# USEA CONSENSUS Program Briefing: *Pore Structure Alteration of Organic-Rich Shale with Sc-$CO_2$ Exposure*

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## INTRODUCTION

## THE BAKKEN

## METHODS

## RESULTS

## DISCUSSION

## CONCLUSION

## APPRECIATION

## QUESTIONS

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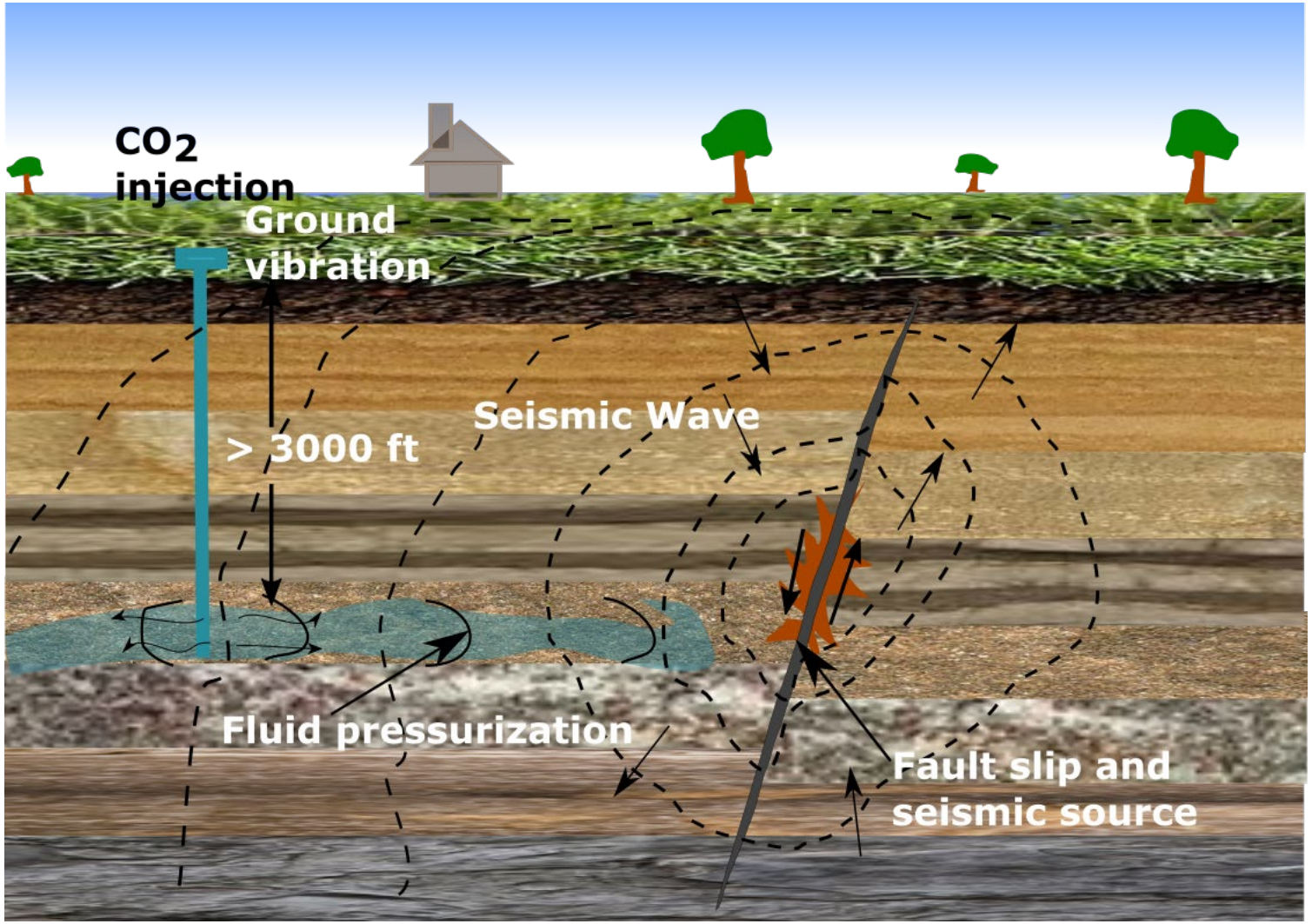
# INTRODUCTION

# Introduction

- The use of fossil fuel in the past century has drastically increased $CO_2$ emission into the atmosphere.
- Approximately two−thirds of proven fossil fuel reserves need to remain un−extracted and CCS technology deployed for the world to achieve the 2 ºC goal by 2050

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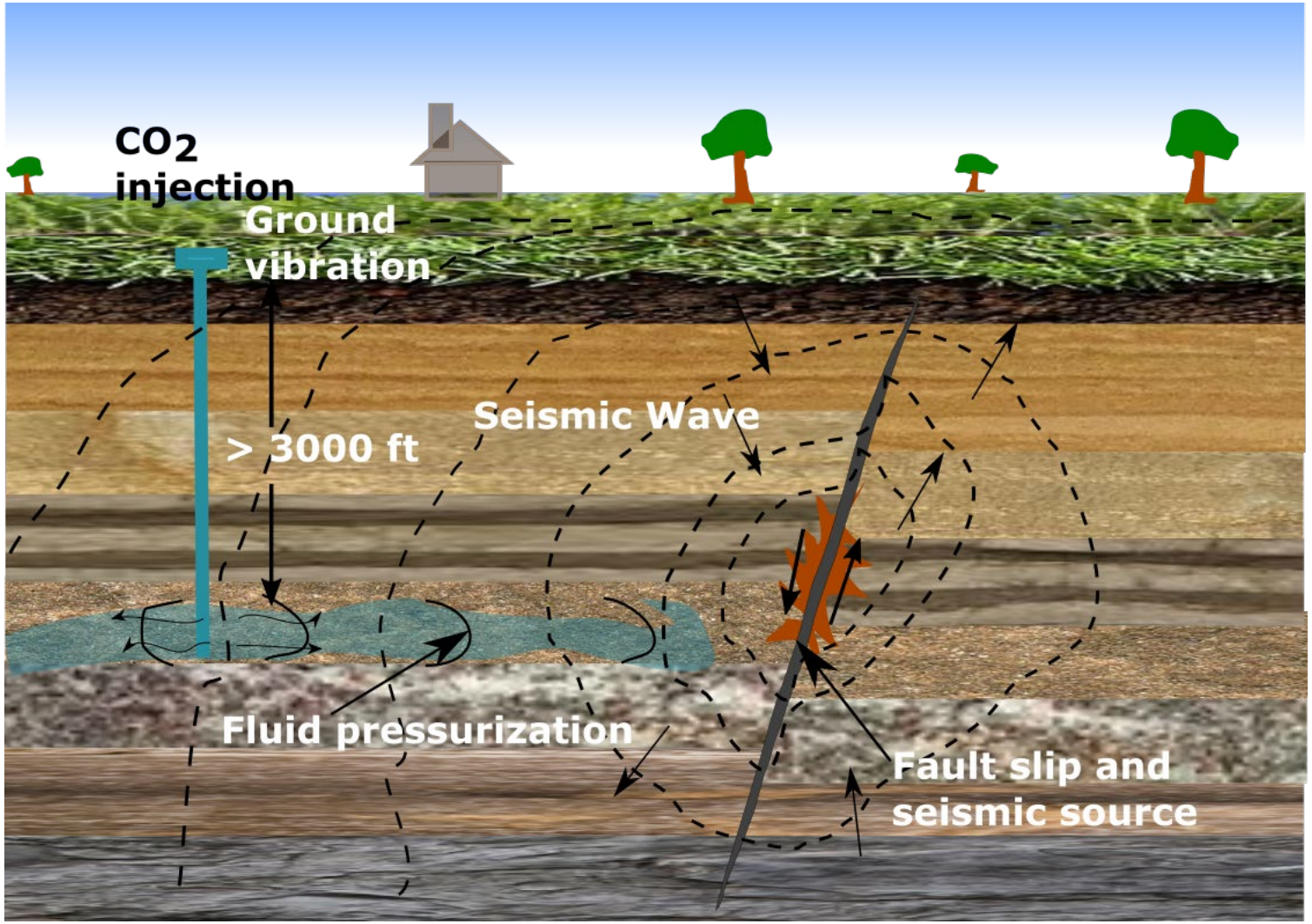
# Introduction

- $CO_2$ EOR and CCS are processes that get rocks exposed to $CO_2$
- When $CO_2$ is injected into the shale layers:
- It dissolves and changes the acid−base equilibrium that triggers the dissolution and precipitation of minerals
- As a result of dissolution, flow channels can be formed in the rock, which will eventually alter the intrinsic permeability and porosity of the rock.

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# Why Gas Adsorption

# Pore structure characterization of shale

- Pore structure evaluation
  - Gas adsorption ($N_2$ and $CO_2$)
  - mercury intrusion porosimetry (MIP)
  - small angle neutron scattering (SANS),
  - ultra-small angle neutron scattering (USANS
  - nuclear magnetic resonance (NMR)
- Direct observation methods:
  - field emission scanning electron microscopy (FE-SEM)
  - atomic force microscopy (AFM)
  - microfocus X-ray computed tomography (u-CT)
  - transmission electron microscopy (TEM).

# Pore structure characterization of shale

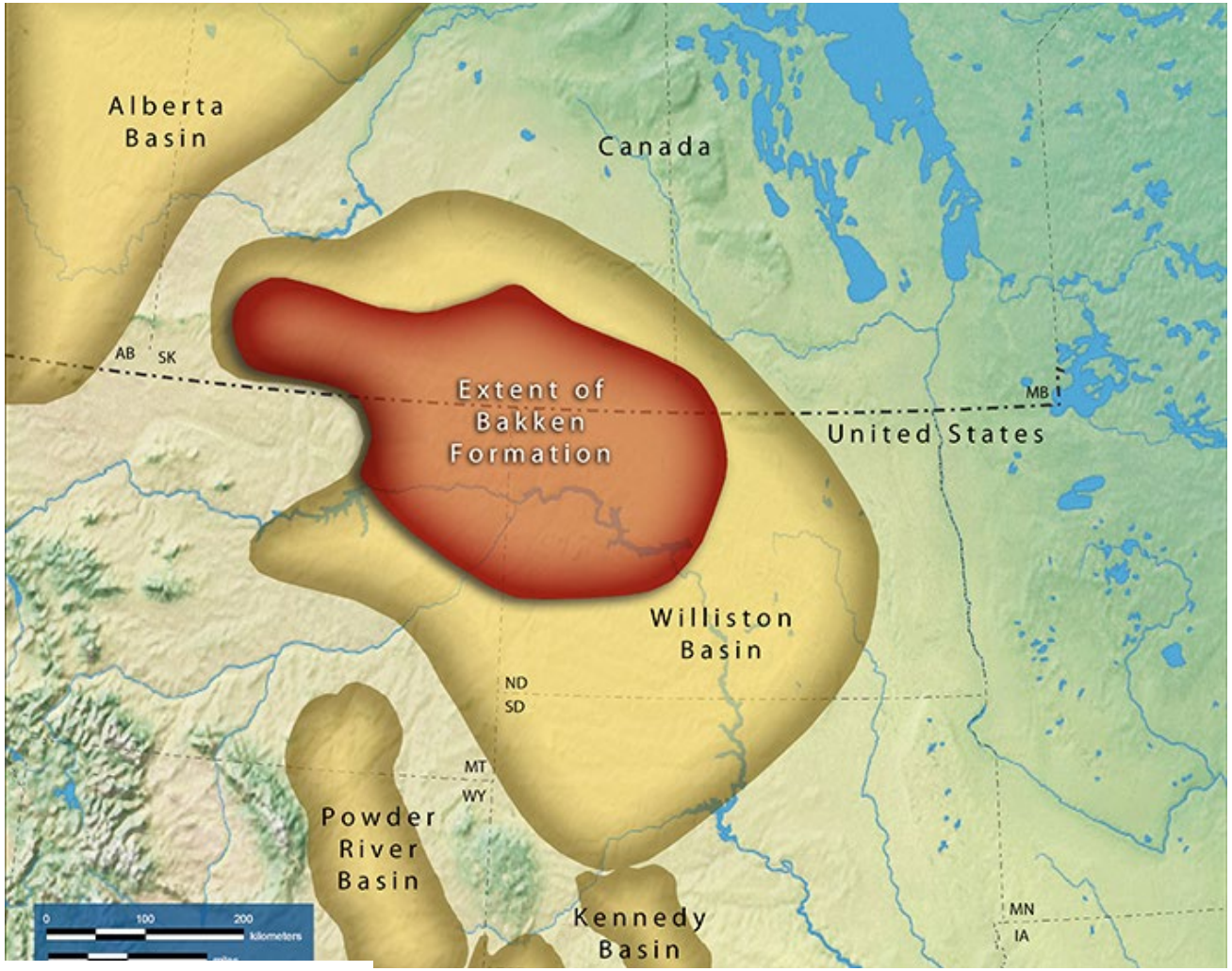
- Gas adsorption ($N_2$ and $CO_2$)
  - Obtain an entire spectrum  of pore size distribution (PSD) from submicron to the macroscale
  - Physisorption isotherm type: I(a), I(b), II, III, IV(a), IV(b), V and VI
  - Hysteresis loop pore shape categories used to determine the morphology of the pore structure: H1, H2(a), H2(b), H3, H4 and H5

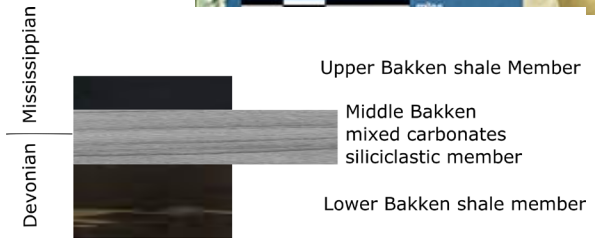
Thommes, et al (2015). Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report). *Pure and applied chemistry*, *87*(9-10), 1051-1069.

# THE BAKKEN

# The Bakken

- Major unconventional play in the Williston Basin
- Consist of the upper, middle and lower members
- Upper and lower  member are dark marine shale with organic content (source and seal rock in the Bakken)
- Middle member is a middle fine−grained combination of clastic and carbonates
- Heterogenous and anisotropic




https://undeerc.org/bakken/bakkenformation.aspx

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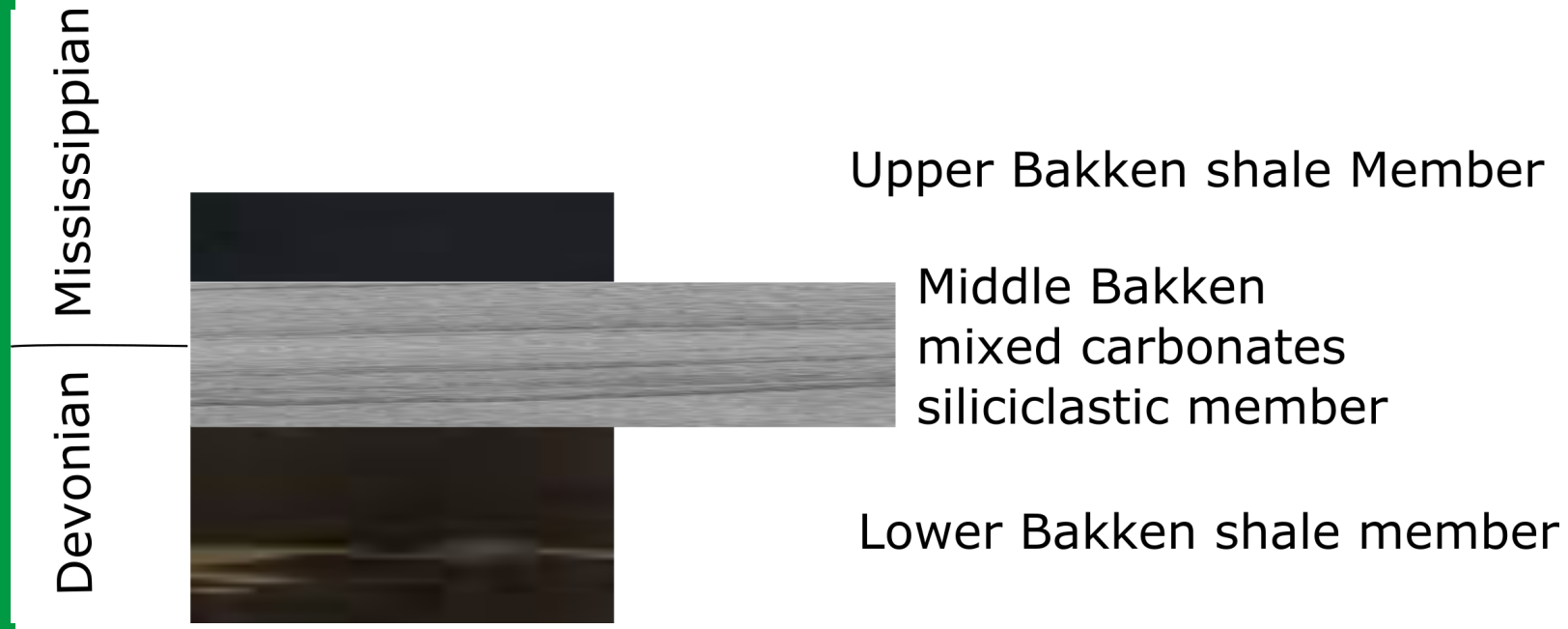


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# METHODS

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# Mineralogical Analysis and TOC

## X−Ray Diffraction (XRD)

- Measure the mineral composition
- Quantify minerals present

- Sampling
  - Upper Bakken: UB−0, UB−3, UB−8, UB−16, UB−30, and UB−60
  - Lower Bakken: LB−0, LB−3, LB−8, LB−16, LB−30, and LB−60

## Total Organic Carbon (TOC)

- Measure TOC content
- Determine the kerogen type
- Determine maturation stage.

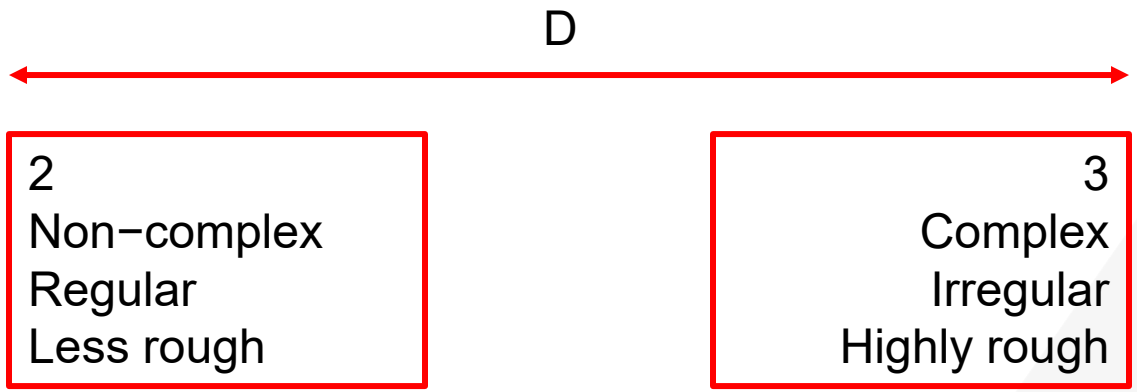
# Gas Adsorption

## Nitrogen ($N_2$) Adsorption

- Determine
  - Pore structure distribution
  - Pore size
  - Pore diameter
  - Pore volume
  - Surface area

## Fractal Analysis

- Characterize the properties of complex structure
- Using Frenkel−Halsey-Hill (FHH)

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# RESULTS

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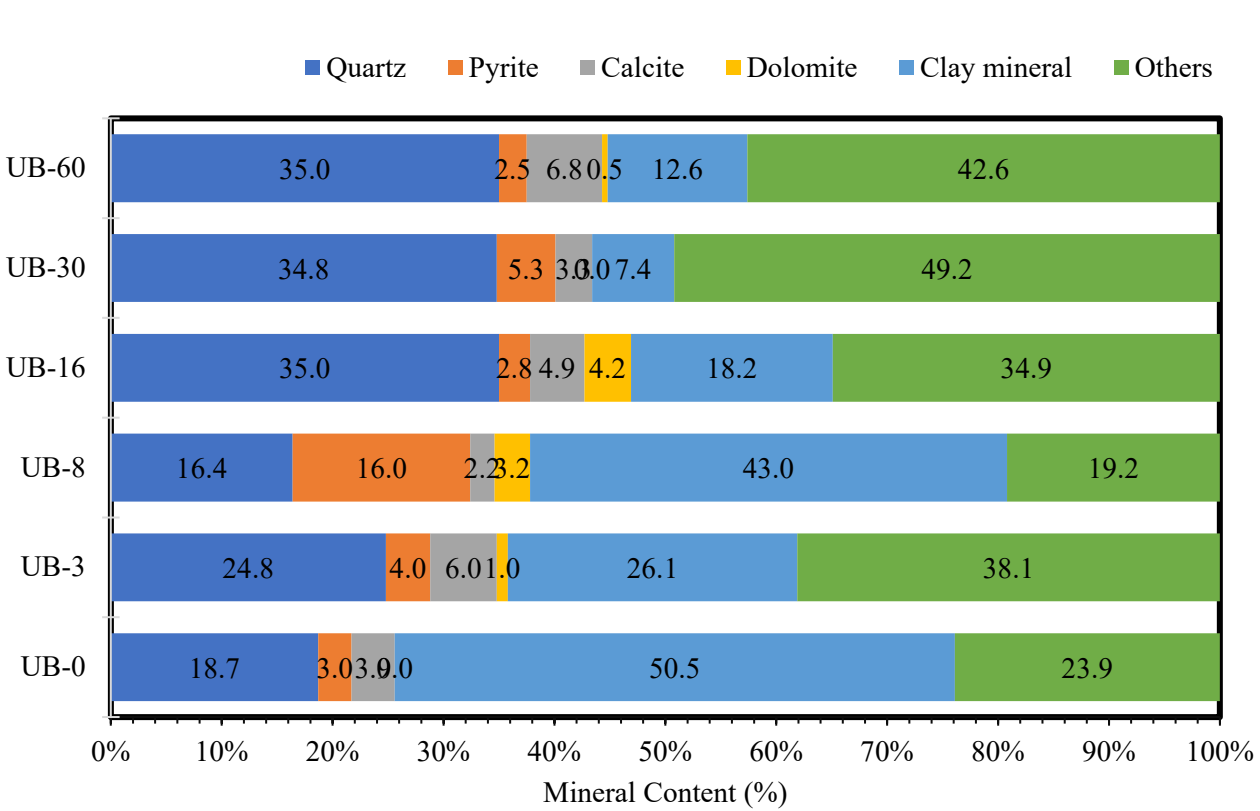
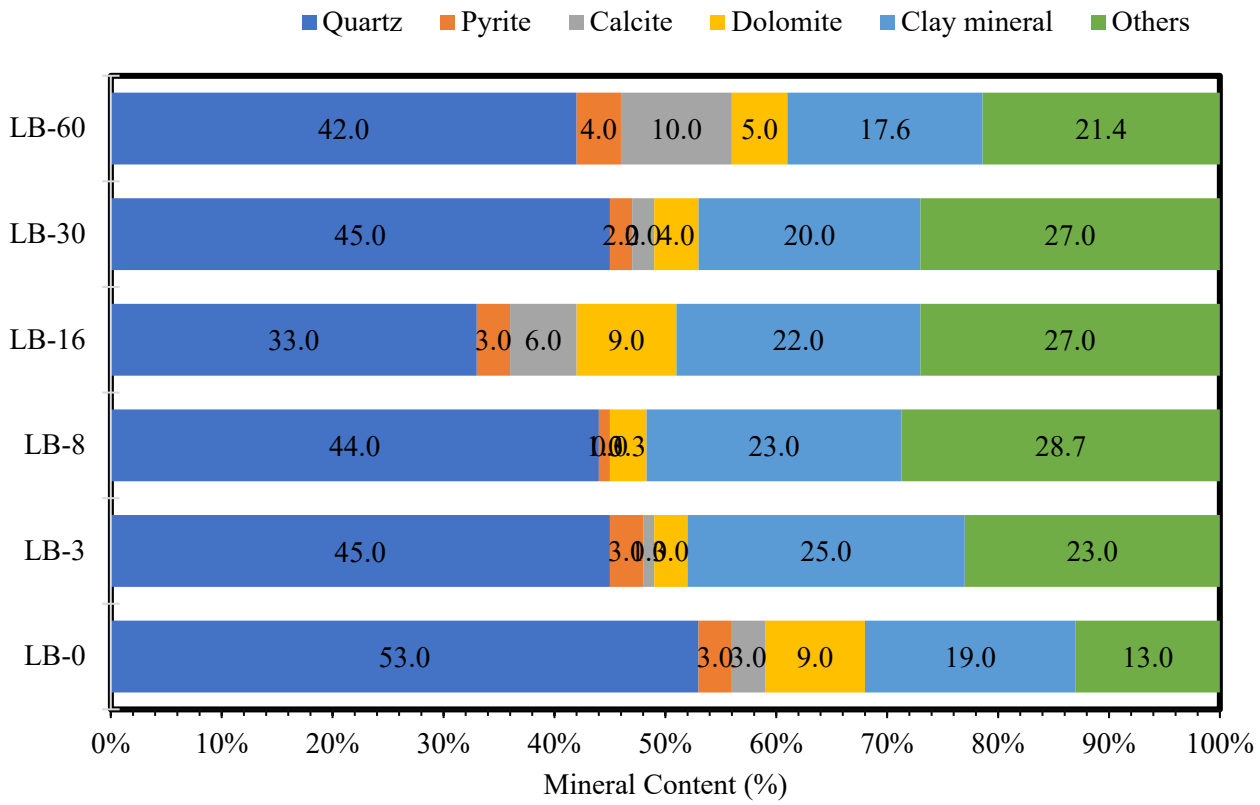
# Mineralogy

| $CO_2$ Exposure days | Name | Quartz | Pyrite | Calcite | Dolomite | Clay Minerals$^{\perp}$ | Others | TOC% | $T_{max}$°C |
|---|---|---|---|---|---|---|---|---|---|
| 0 day | UB-0 | 18.7 | 3.0 | 3.9 | 0.0 | 50.5 | 23.9 | 13.3 | 449.0 |
| 0 day | LB-0 | 53.0 | 3.0 | 3.0 | 9.0 | 19.0 | 13.0 | 14.4 | 448.0 |

$^{\perp}$Clay minerals: illite + kaolinite+chlorite

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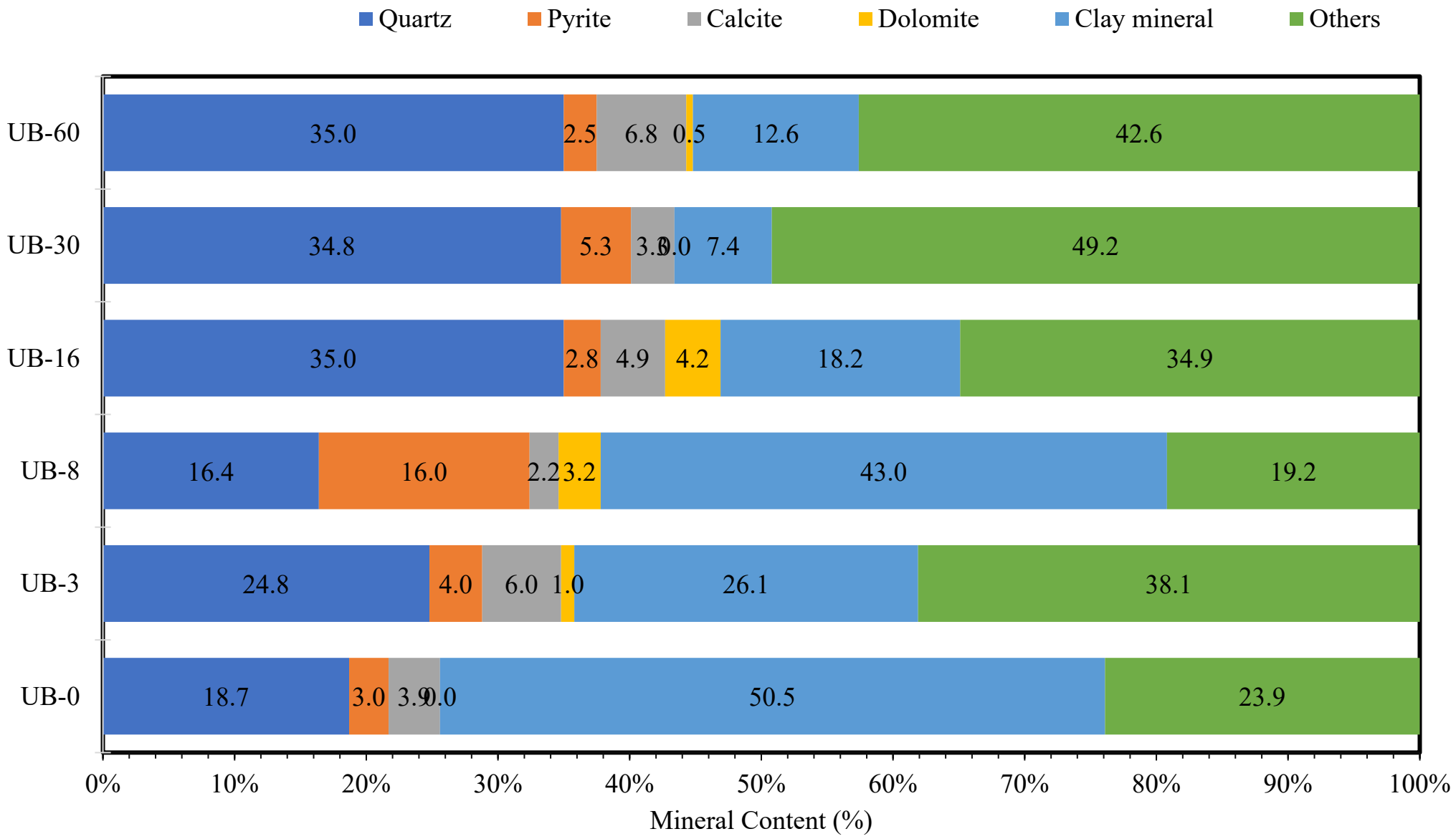


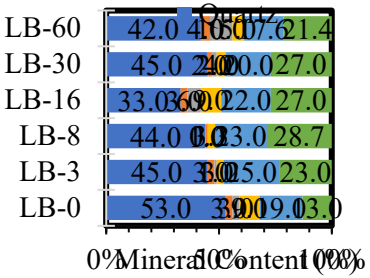


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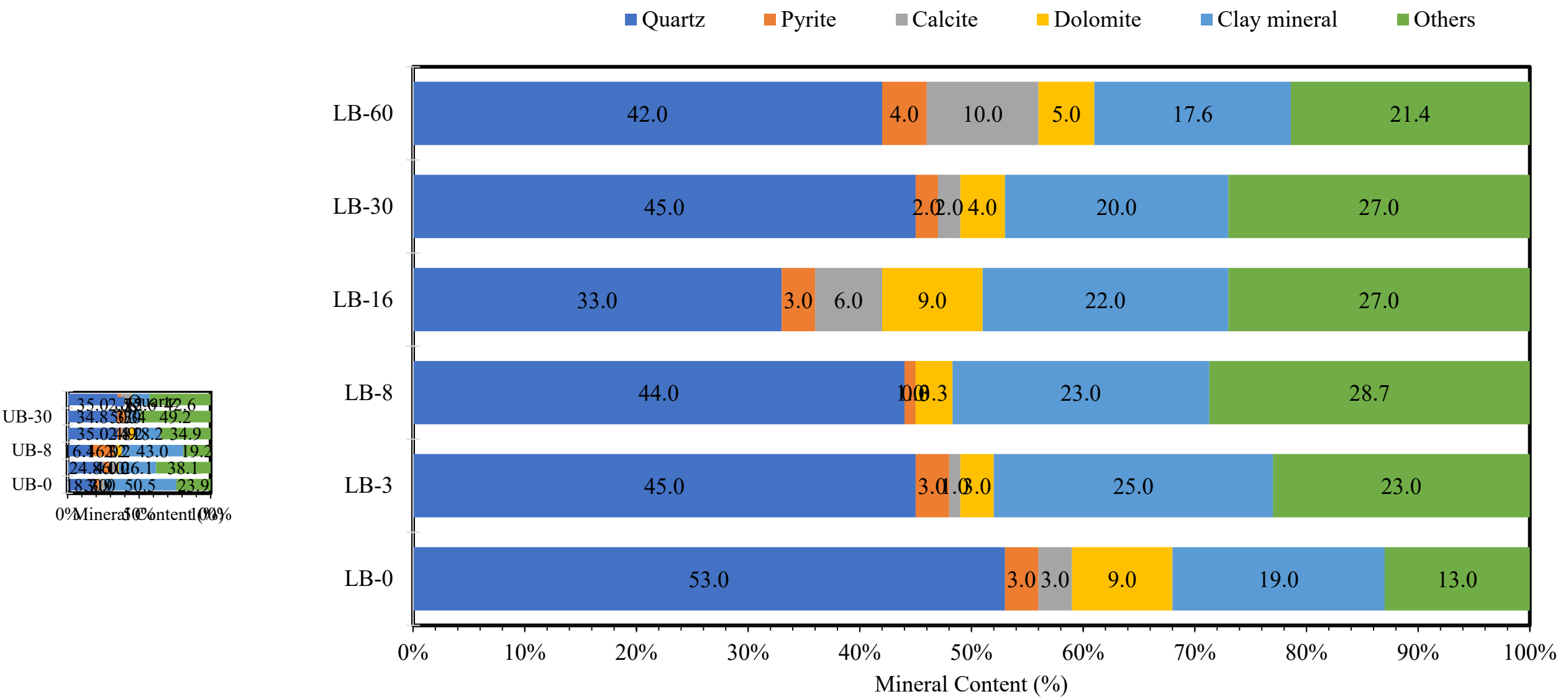


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# Dissolution and precipitation of minerals

$$H_2O + CO_2 \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^- \quad (1)$$

$$CaCO_{3(Calcite)} + 2H^+ \leftrightarrow Ca^{2+} + CO_2 + H_2O \quad (2)$$

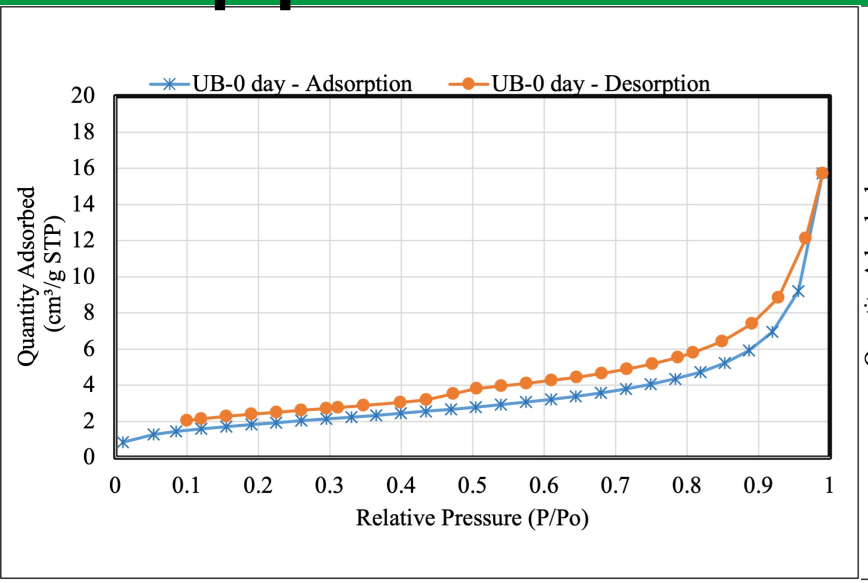
$$CaMg(CO_3)_{2\ (Dolomite)} + 4H^+ \rightarrow Ca^{2+} + Mg^{2+} + 2CO_2 + 2H_2O \quad (3)$$

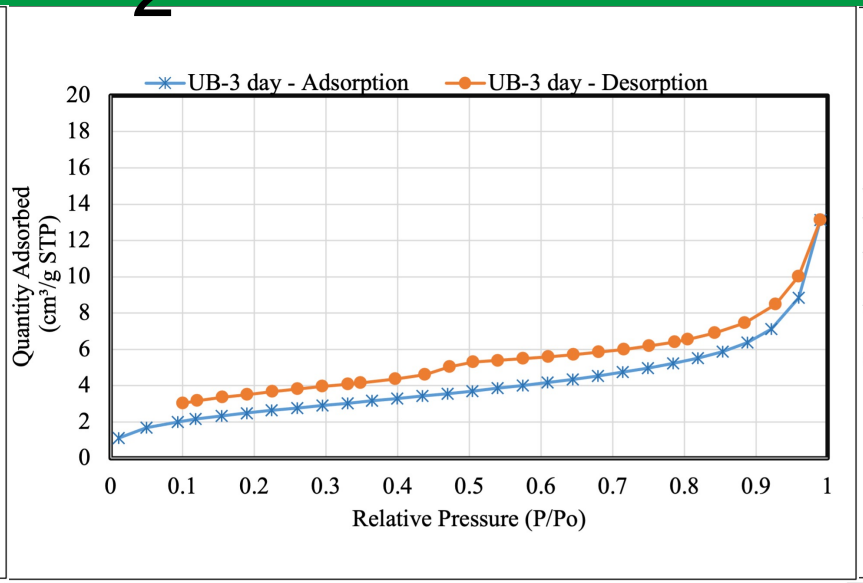
$$Illite + 8H^+ \leftrightarrow 0.6\ K^+ + 2.3Al^{3+} + 0.25Mg^+ + 3.5SiO_2 + 5H_2O \quad (4)$$

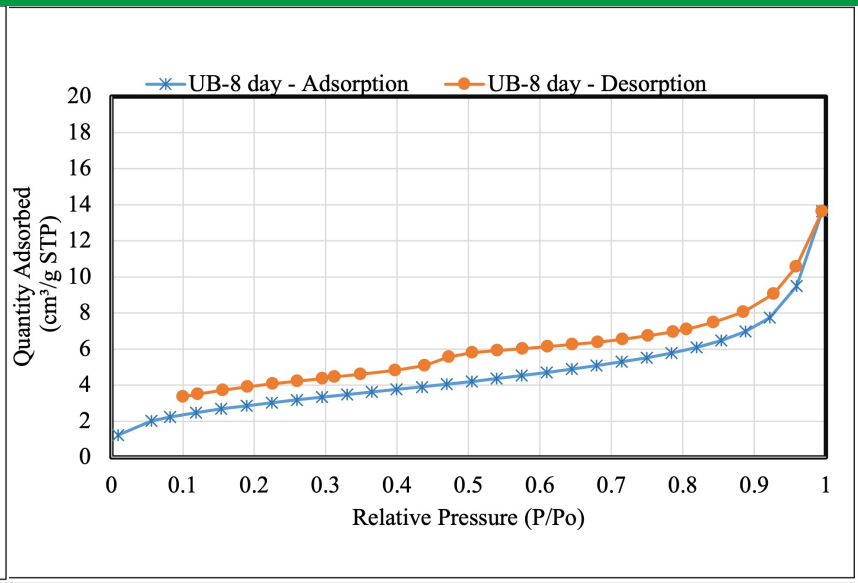
$$Chlorite + 16H^+ \leftrightarrow 5Fe^{2+} + 2.3Al^{3+} + 3SiO_2 + 12H_2O \quad (5)$$

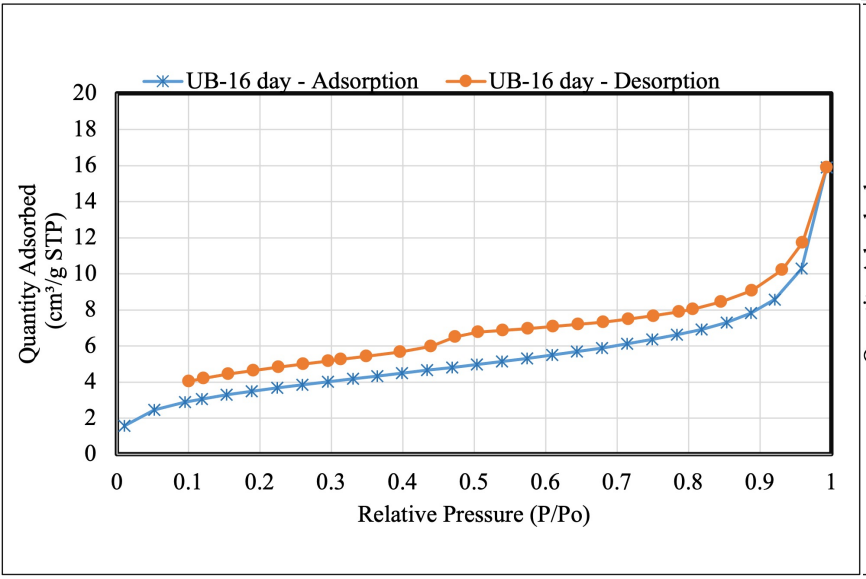
$$Quartz + 4H^+ \leftrightarrow Si^{4+} + H_2O \quad (6)$$

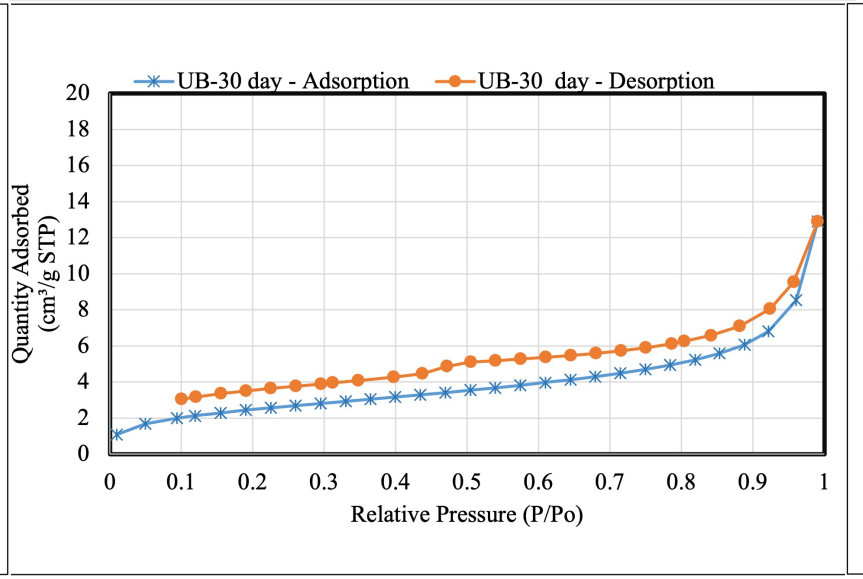
# Upper Bakken $N_2$ Isotherm

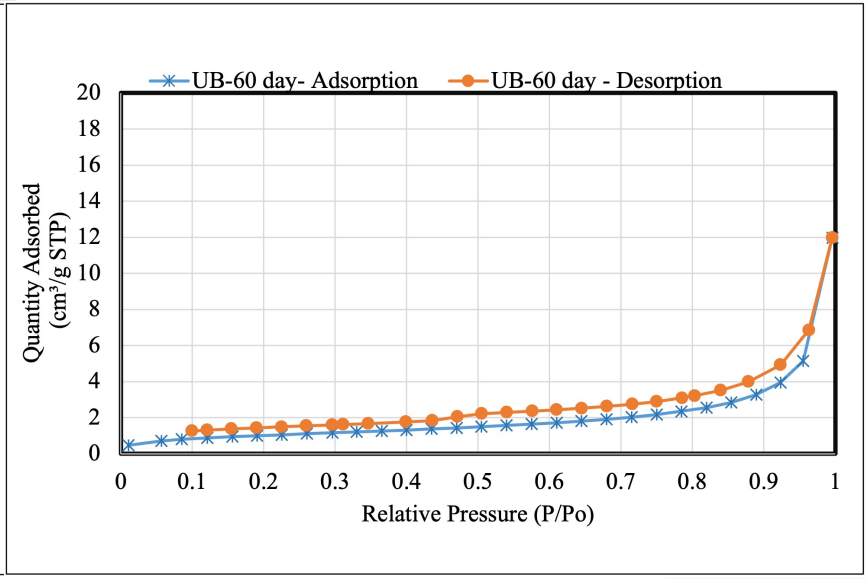
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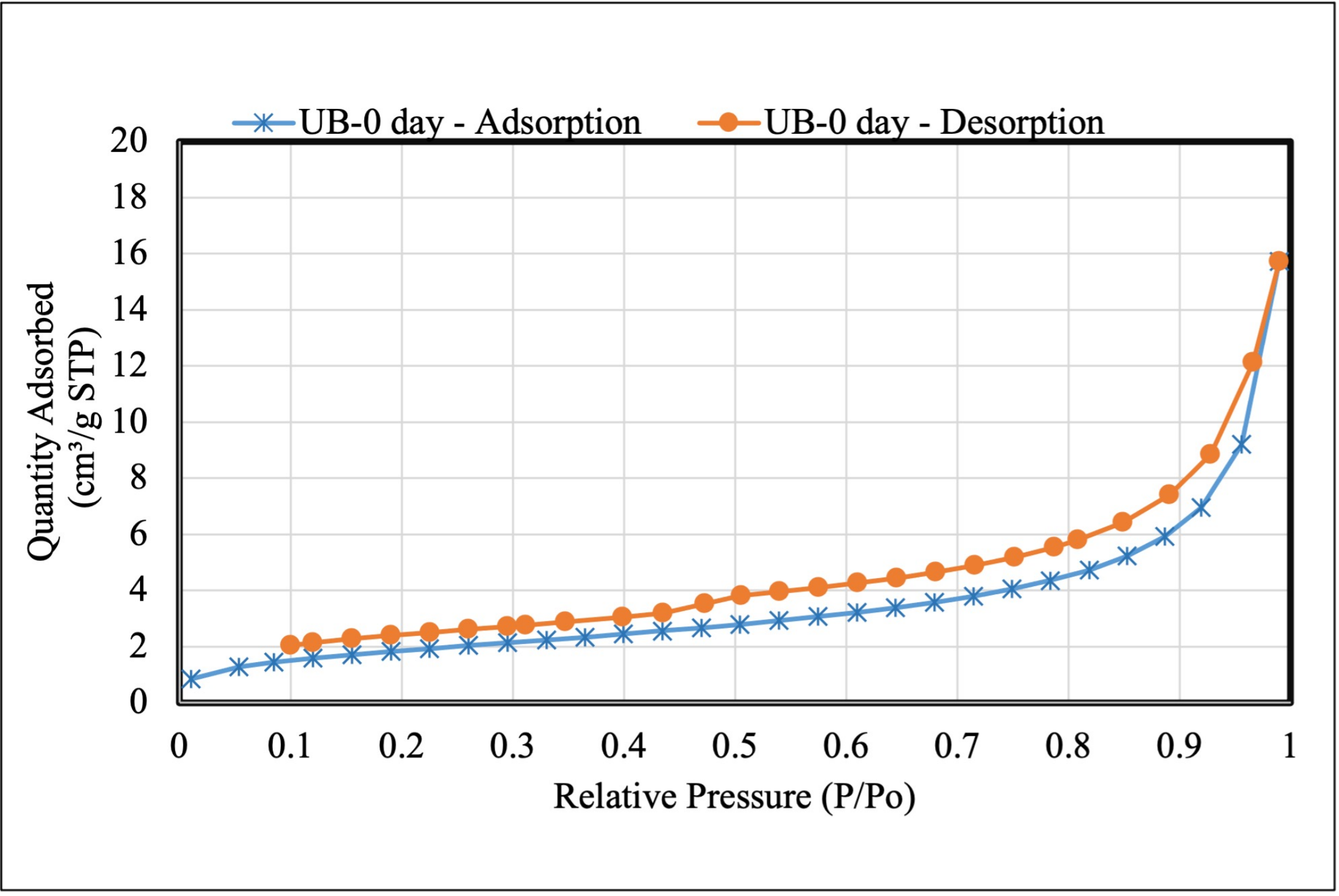


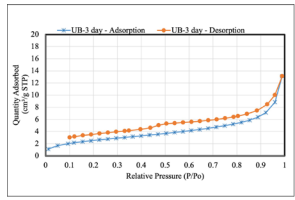


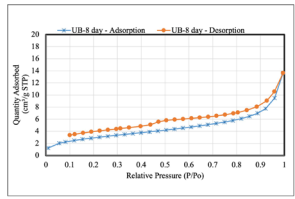


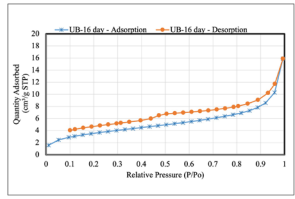


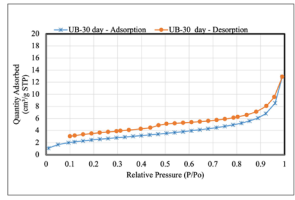


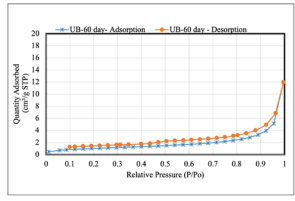


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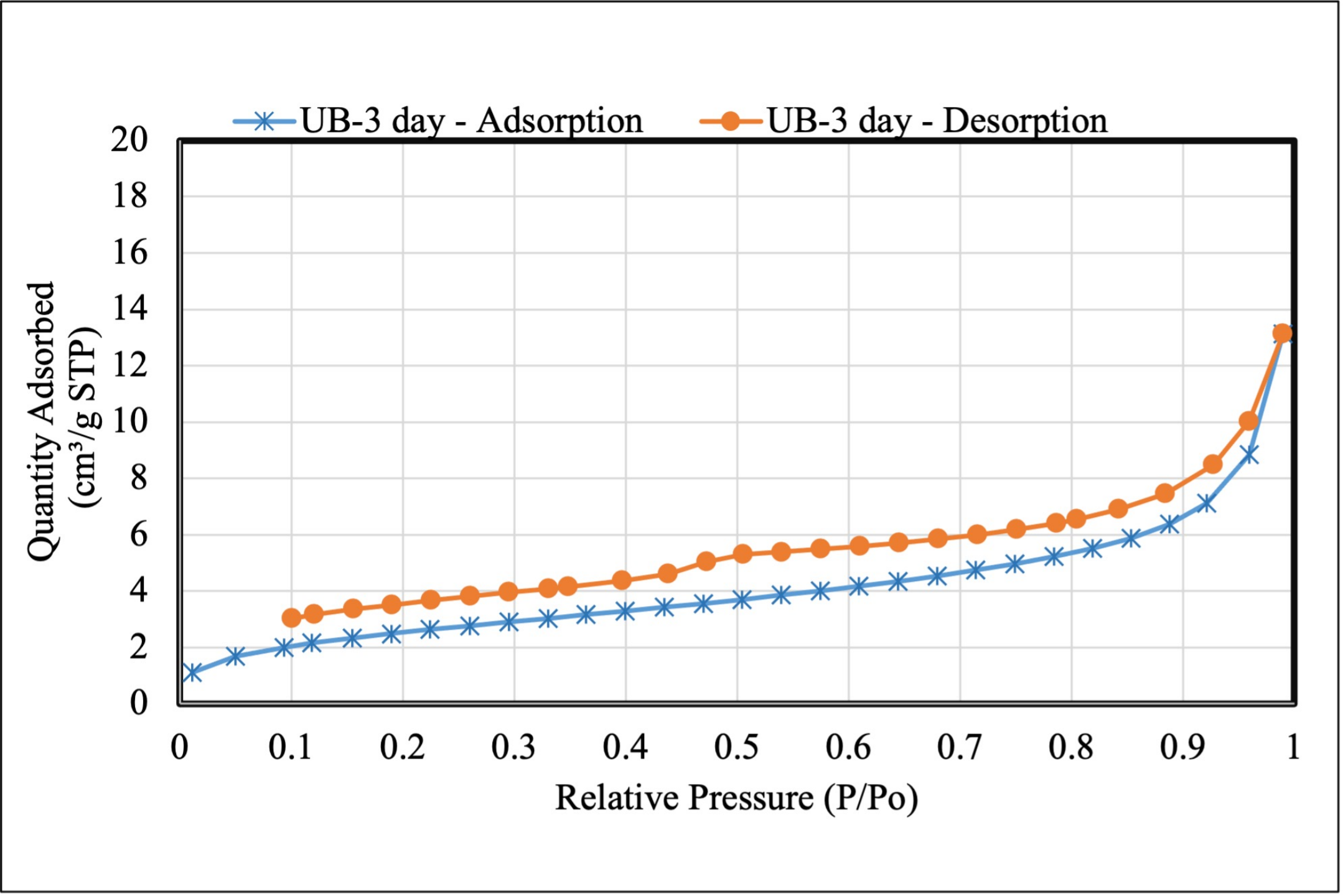


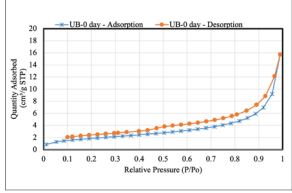


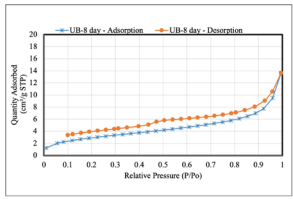


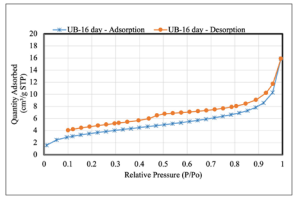


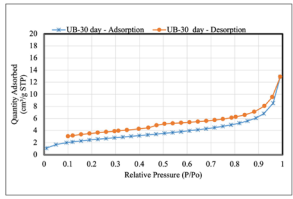


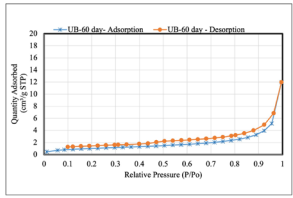


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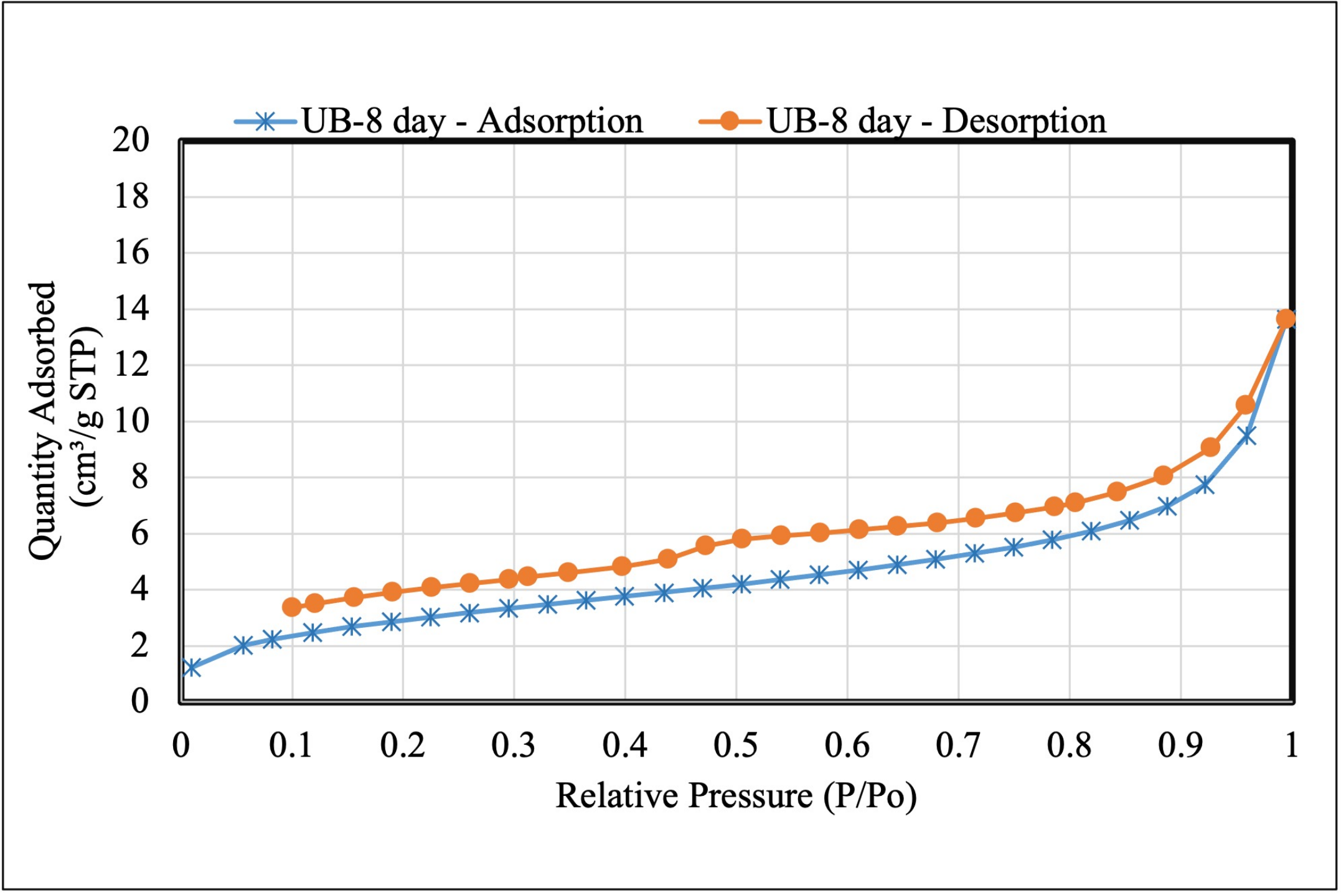


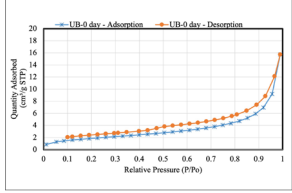


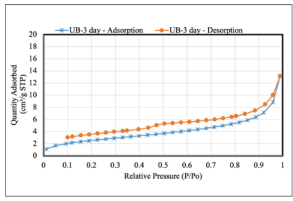


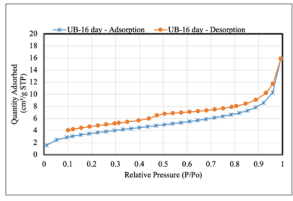


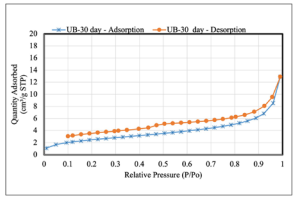


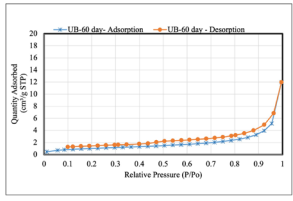


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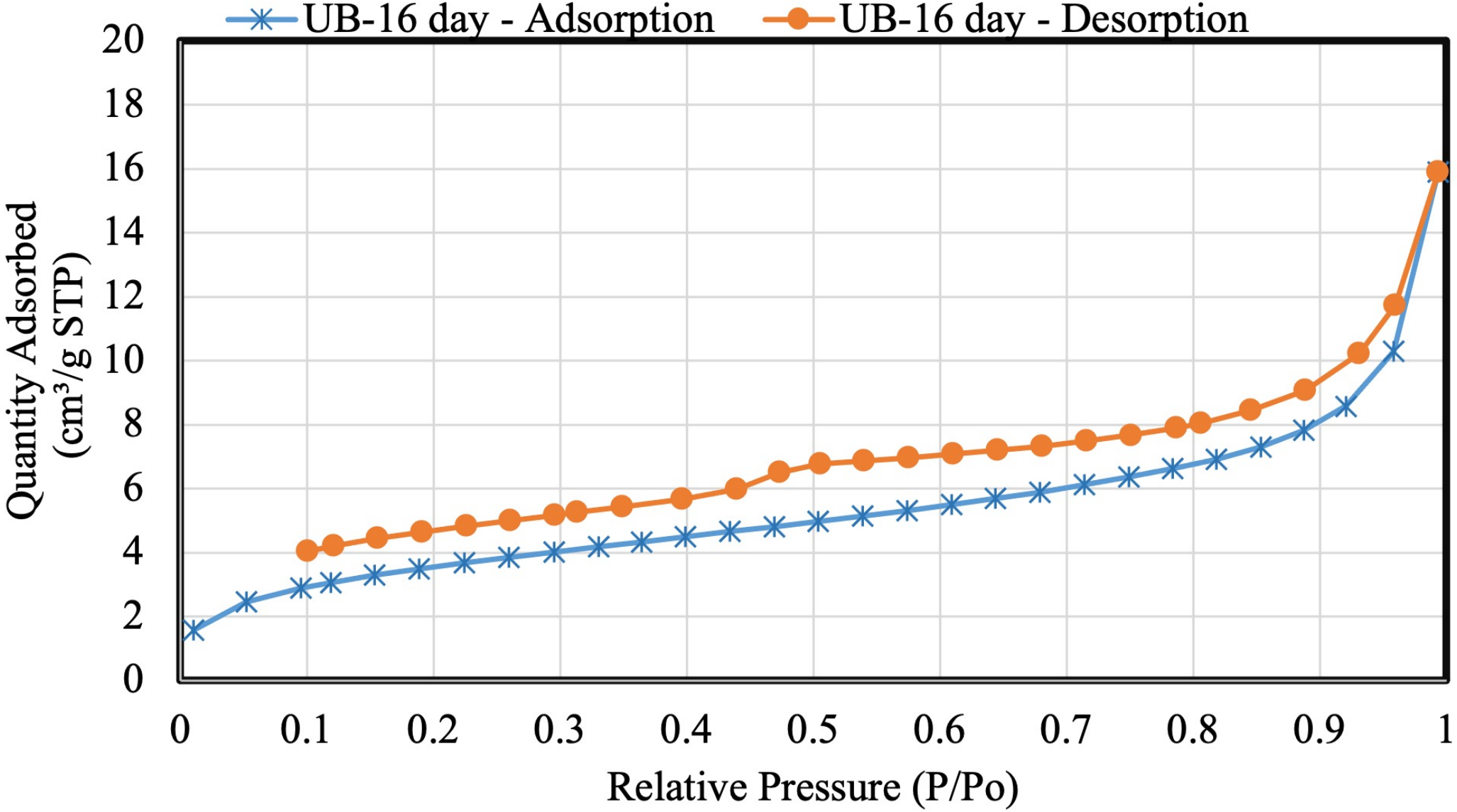


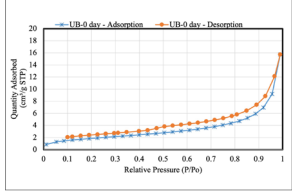


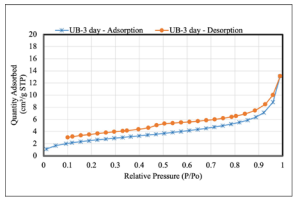


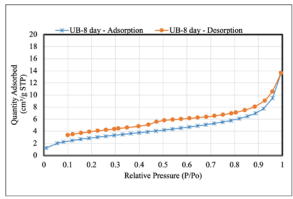


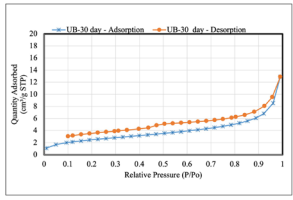


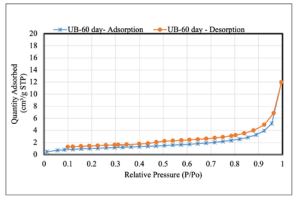


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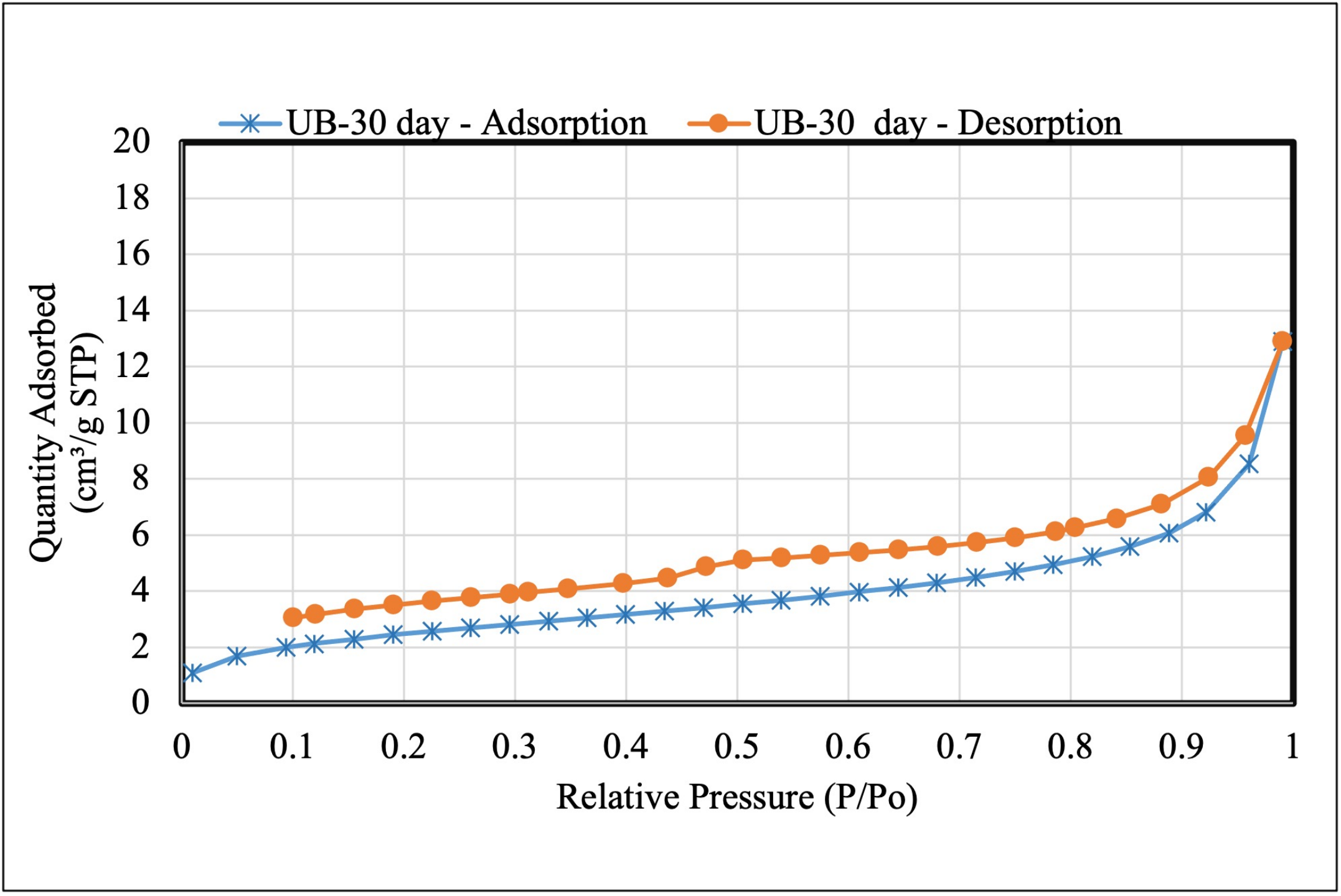


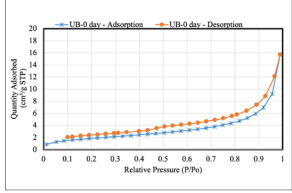


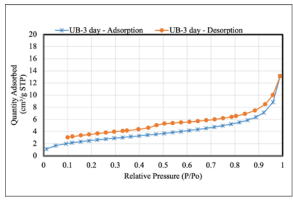


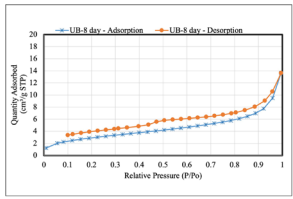


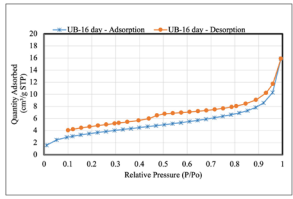


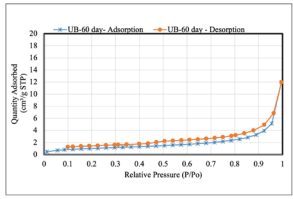


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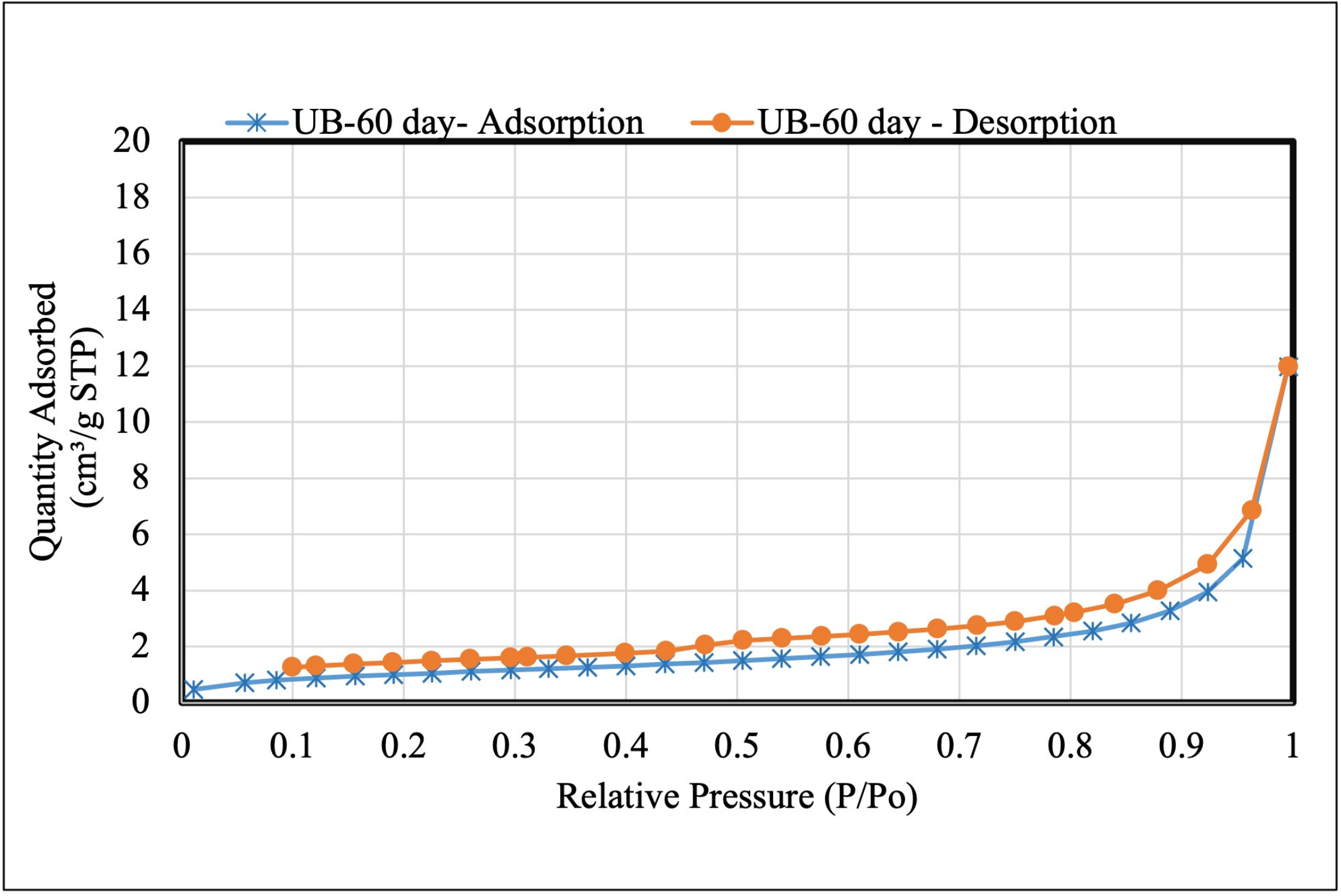


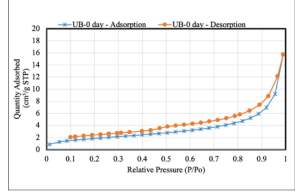


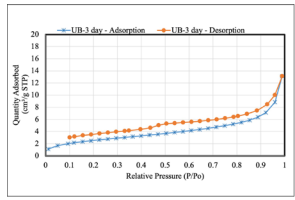


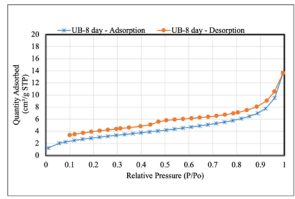


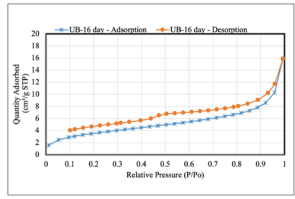


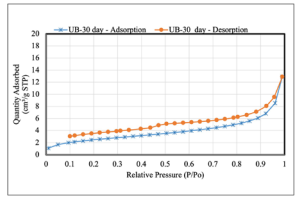


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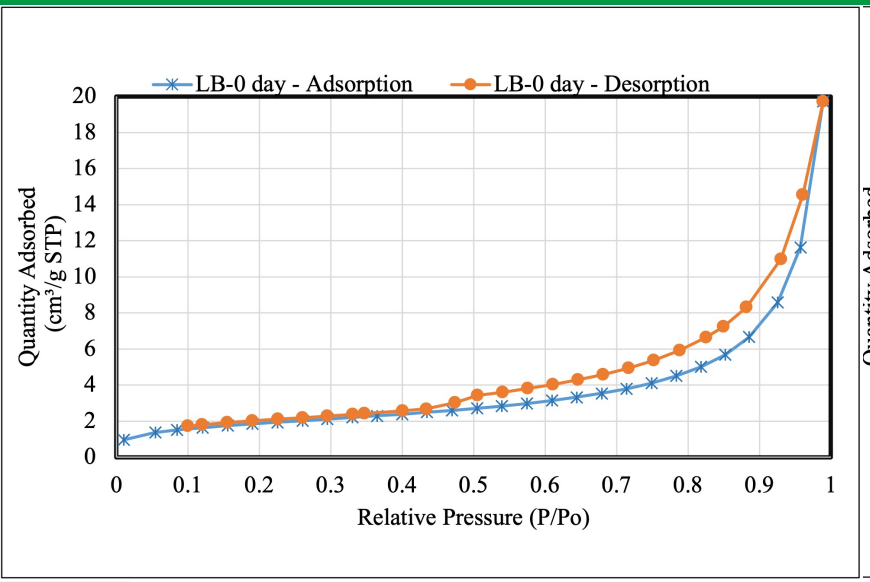
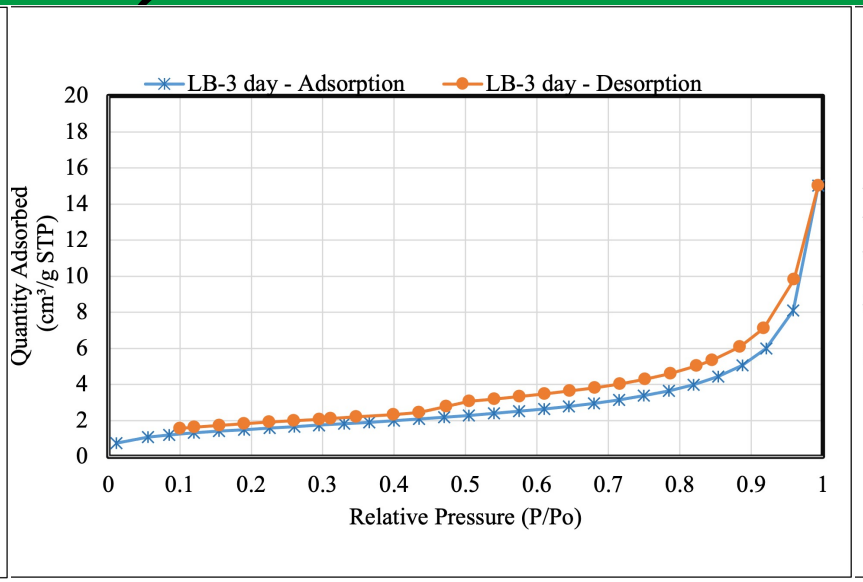
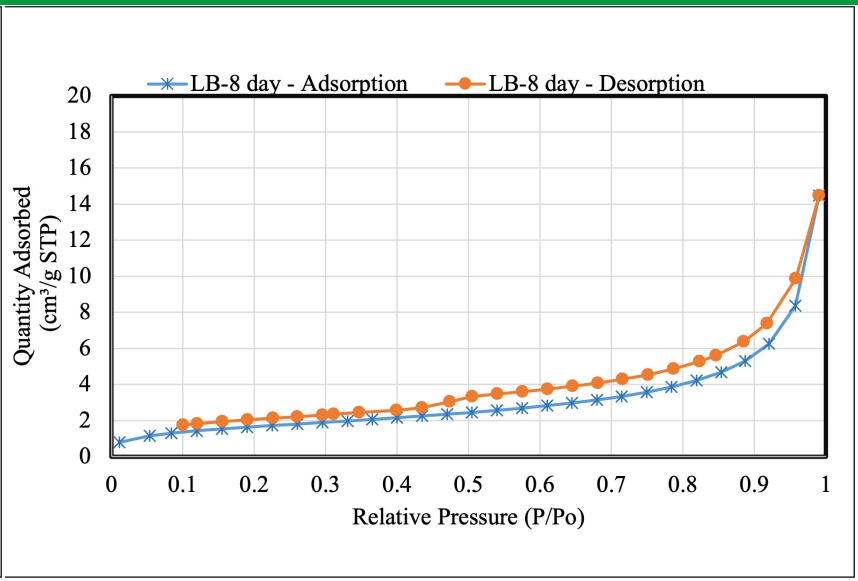
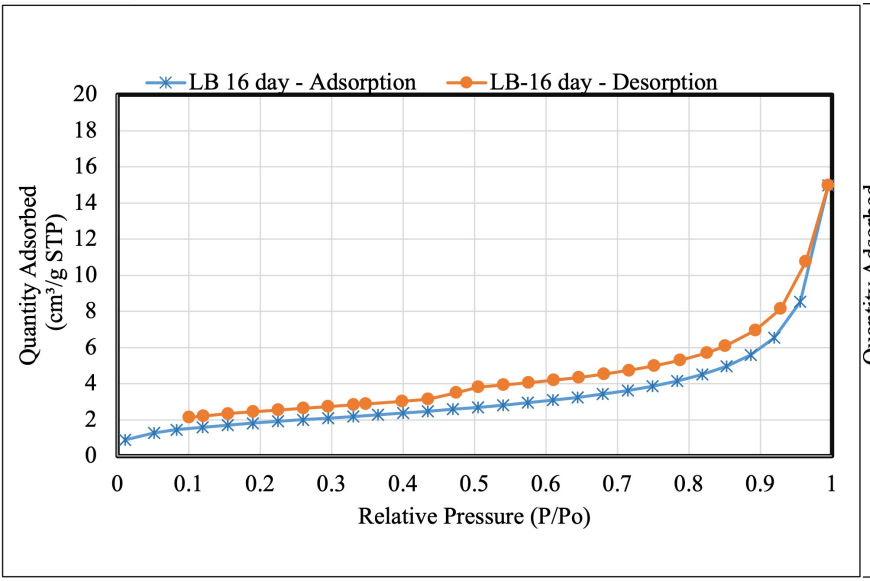
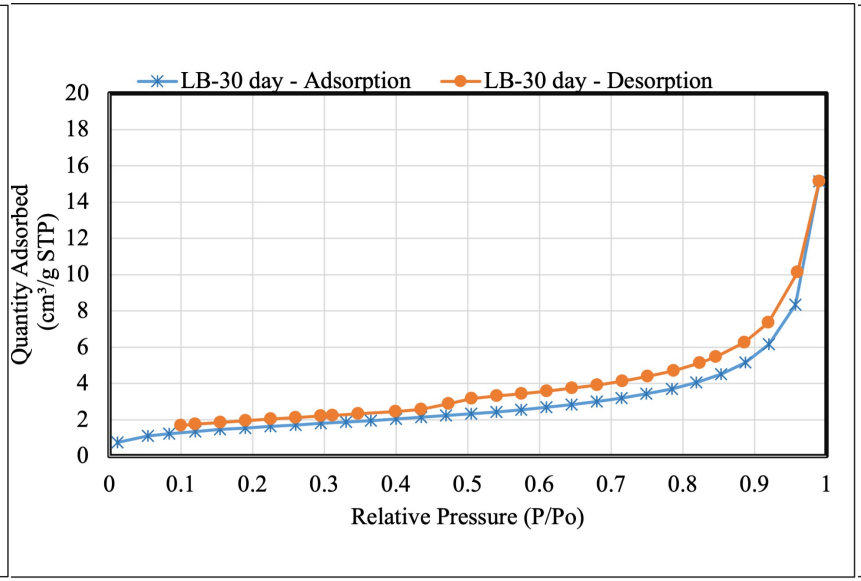
# Lower Bakken $N_2$ Isotherm

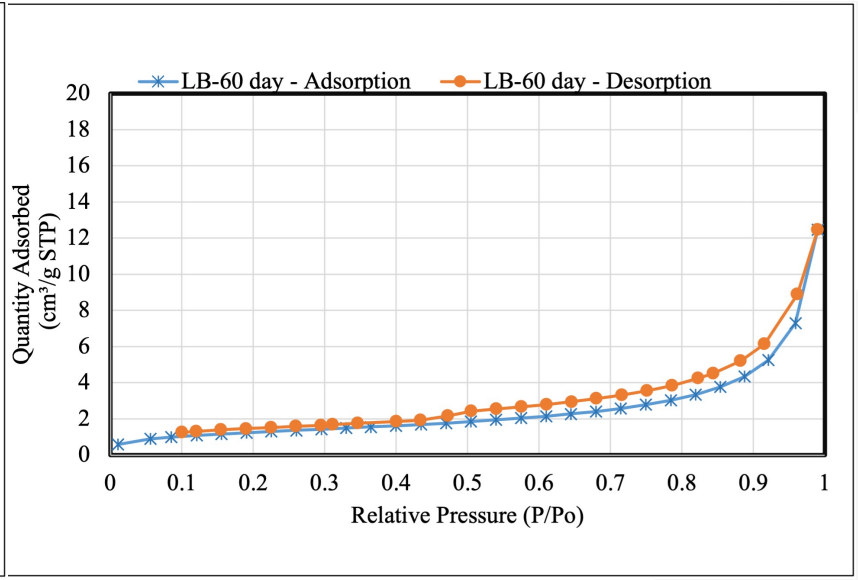
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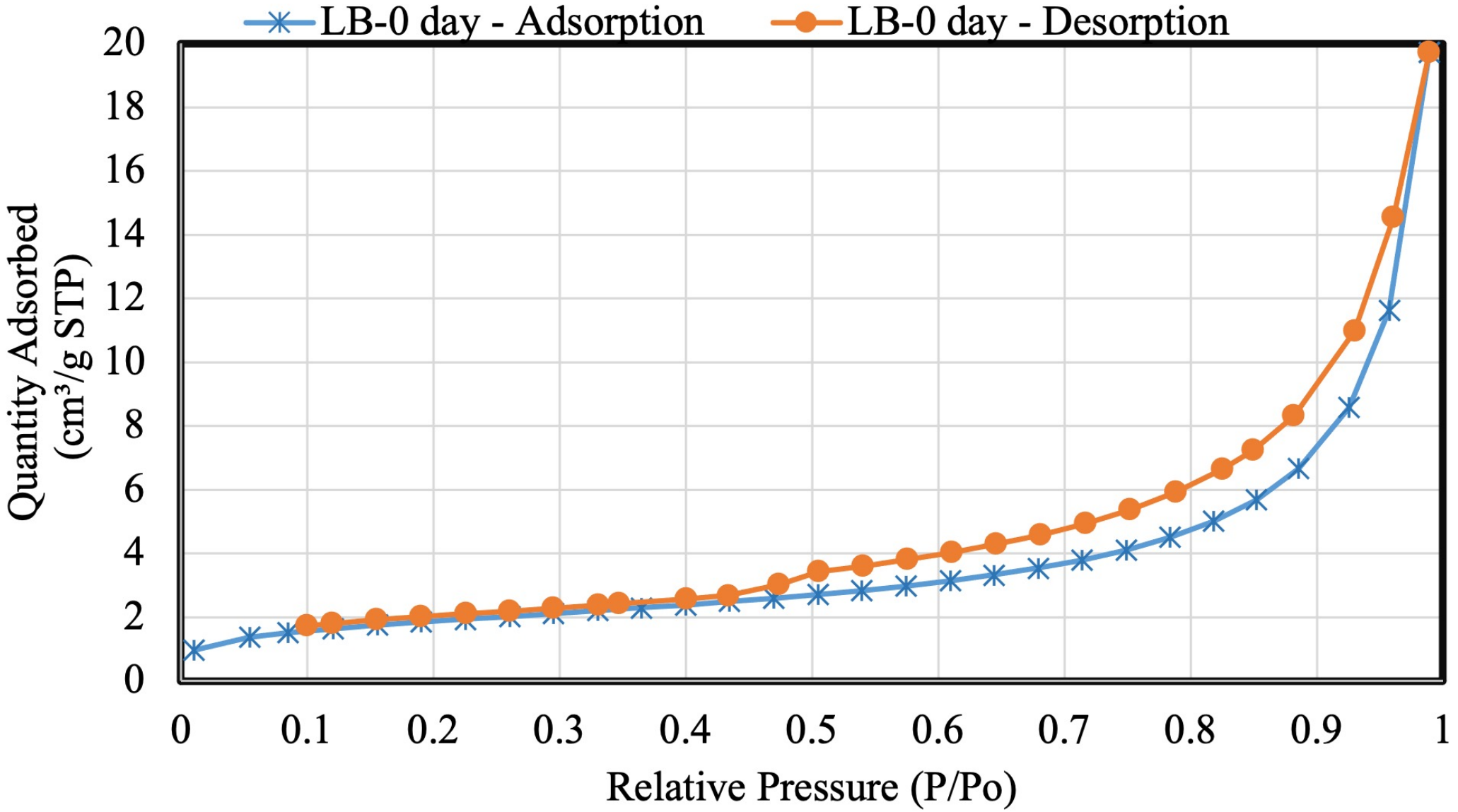


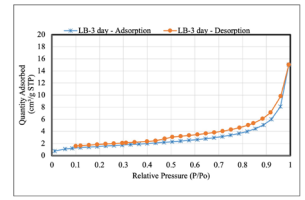


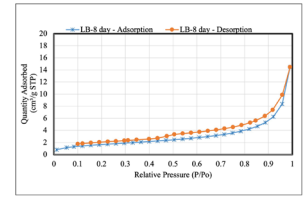


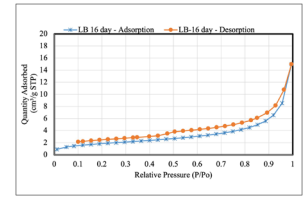


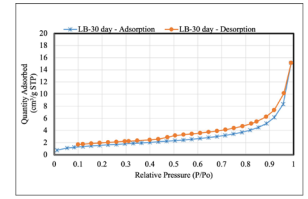


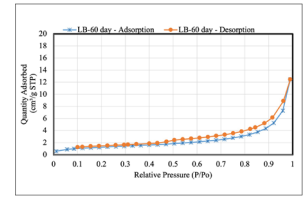


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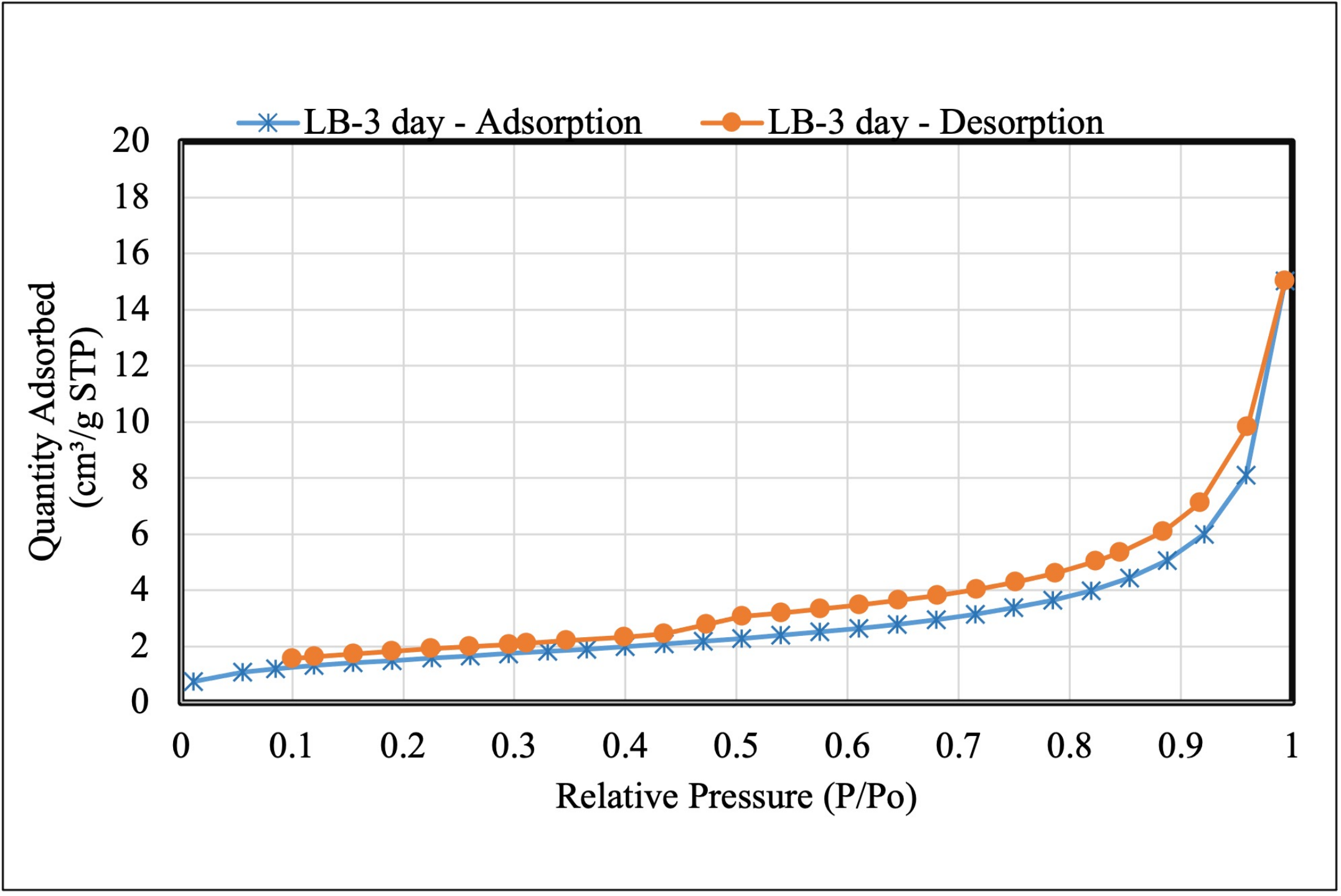


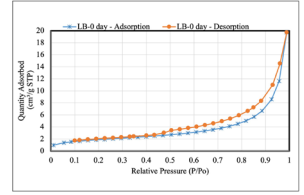


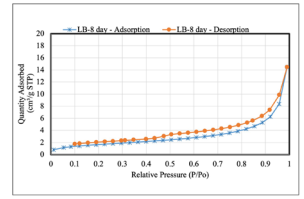


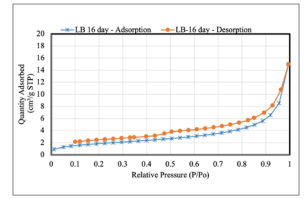


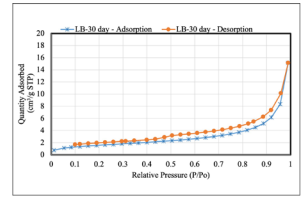


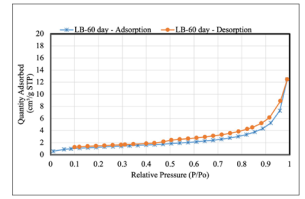


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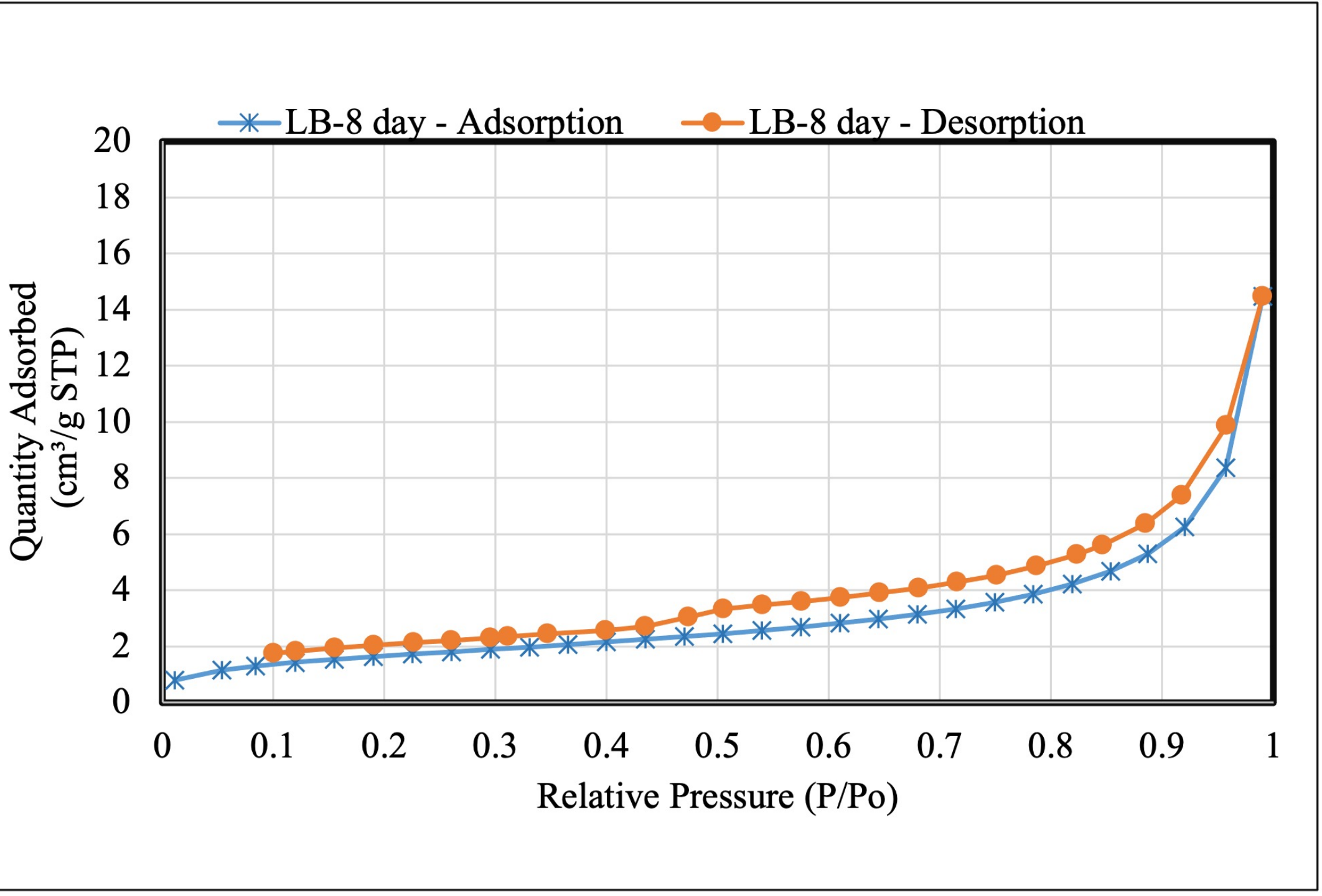


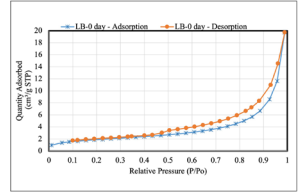


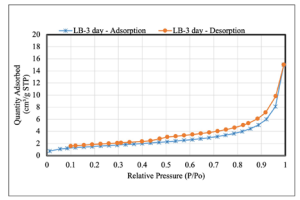


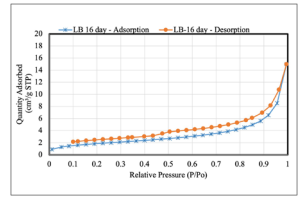


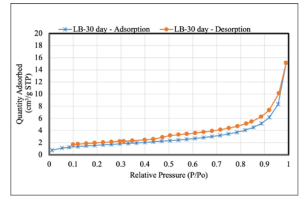


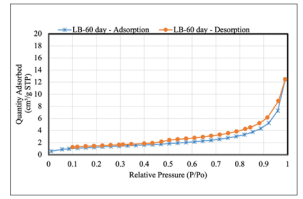


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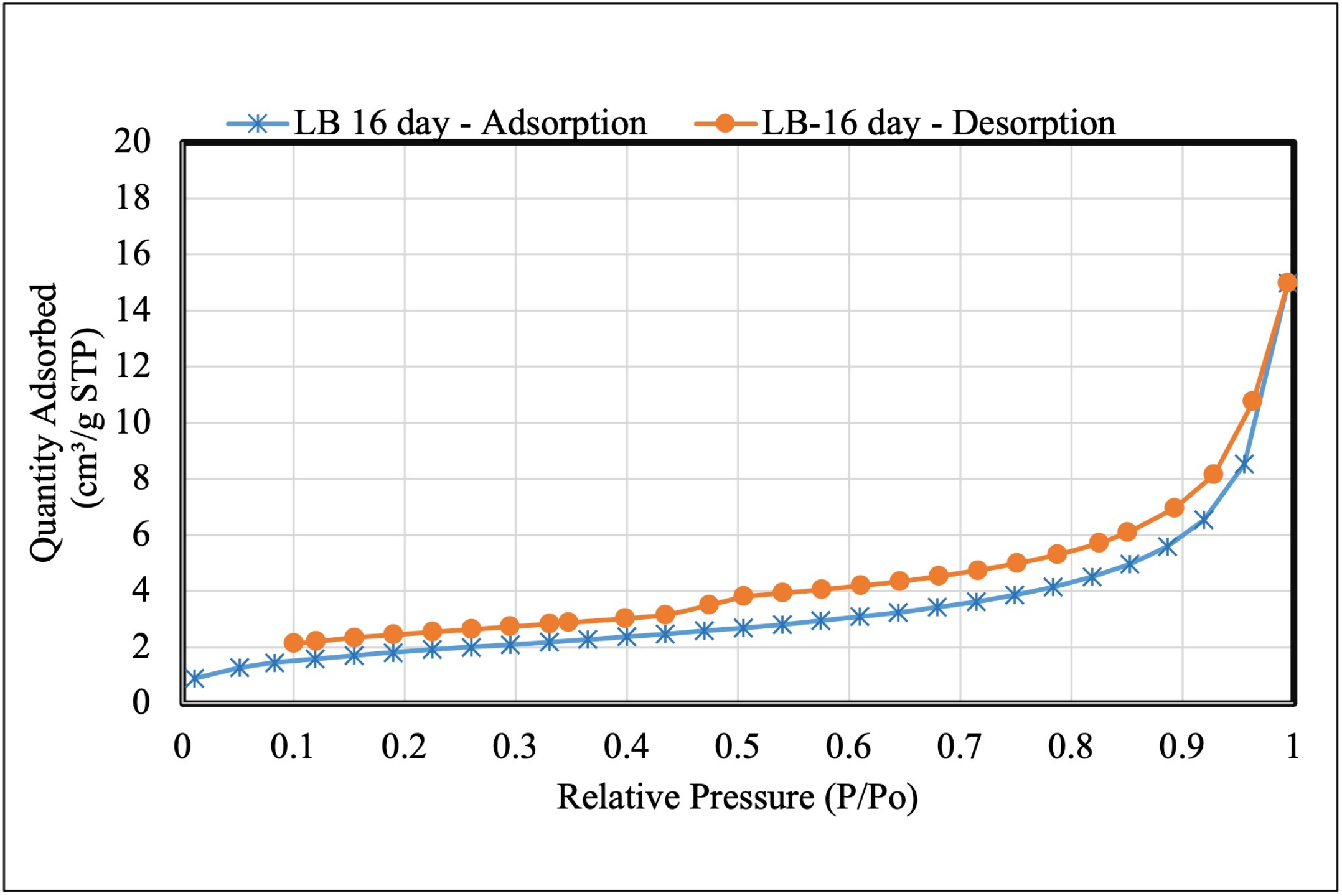


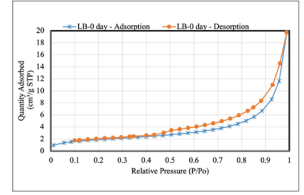


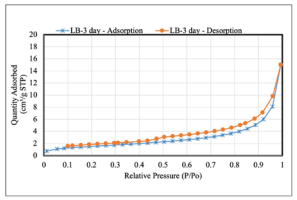


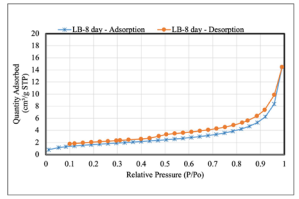


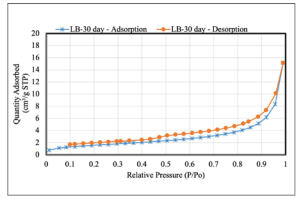


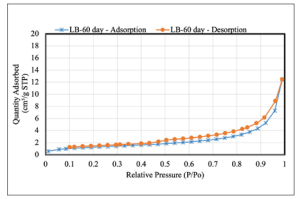


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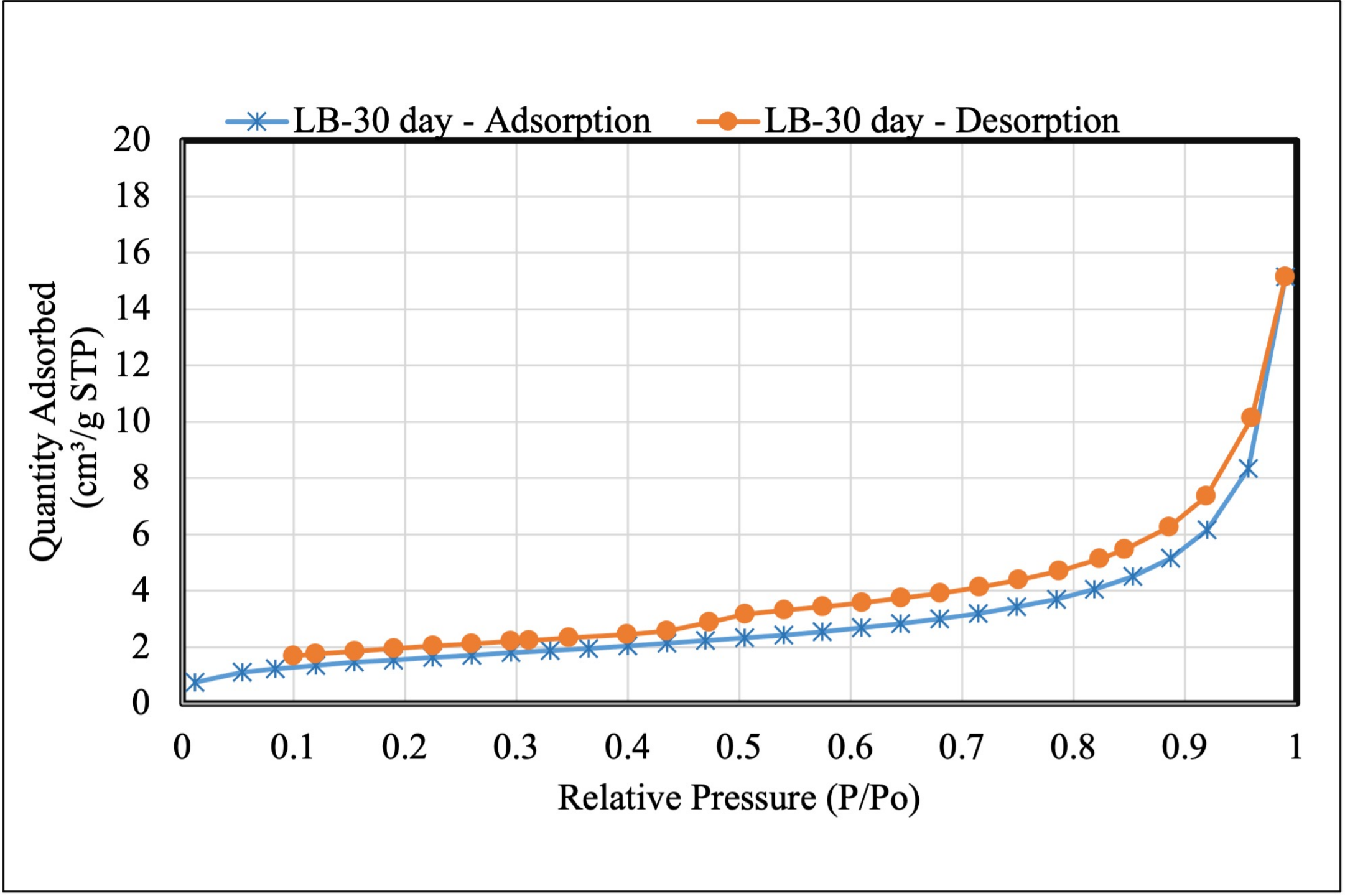


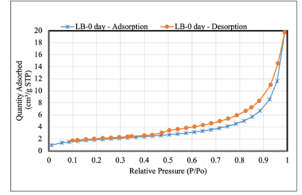


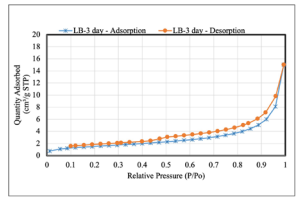


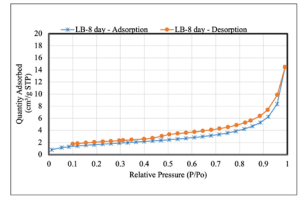


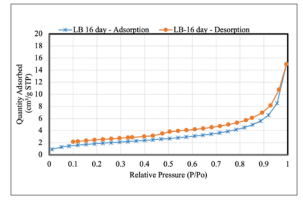


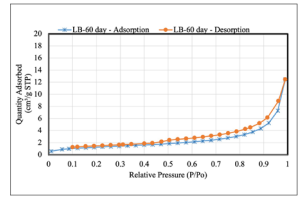


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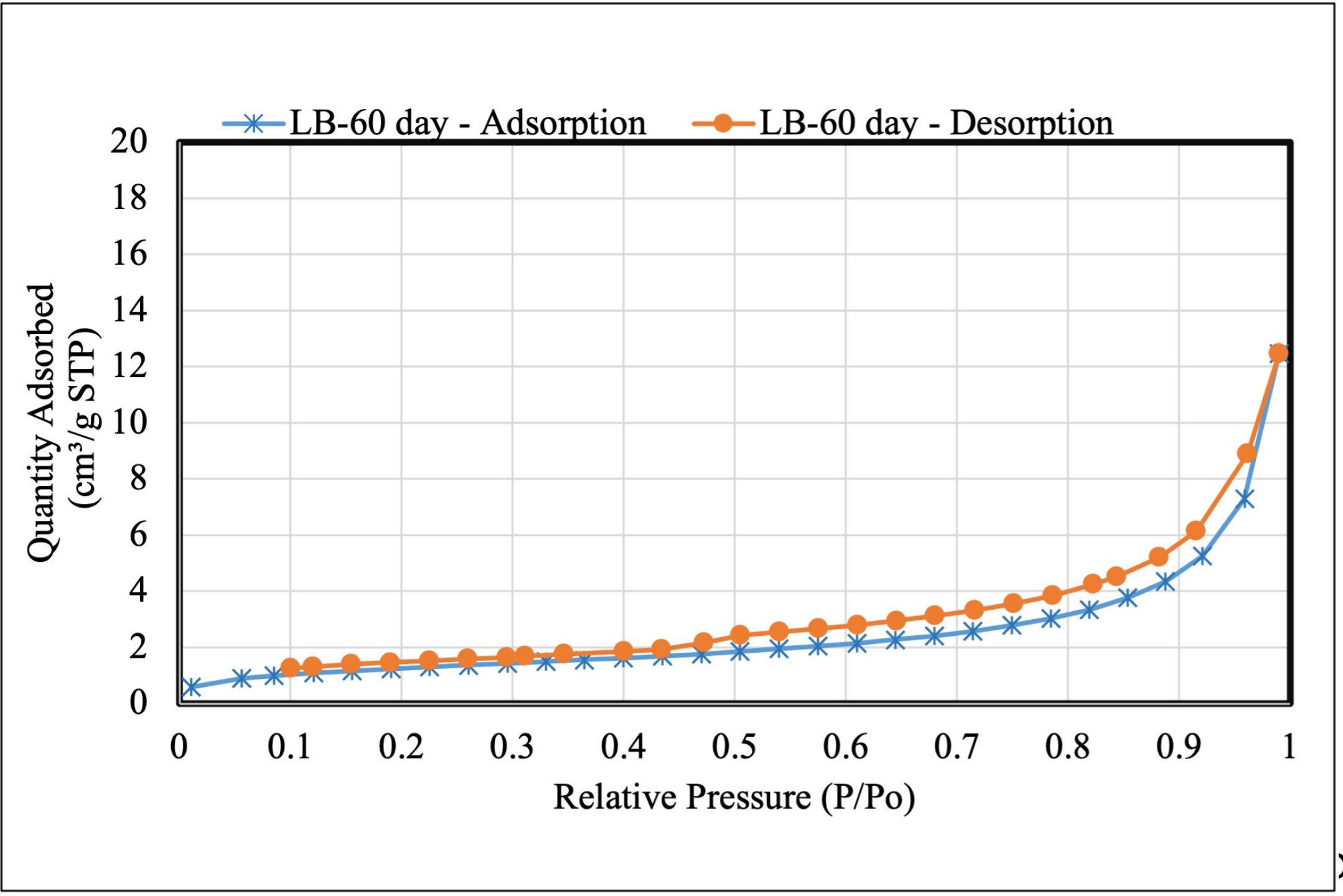


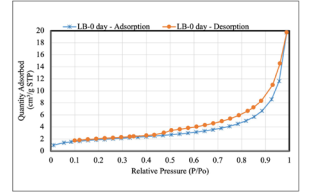


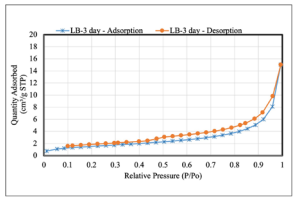


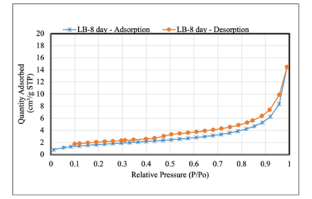


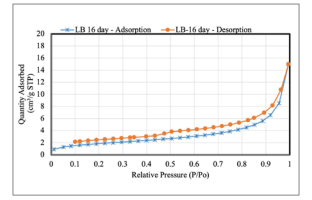


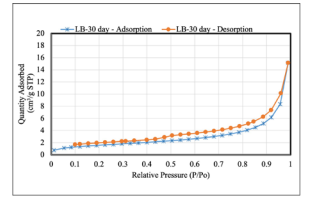


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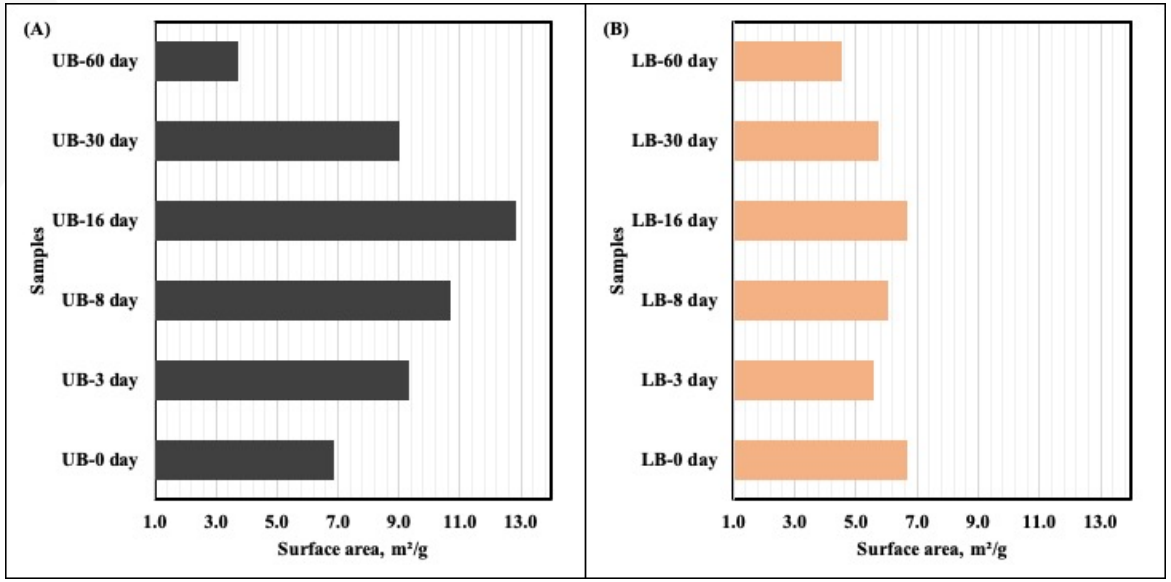
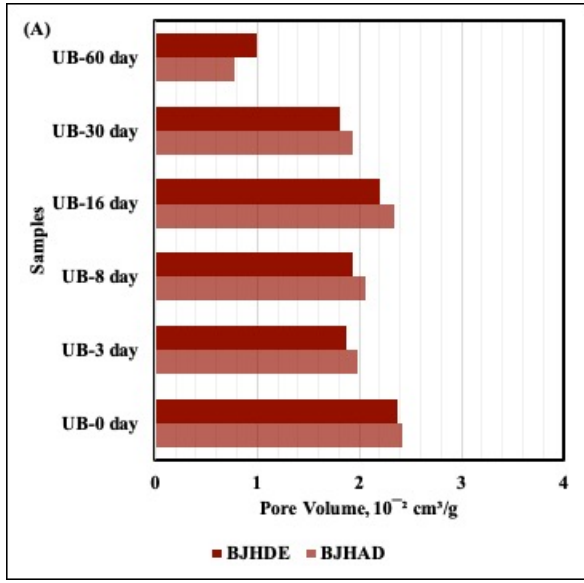
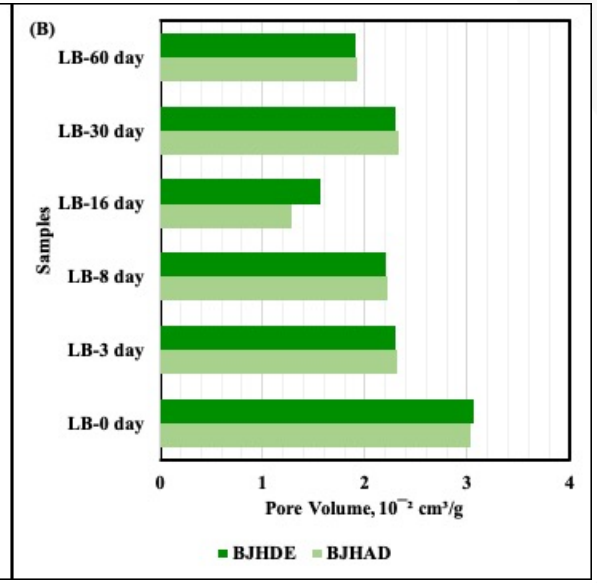
# Pore Structure Analysis







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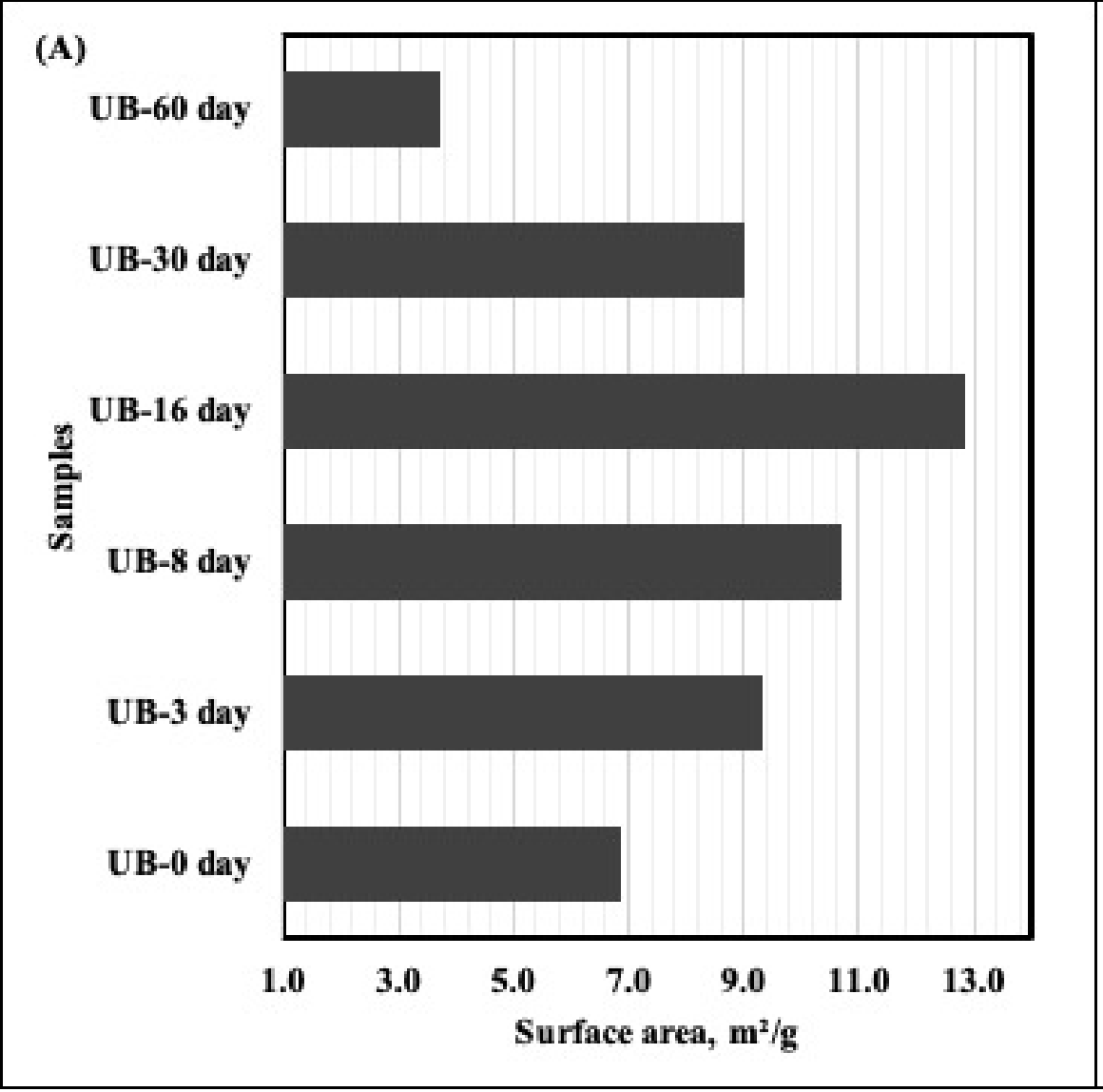


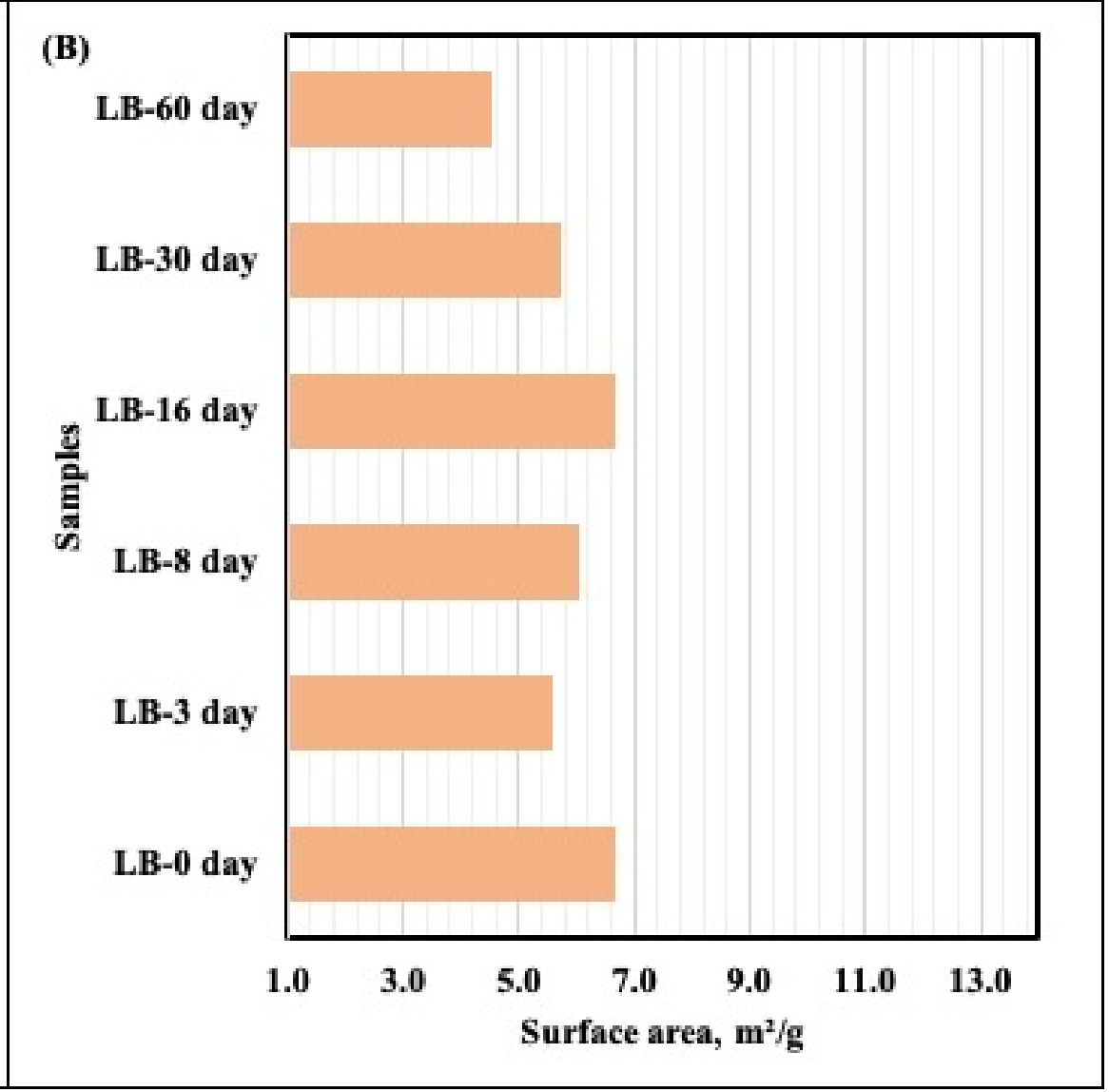


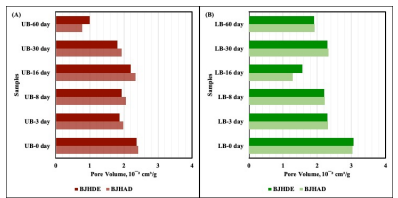

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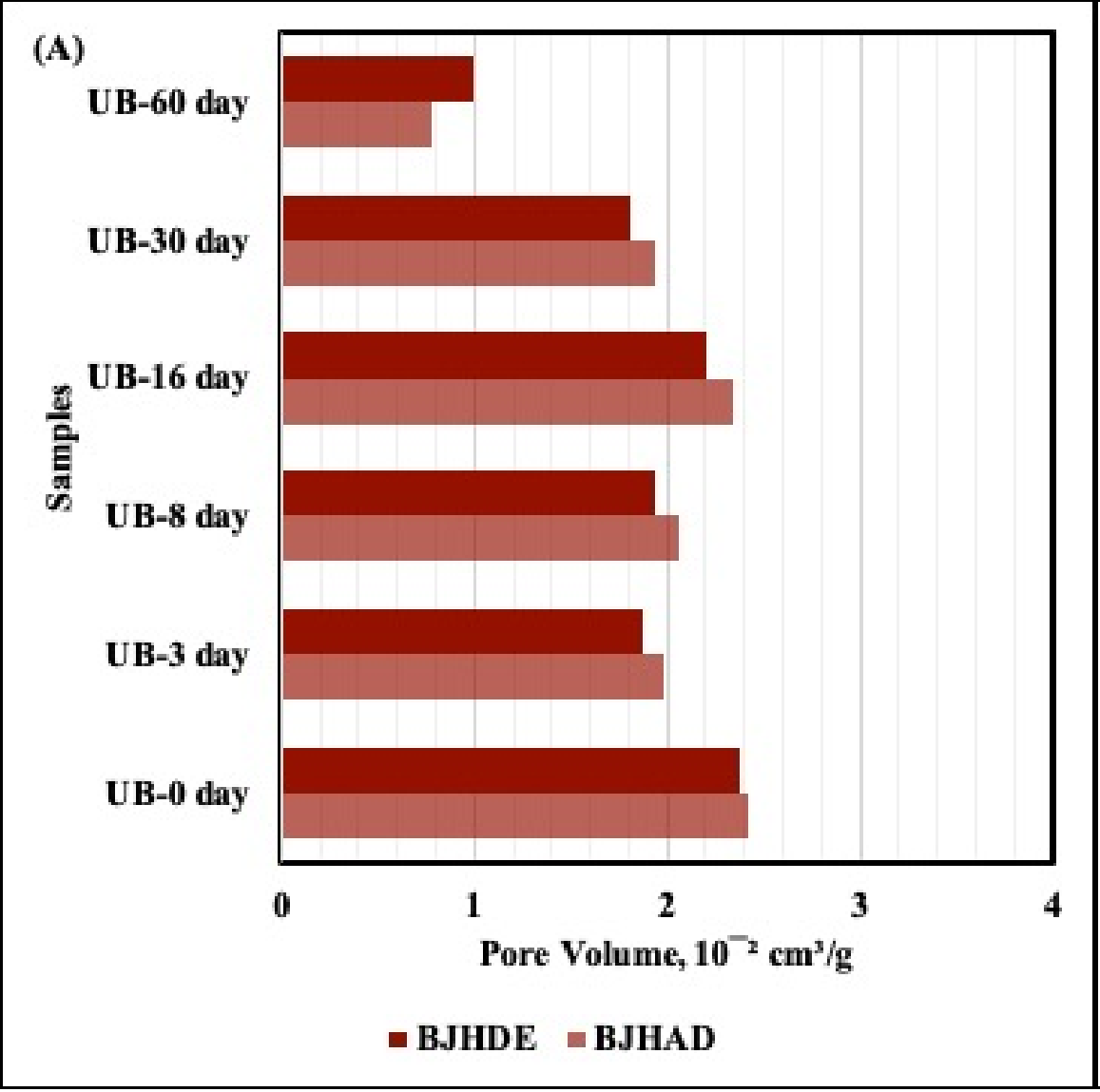


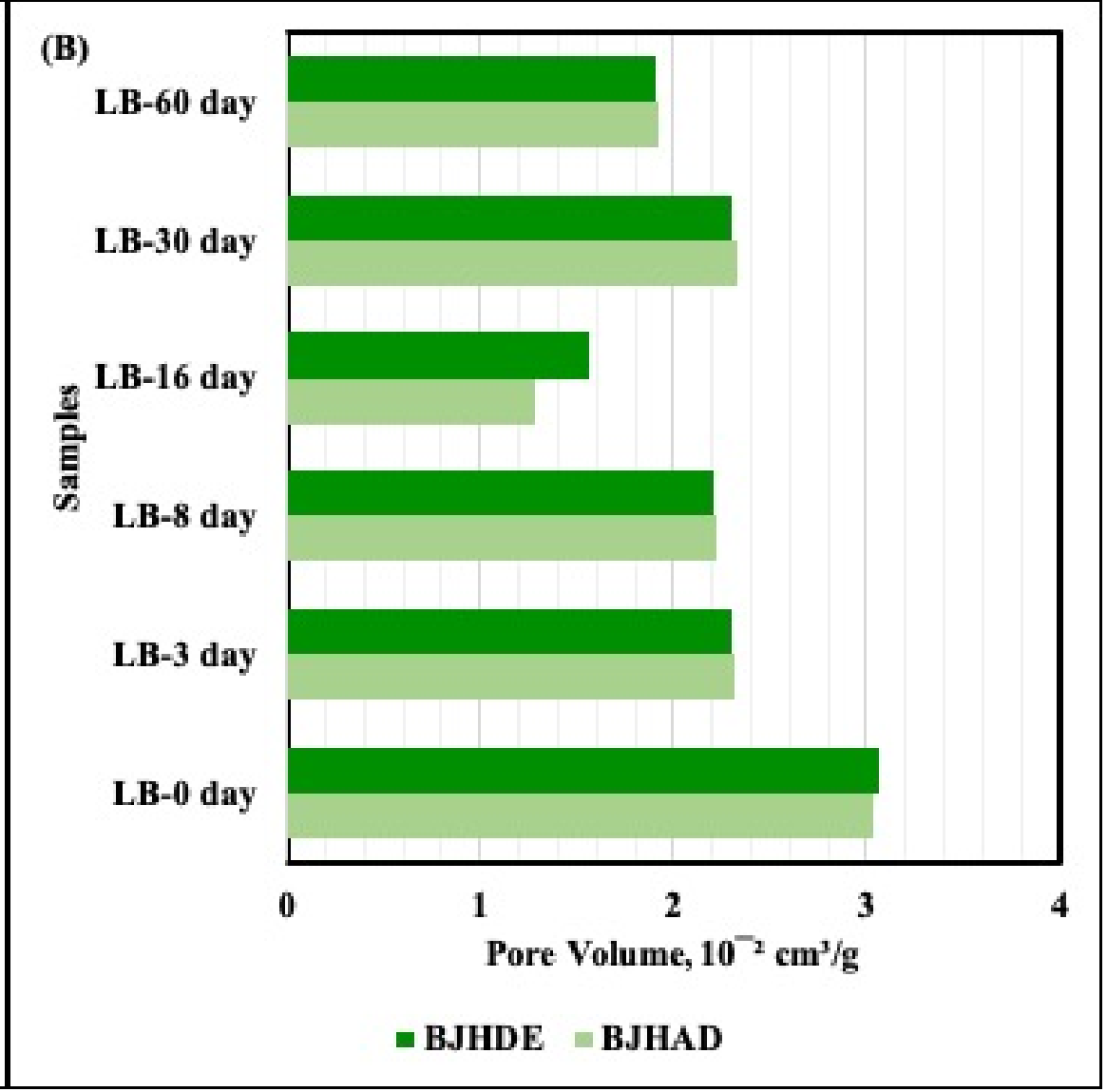


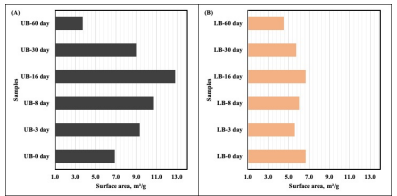

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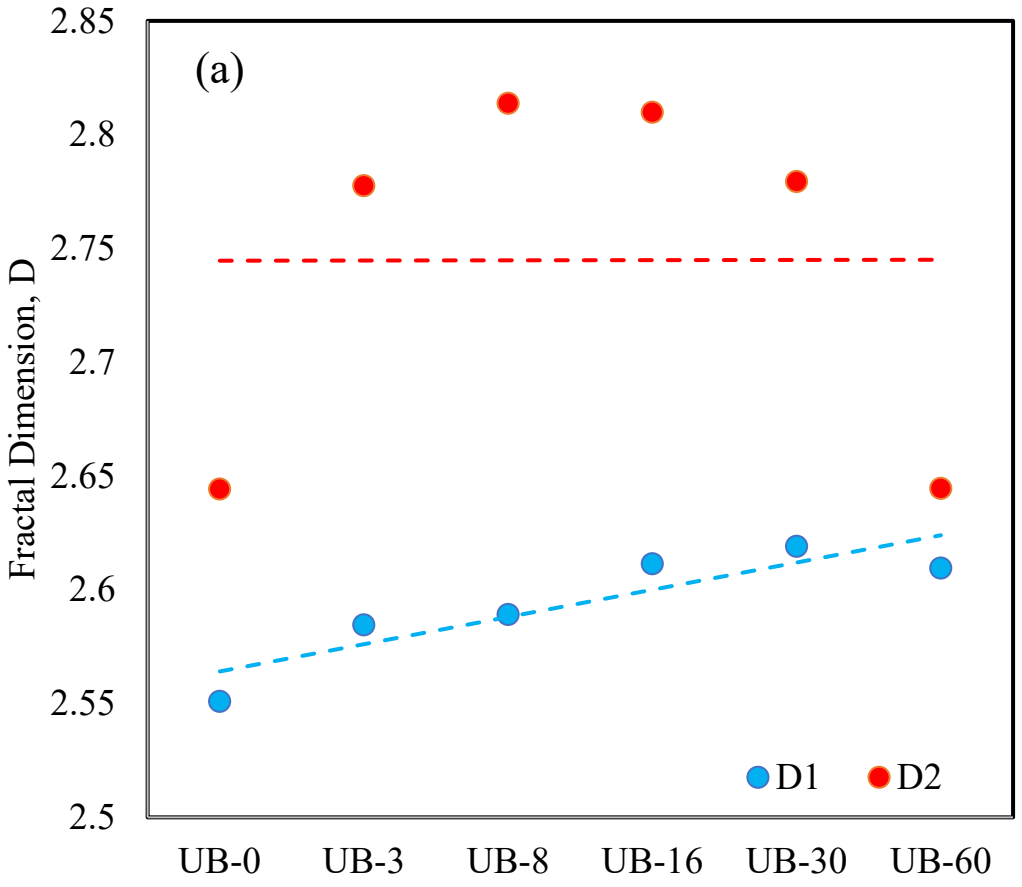


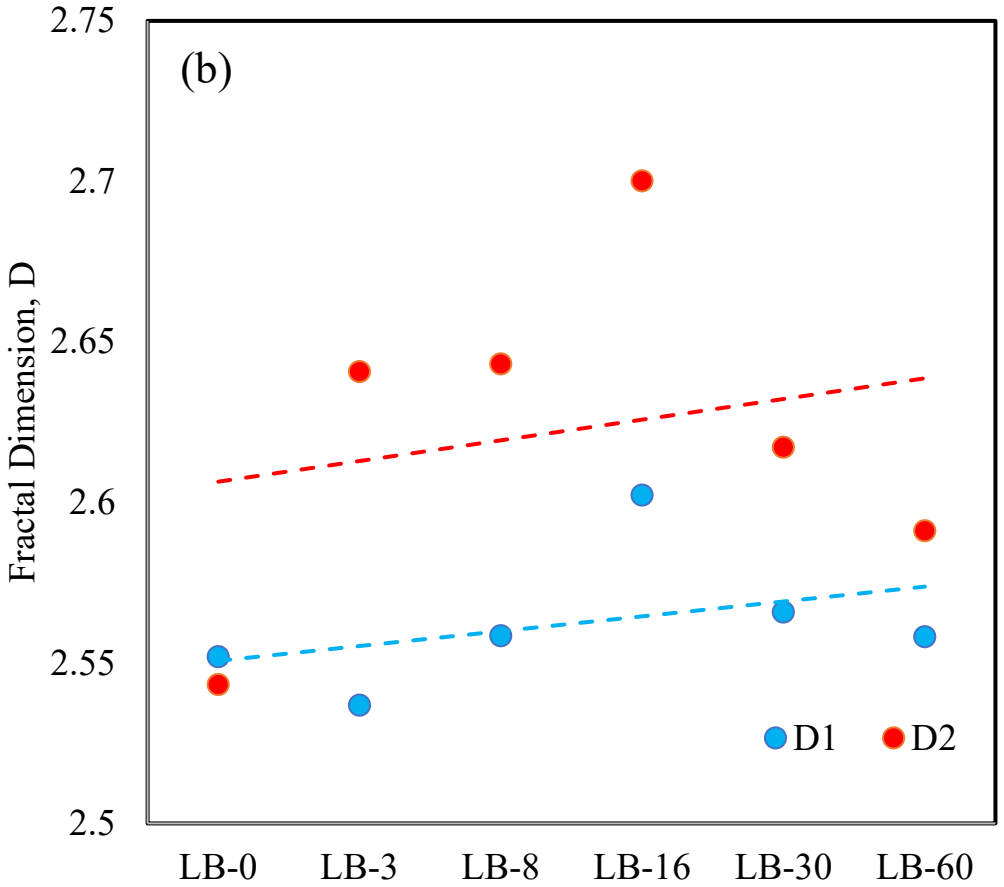


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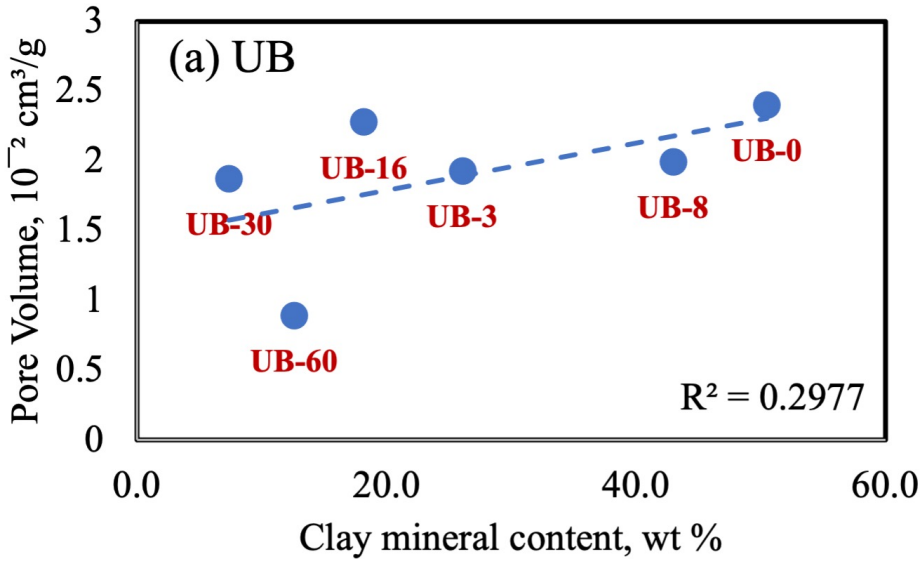
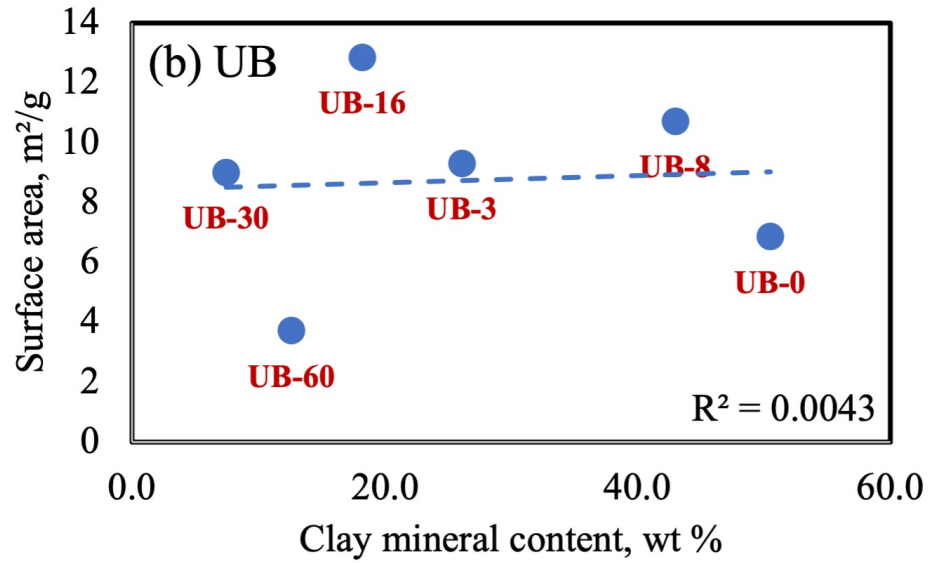
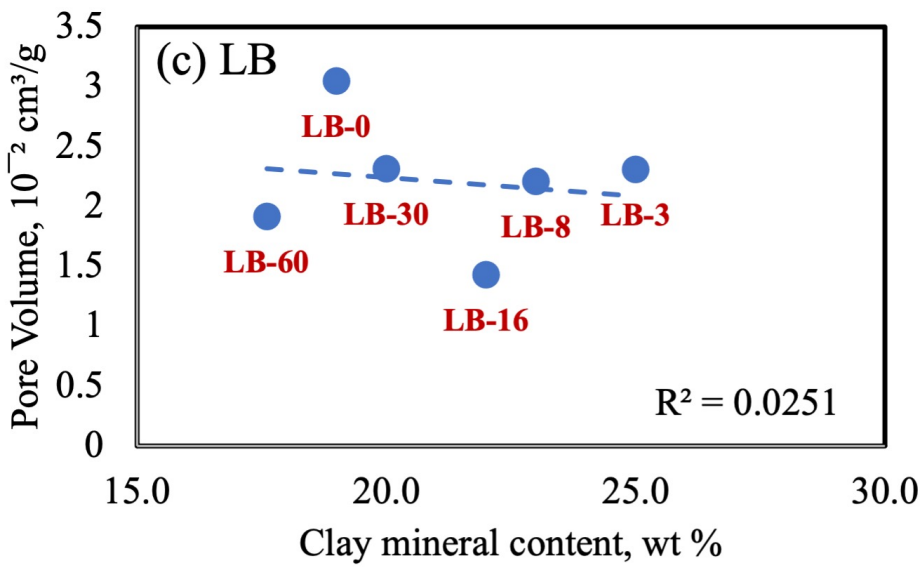
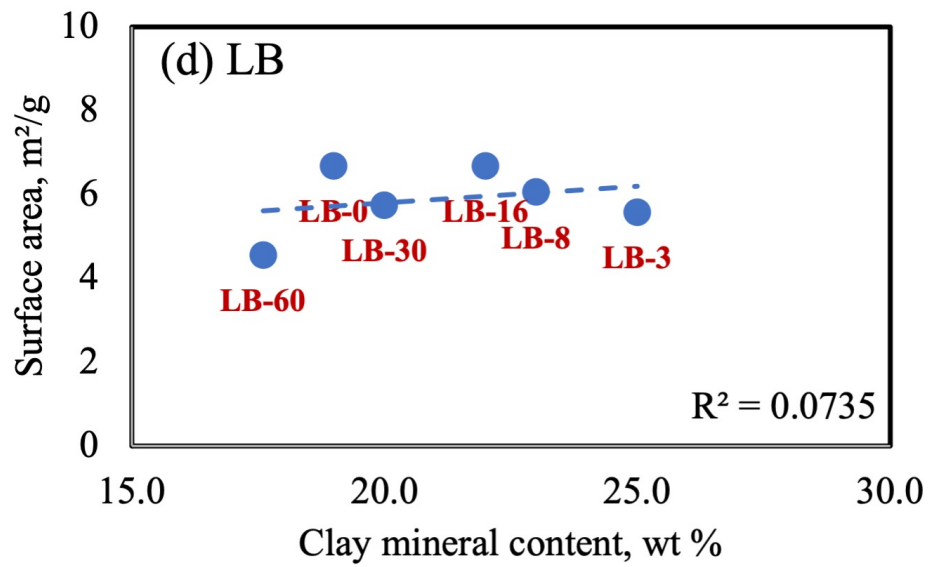
# DISCUSSION

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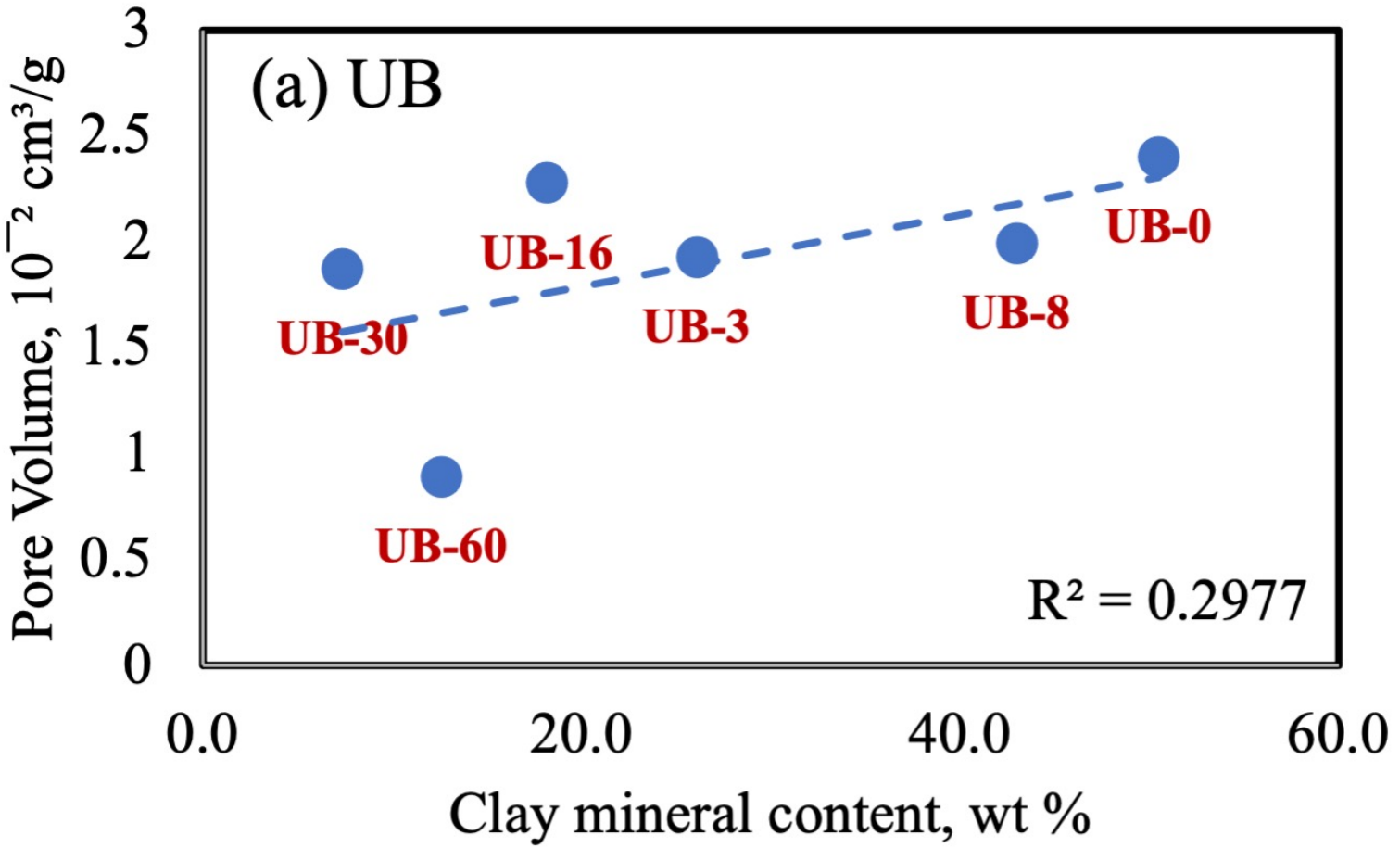
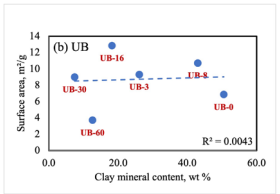
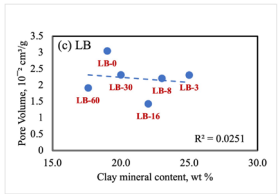
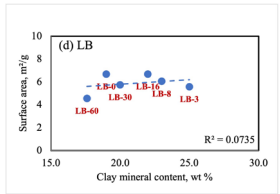



Weak positive linear correlation

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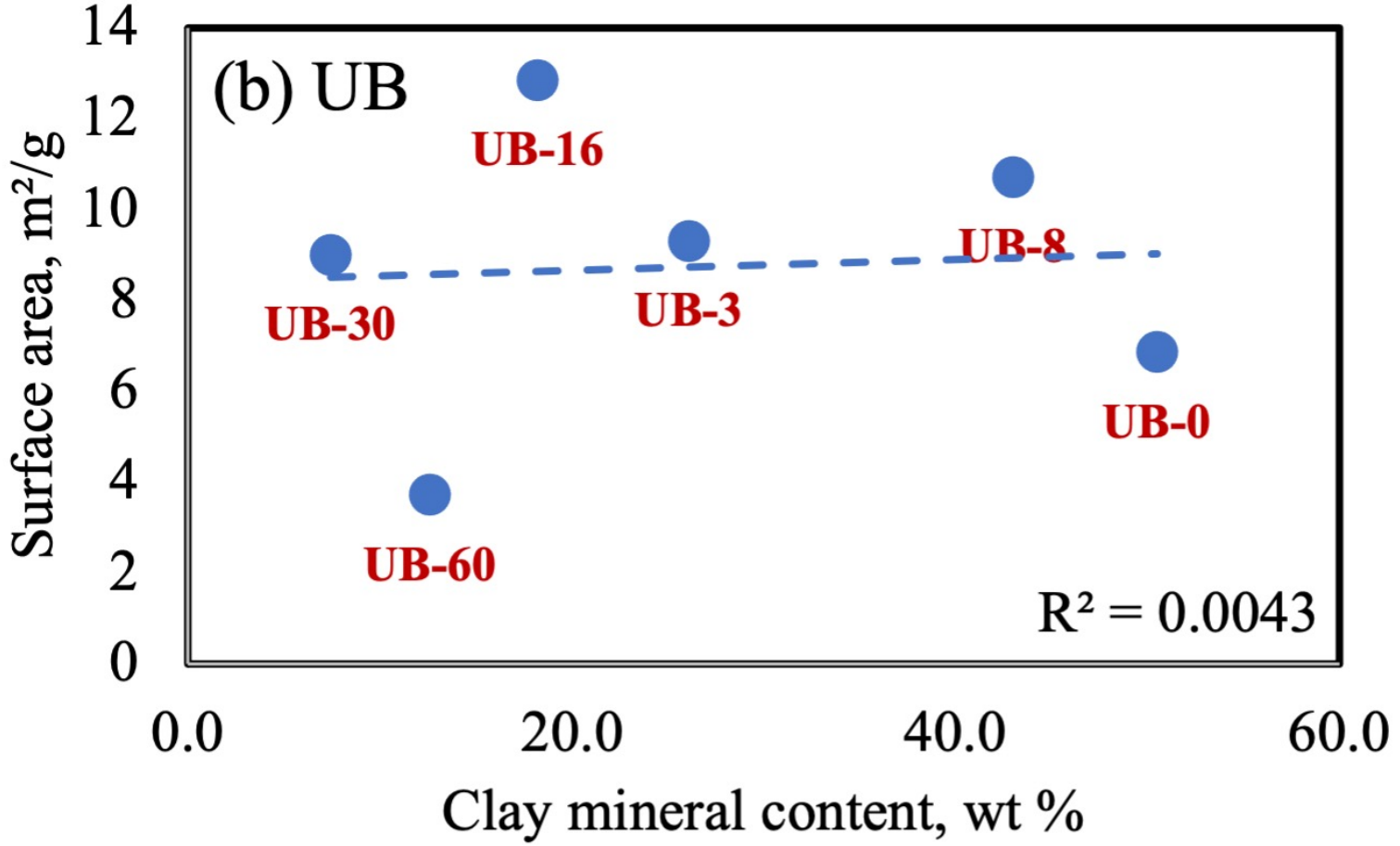


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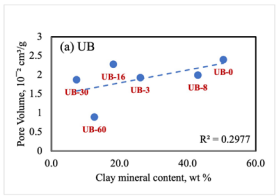


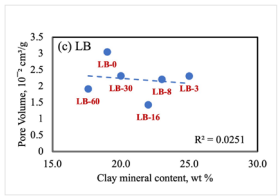


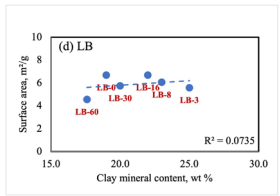


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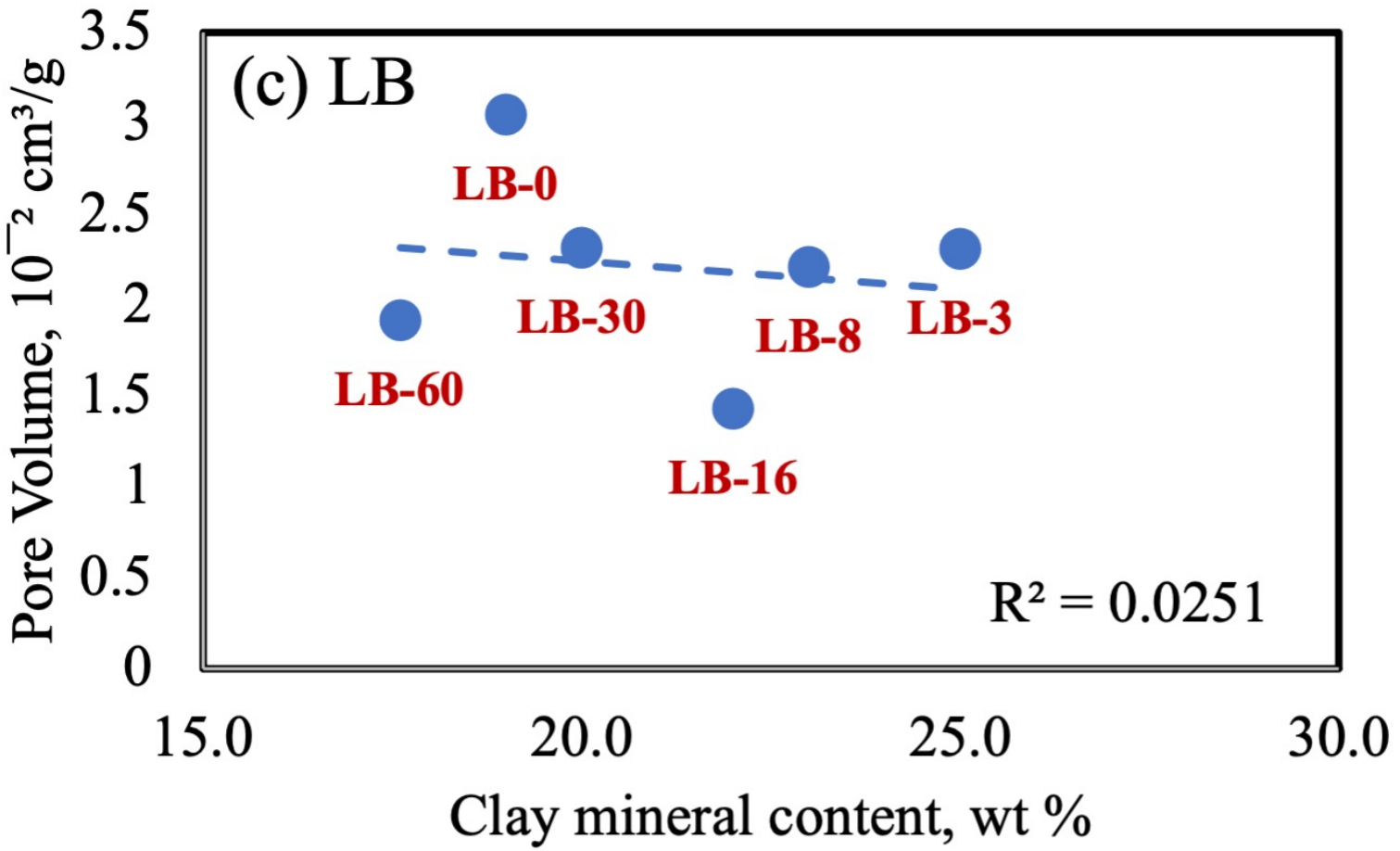


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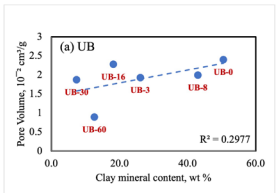


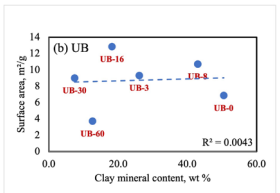


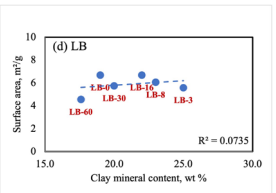


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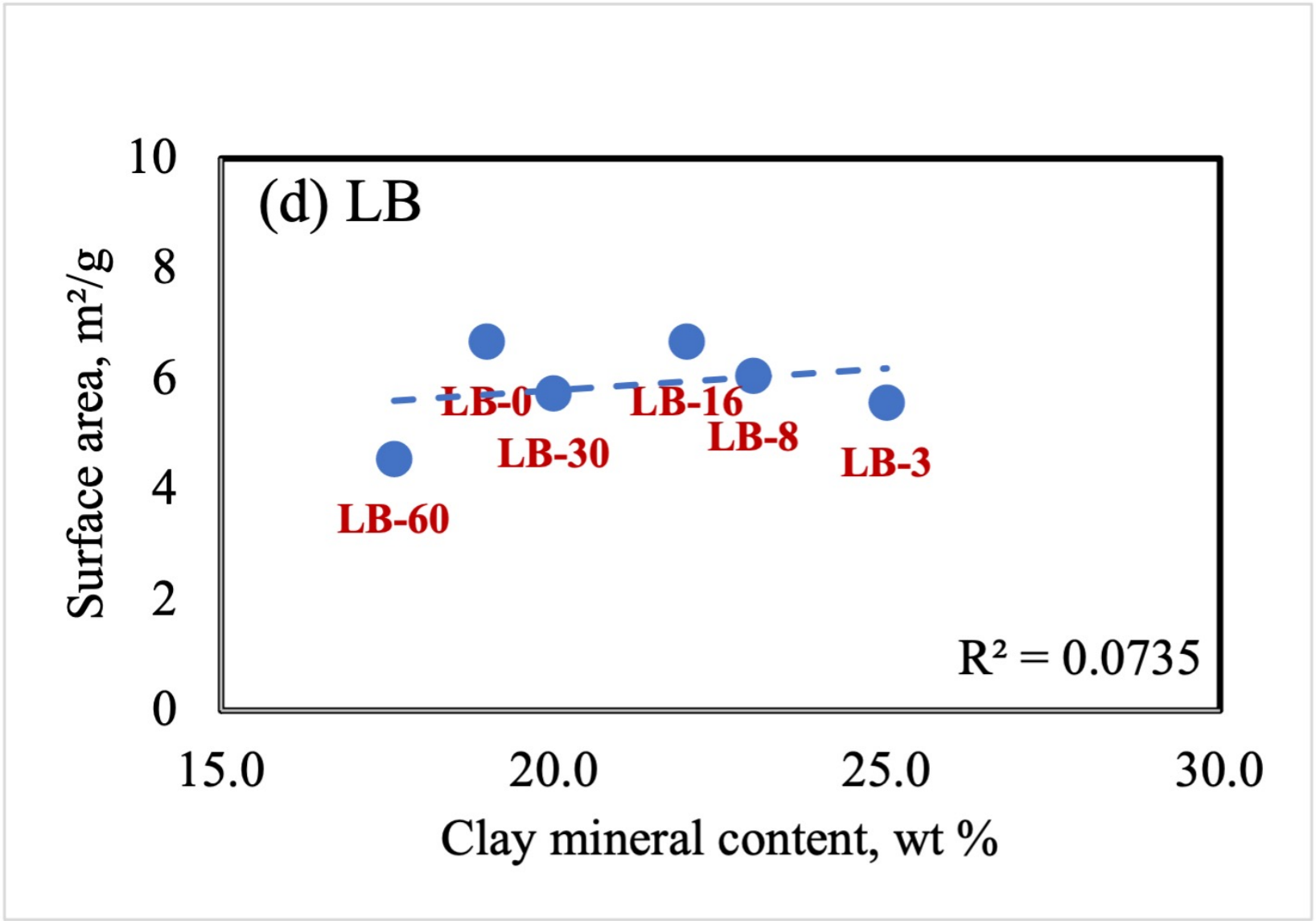


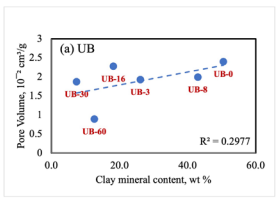


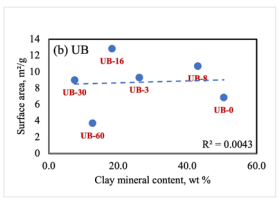


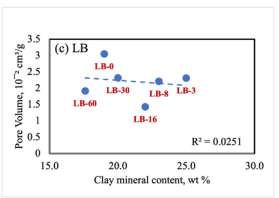


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# Discussion

- The UB shale sample has larger quantities of clay minerals and carbonates compared to LB, while LB shale sample has more quartz.
- This explains why the LB has a larger pore volume and pore size as a result of the exposure to $CO_2$ causing the dissolution of the clay minerals and carbonates
- Larger adsorption capacity in the LB sample was to some extent related to the pore size, pore volume, mineral composition and TOC of the sample.
- Carbonate dissolution will increase the pore size of the shale samples, so the dissolution of carbonate exhibits a positive relationship with the increase in pore volume and the overall adsorption potential of the samples

# CONCLUSION

# Conclusion

- The presence of quartz seems to be playing a role in the pore size structure of the shale sample.
- The dissolution of organic matter or clay minerals in the shale after $CO_2$ saturation causes some of the pores to disappear or convert, thereby increasing and decreasing specific surface area
- Surface area is larger in the sample with larger TOC
- The fractal dimension increased as samples were saturated with $CO_2$ with peak after 8 and 16 days and decreased at 30 and 60 days for both UB and LB samples.
- Pore morphology transformation from regular to complex (dissolution) and back to more homogenous structure (precipitation).

# APPRECIATION

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# QUESTIONS

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