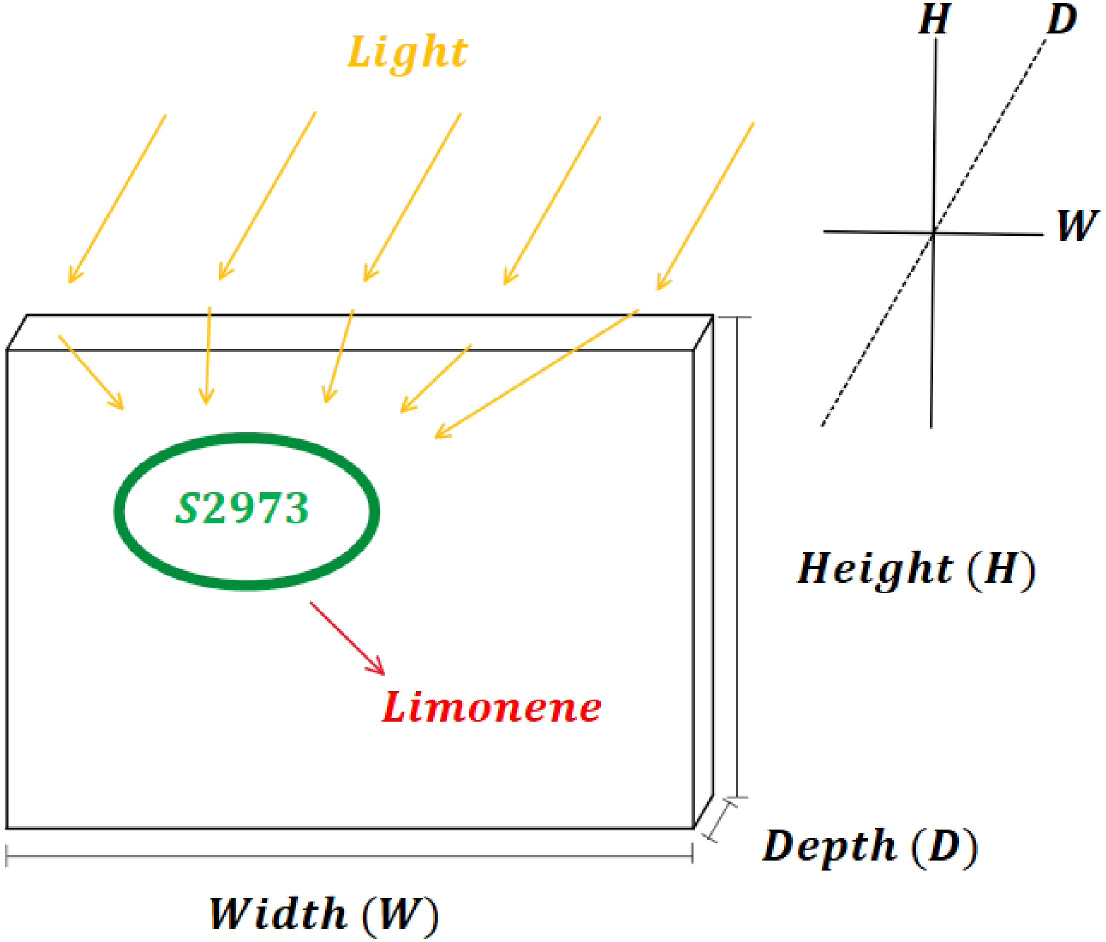
Nonlinear regression for fitting models to data


Home
Components
Environment
Mass Transfer
Reactions
Solver
Model Review
Parameters
Regression
Plot Customization
Component
S2973 (Liquid Phase)
Governing Function:
$$\frac{dX_1}{dt} = \mu_{max} X_1 \left(\frac{I}{(K_I + I)}\right) - k_d X_1$$
Saved
Edit Functions
mu_max*X_1*(I/(K_I+I))-k_d*X_1
Update
Open Expressions Reference
Monod
Add Expression
Set Piecewise Limits on Functions
Expression
Add
If
<=
t
<=
Else
0
Remove
Lower Bound
Upper Bound
Variable
Value Outside Bounds
System Variable
Expression
limonene (Liquid Phase)
C_1
N (Liquid Phase)
C_2
P (Liquid Phase)
C_3
C (Liquid Phase)
C_4
Equilibrium Hydrionium Concen…
H3O_eq
Equilibrium Hydroxide Concentr…
OH_eq
pH
pH
pOH
pOH
Light Intensity
I
Helper Functions
Add New
Update
Remove
Saved
Clear Console
Show Console
Stop Calculation

Fitting algal limonene model to experimental data

- Focus on effect of light availability on algal biomass growth
- Experimental data obtained from flat-panel PBR trials
- Assumes light is the only significantly growth-limiting substrate in experimental trials

A simplified model is fit to experimental data to obtain kinetic parameters describing the impact of light intensity on biomass growth



Average Light Intensity $[ppf]$:

$$I = \frac{\int_0^D I_0 \exp(-A \cdot l \cdot X_1)\, dl}{D}$$

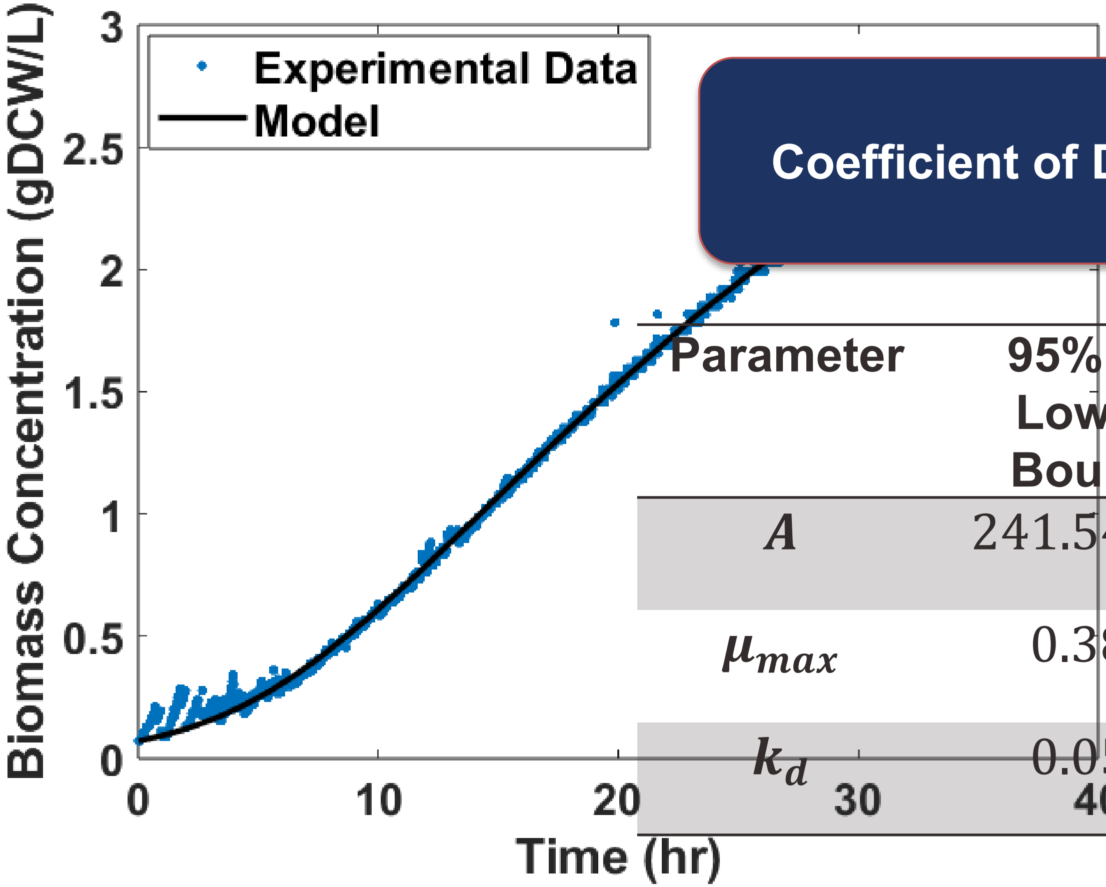
Biomass Concentration $\left[\frac{g}{L}\right]$:

$$\frac{dX_1}{dt} = \mu_{max} X_1 \cdot \left(\frac{I}{K_I + I}\right) - k_d X_1$$

Limonene Concentration $\left[\frac{g}{L}\right]$:

$$\frac{dC_1}{dt} = Y_{1_1} \mu_{max} X_1 \cdot \left(\frac{I}{K_I + I}\right)$$

Model fitting was successful, yielding 3 important kinetic parameters



Coefficient of Determination (R^2)= 0.9985

Parameter	95% CI Lower Bound	Predicted Value	95% CI Upper Bound
A	241.5404	**249.7295**	257.9187
μ_{max}	0.3835	**0.3854**	0.3873
k_d	0.0536	**0.0556**	0.0577

Further experiments can determine more kinetic parameters describing the effect of other relevant factors on biomass growth

Batch cultivation with single limiting substrate

- Impact of C, N, P nutrients on biomass growth rate
- Nutrient-to-biomass yields

Batch cultivation with light as limiting substrate

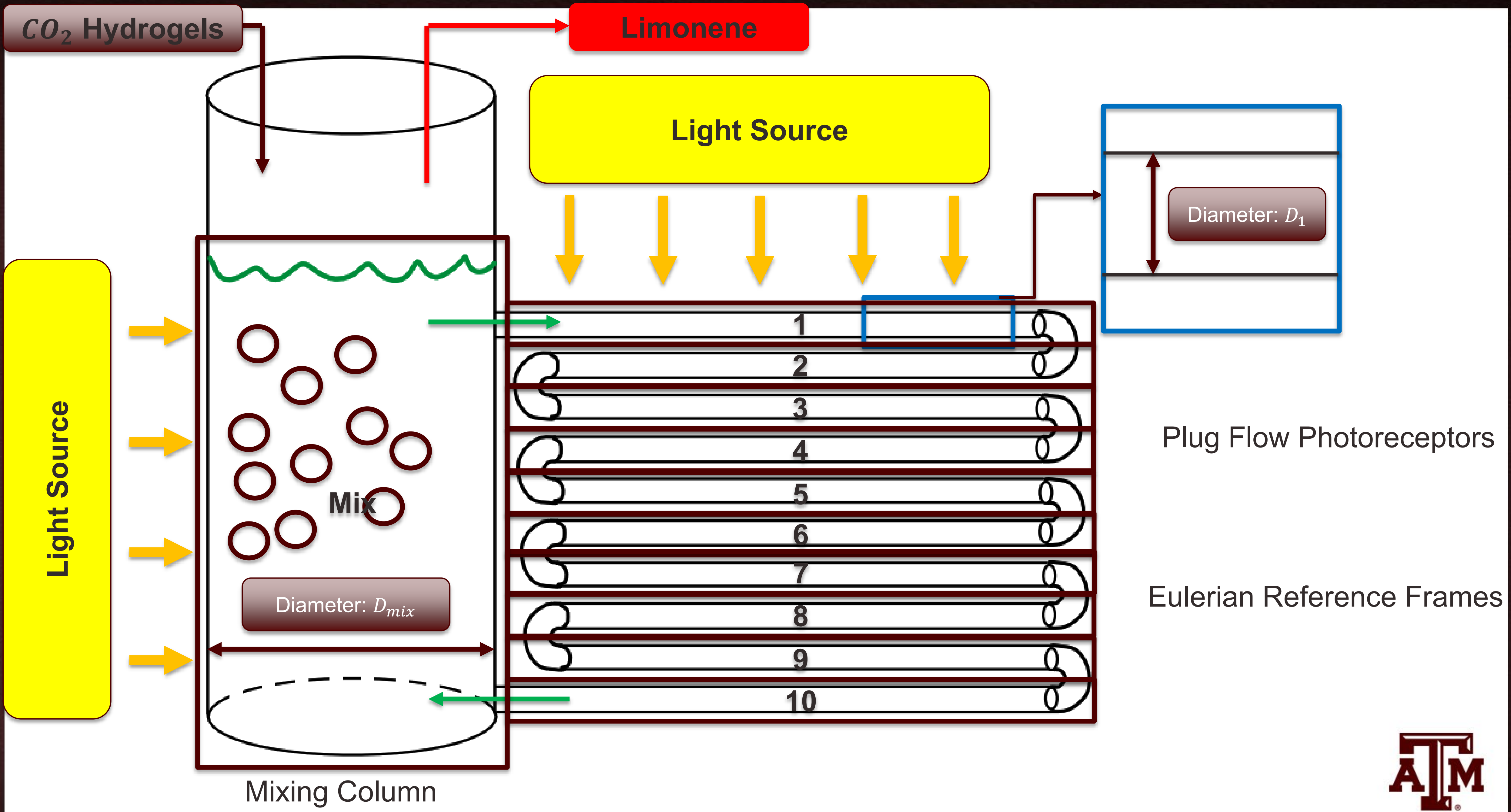
- Obtain accurate value for K_I parameter (assumed in current model)

Goal: develop model useful for photobioreactor control and bioprocess optimization

Predicting performance of photobioreactor for producing Limonene from light and CO_2 via cyanobacteria

Simulating impact of light and nutrient concentration on biomass and product formation

- Biomass light shading
- Effect of PBR geometry on light availability
- Experiment-calibrated light modeling



CO_2 Hydrogels
Limonene
Light Source
Light Source
Mix
Diameter: D_{mix}
Mixing Column
1
2
3
4
5
6
7
8
9
10
Diameter: D_1
Plug Flow Photoreceptors
Eulerian Reference Frames

Biochemical Reaction Functions for Algal PBR System

$$for\ n = mix, 1,2, \dots, 10:$$

$$Biomass: \frac{dX_n}{dt} = \mu_{max} X_n \left(\frac{N_n}{N_n + K_N}\right)\left(\frac{P_n}{P_n + K_P}\right)\left(\frac{CO_{2,n}}{CO_{2,n} + K_{CO_2}}\right)\left(\frac{I_n}{I_n + K_I}\right) - k_d X_n$$

$$CO_2: \frac{dCO_{2n}}{dt} = -Y_{CO_2} \mu_{max} X_n \left(\frac{N_n}{N_n + K_N}\right)\left(\frac{P_n}{P_n + K_P}\right)\left(\frac{CO_{2,n}}{CO_{2,n} + K_{CO_2}}\right)\left(\frac{I_n}{I_n + K_I}\right)$$

$$\boldsymbol{\frac{dCO_{2,mix}}{dt} = 0}$$

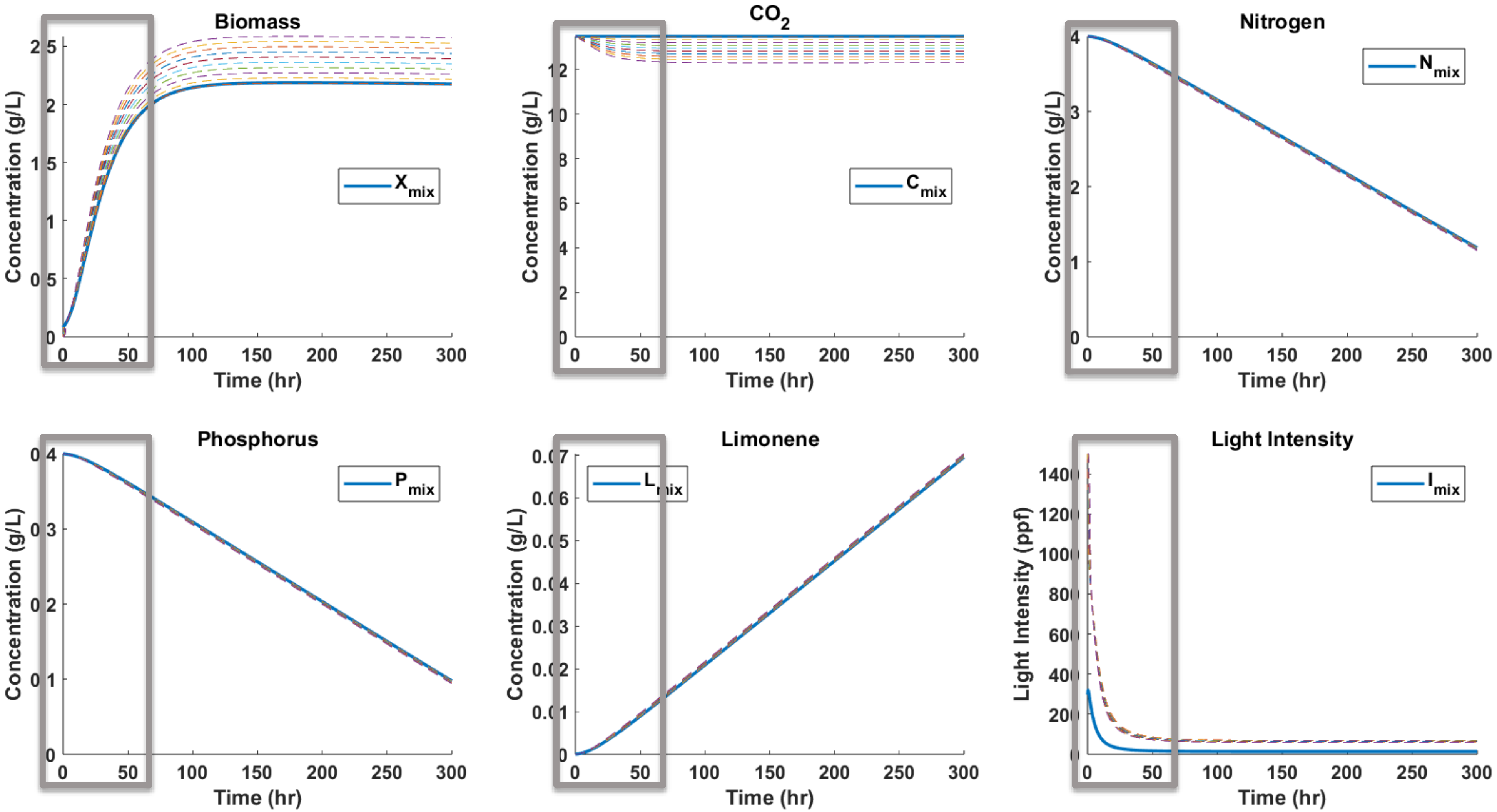
$$Nitrogen: \frac{dN_n}{dt} = -Y_N \mu_{max} X_n \left(\frac{N_n}{N_n + K_N}\right)\left(\frac{P_n}{P_n + K_P}\right)\left(\frac{CO_{2,n}}{CO_{2,n} + K_{CO_2}}\right)\left(\frac{I_n}{I_n + K_I}\right)$$

$$Phosphorus: \frac{dP_n}{dt} = -Y_P \mu_{max} X_n \left(\frac{N_n}{N_n + K_N}\right)\left(\frac{P_n}{P_n + K_P}\right)\left(\frac{CO_{2,n}}{CO_{2,n} + K_{CO_2}}\right)\left(\frac{I_n}{I_n + K_I}\right)$$

$$Light: I_n = \frac{\int_0^{D_n} \int_0^{\sqrt{D_n^2 - w^2}} I_0 \exp(-A \cdot (w \cdot X_n))\, dh\, dw}{\pi \left(\frac{D_n}{2}\right)^2}$$

Calculates the average light intensity in each Eulerian reference frame

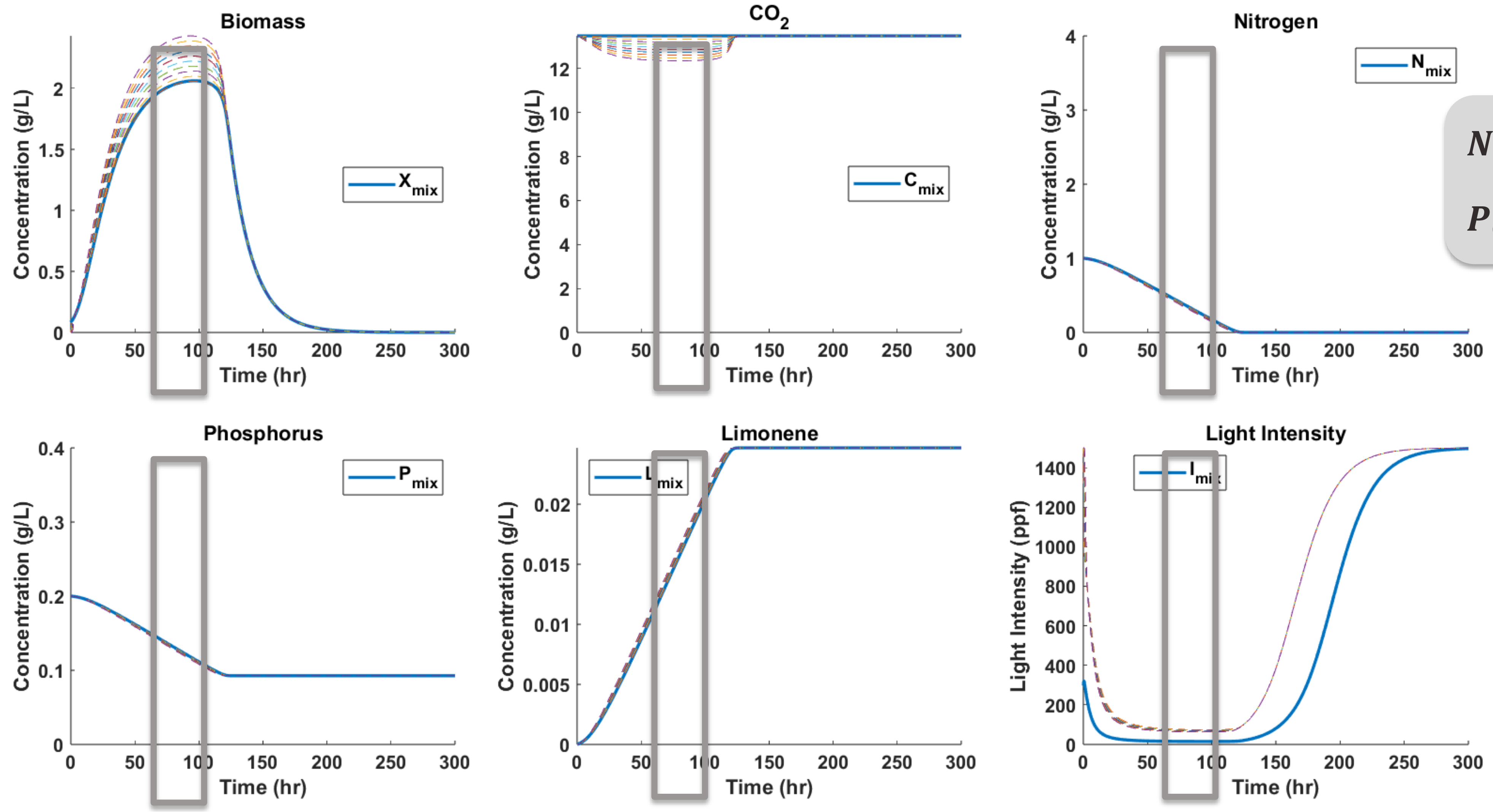
Growth Limited By Light Resources



$$N_0 = 4\frac{g}{L}$$

$$P_0 = 0.4\frac{g}{L}$$

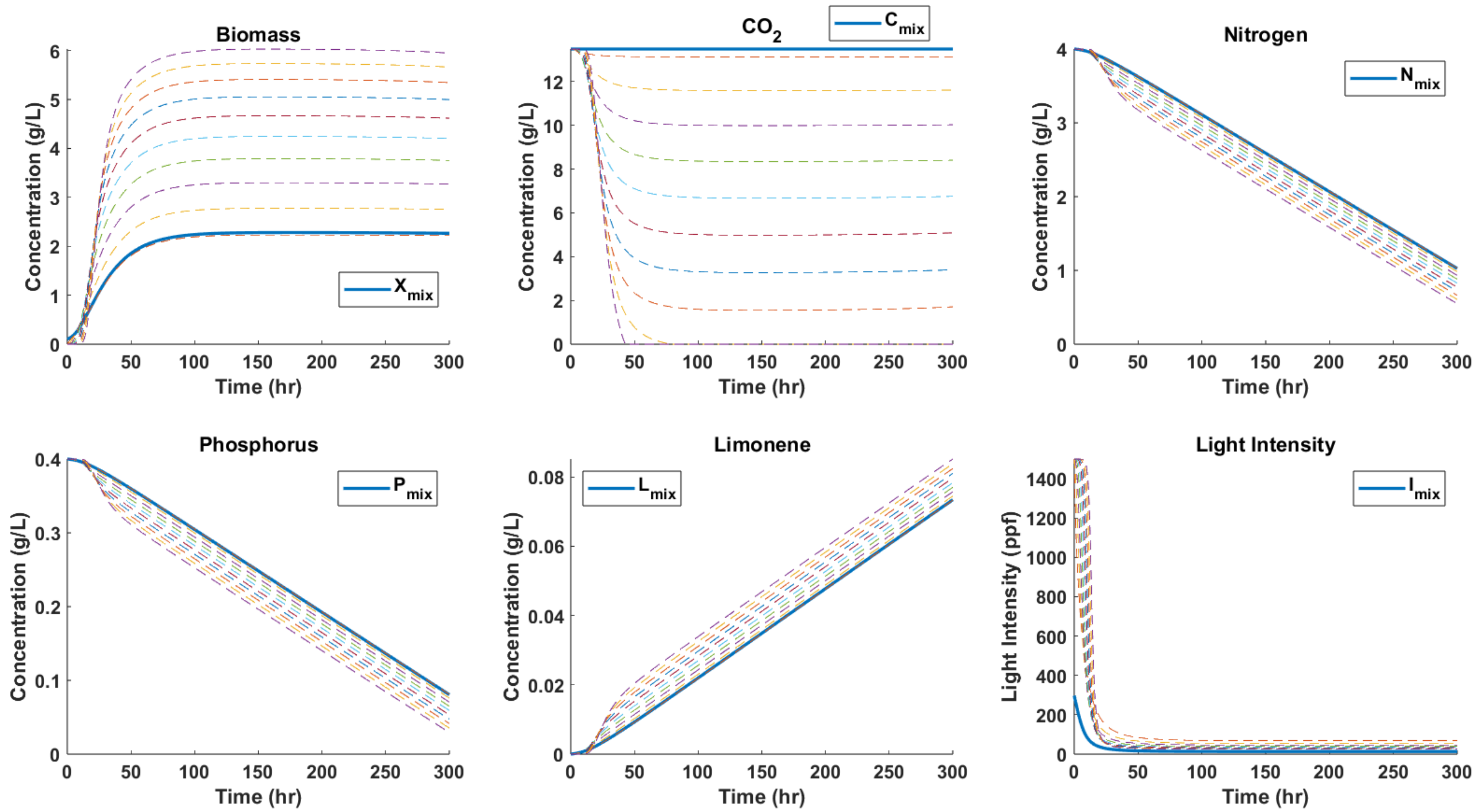
Growth Limited By Nutrient Resources



$$N_0 = 1\frac{g}{L}$$

$$P_0 = 0.2\frac{g}{L}$$

Slower PFR Flowrate (Nutrient Limitation Case)



$$dV_o = 5\,\frac{L}{hr}$$
$(10\%\ of\ original)$

Lessons Learned

- Scale up: what you can plan and what you cannot
  1. Cultivation scale-up
  2. Sorbent synthesis
  3. Hydrogel synthesis

- Modeling can be very helpful for scale up

- CO2 concentration

Future Plans

- Scale-up: 20-liter and 100-liter cultivation/sorbent and hydrogel synthesis and testing
- Work with NCCC for on-site CO2 conversion
- System integration

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- Questions?