Evaluating the Adsorption Performance of Economical and Environment-friendly Arsenic Adsorbents: A Comparison between CMDS-Bead and GFH

Ki-Rim Lee[1], Duk-Min Kim[1], Hye-Lim Kwon[1], Nam-Kyu Kim[1], Young-Min Kim[1], Dae-Gyu Im[2], Sin-Dong Kim[3], Oh-Hun Kwon[4], Mi-Sun Park[4]

[1]Department of New Energy and Mining Engineering, Sangji University (South Korea)

[2]Department of Earth and Environmental Sciences, Korea University (South Korea)

[3]Environment Energy & Chemical Solution (South Korea)

[4]Korea Mine Rehabilitation and Mineral Resources Corporation (KOMIR, South Korea)

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Introduction

✓ **The problem of arsenic contamination**

- Arsenic emanating from **mine drainage** substantially endangers our health and crops through the contamination of surface and groundwater
- **World Health Organization (WHO) drinking water** standard for arsenic: **0.01 mg/L**

✓ **The effective removal technique <Adsorption>**

- Adsorption technology is widely used due to its **simplicity, cost-effectiveness, and high removal efficiency**
- In particular, adsorbents **based on ferric hydroxides** are known to be excellent for arsenic removal due to their **strong binding capacity with arsenic**

Introduction

✓ **Characteristics of ferric hydroxides**

- **Large surface area**

- GFH has a large specific surface area of 222 m^2/g (Kumar et al. 2020)

- **High point of zero charge (PZC)**

- Shows excellent effectiveness in adsorbing arsenic, which behaves as oxidized anions

- **High chemical affinity between arsenic and iron**

- Arsenic ions can be electrochemically adsorbed onto ferric hydroxides

➢ **Adsorbents made of ferric hydroxides**

- GFH (Granular Ferric Hydroxides), CMDS (Coal Mine Drainage Sludge), etc.

Materials and methods

✓ Adsorbent Introduction

- **CMDS-Bead and CMDS-Pellet** : Processed into beads and pellets from sludge of the Yeongdong coal mine drainage treatment facilities
- **GFH** : Commercially manufactured ferric hydroxides

GFH

($9)

CMDS-Bead

CMDS-Pellet

($6)

Materials and methods

✓ Batch experiment

- **Adsorption isotherm experiments**

❖ This experiment was conducted in duplicate

1) Prepared solutions of arsenic (As(V)) at **different concentrations** : **(1, 5, 10, 15, 25, 40, 60, 80, 100 mg/L)** Deionized water + $Na_2HAsO_4 \cdot 7H_2O$(98%)
2) 40 mL of As(V) solution was added to 50 mL conical tubes, and 0.2 g of each adsorbent was dosed into them
3) The samples were reacted in a constant temperature shaker at 25±1°C and 150 rpm for either **3 days or 30 days**, and then filtered using 0.45 μm filter paper
4) After sampling in conical tubes, the pH was lowered to below 2 using HNO_3, and the samples were refrigerated at 4°C
5) Arsenic concentrations were then measured using Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES)

- The adsorption isotherm results for three different adsorbents were analyzed using **Langmuir** and **Freundlich models** to assess their characteristics

Materials and methods

✓ **Batch experiment**

- **Adsorption kinetic experiments**

❖ **This experiment was conducted in duplicate**

❖ **The pH was adjusted to 6 using NaOH and HCl**

1) Prepared solutions of arsenic (As(V)) at a **concentration of 29.49 mg/L** : Deionized water + $Na_2HAsO_4 \cdot 7H_2O$(98%)
2) 40 mL of As(V) solution was added to 50 mL conical tubes, and 0.2 g of each adsorbent was dosed into them
3) The solution was reacted for up to **720 hours** at 25± 1°C and 150 rpm, then filtered using a 0.45 μm filter paper
4) After sampling in conical tubes, the pH was lowered to below 2 using HNO_3, and the samples were refrigerated at 4°C
5) Arsenic concentrations were then measured using ICP-OES

- The results of the dynamic adsorption experiments for each of the three adsorbents, based on reaction time, were analyzed using **Pseudo-First-Order (PFO)** and **Pseudo-Second-Order (PSO) kinetic models** to evaluate the characteristics of each adsorbent

Materials and methods

✓ Column experiment methodology

- **Column Specifications**

- H: 30 cm, D: 5 cm, V: 588 mL

- **Raw Water Sources**

- The adsorption experiments were conducted using raw water from the **Goro (GR; As: 0.2-0.5 mg/L)** and the **Geumjeong (GJ; As: 0.4-0.7 mg/L) mine drainages**

- **EBCT and Flow Rate**

- Set an **Empty Bed Contact Time (EBCT) of 22.4 min**, with **a flow rate of 14 mL/min** and a media height of 16 cm

- **Sample Collection and Storage**

- Weekly sampled, acidified with HNO_3 to pH below 2, and stored at 4°C

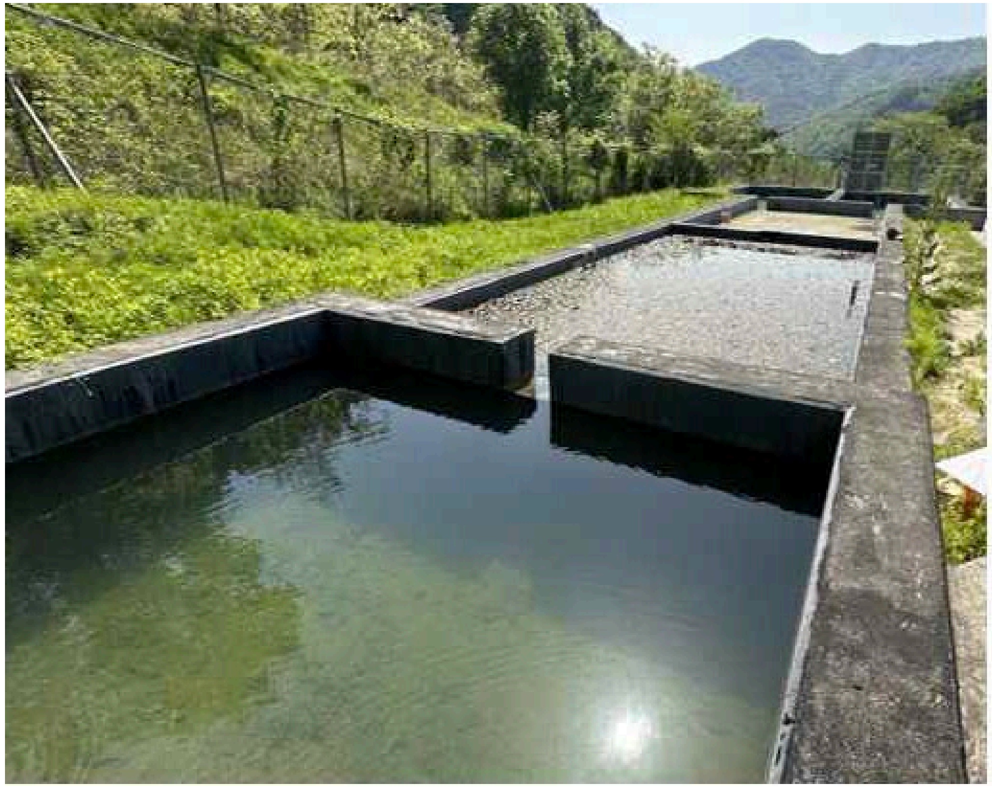
- **Analysis**

- Arsenic concentration was analyzed using ICP-MS

Materials and methods

✓ Column experiment methodology

- Goro mine drainage (GR)



- Geumjeong mine drainage (GJ)

Materials and methods

✓ Column experiment methodology

- Photo of the progress of the column experiment

- Shape and size of adsorbents

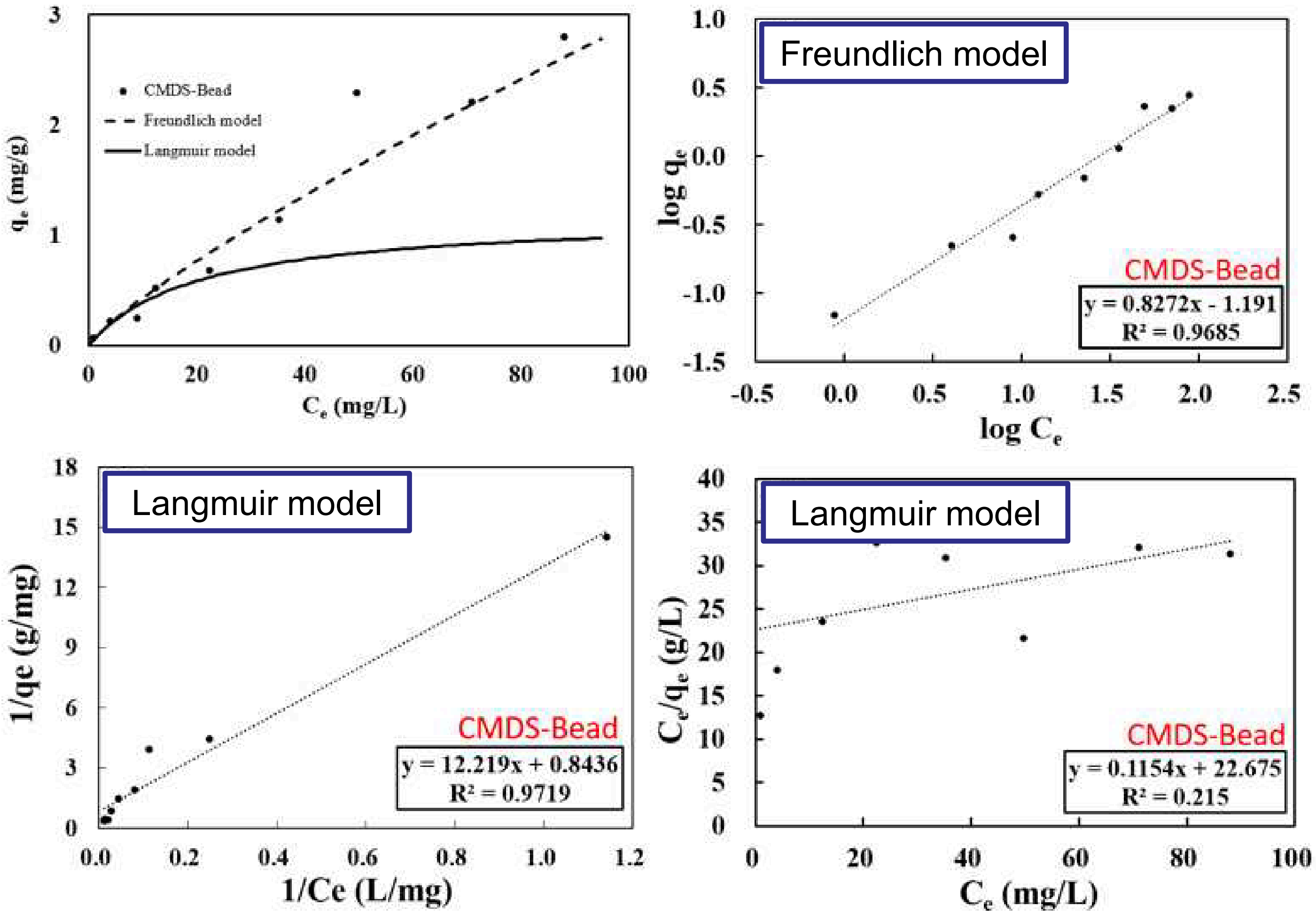
Results & discussion

✓ **Results for adsorption isotherm experiment (CMDS-Bead)**

- **3 days**

- A **higher R^2** of 0.9719 was observed using the **Langmuir model**
- **Langmuir K(K_L) : 0.069 L/mg**
- **Maximum adsorption capacity (Q_{max}) : 1.1855 mg/g**

Arsenic Concentration	Adsorption Rate
1 mg/L	12.4 %
80 mg/L	11.3 %
100 mg/L	12.0 %



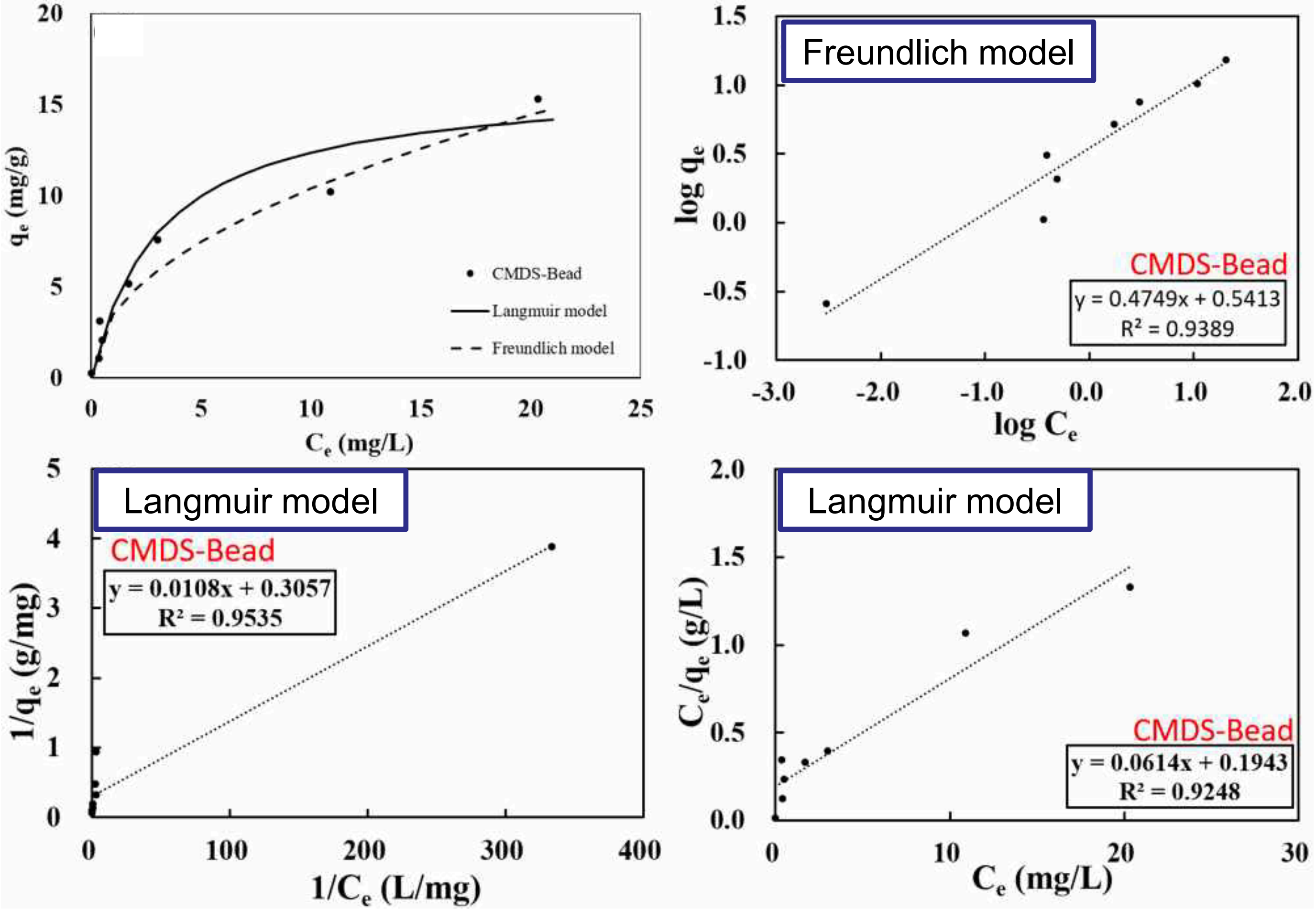
Results & discussion

✓ **Results for adsorption isotherm experiment (CMDS-Bead)**

- **30 days**

- A **higher R^2** of 0.9535 was observed in the **Langmuir model**
- **K_L : 0.31596 L/mg**
- **Q_{max} : 16.285 mg/g**

Arsenic Concentration	Adsorption Rate
1 mg/L	100 %
60 mg/L	81.9 %
100 mg/L	79.7 %



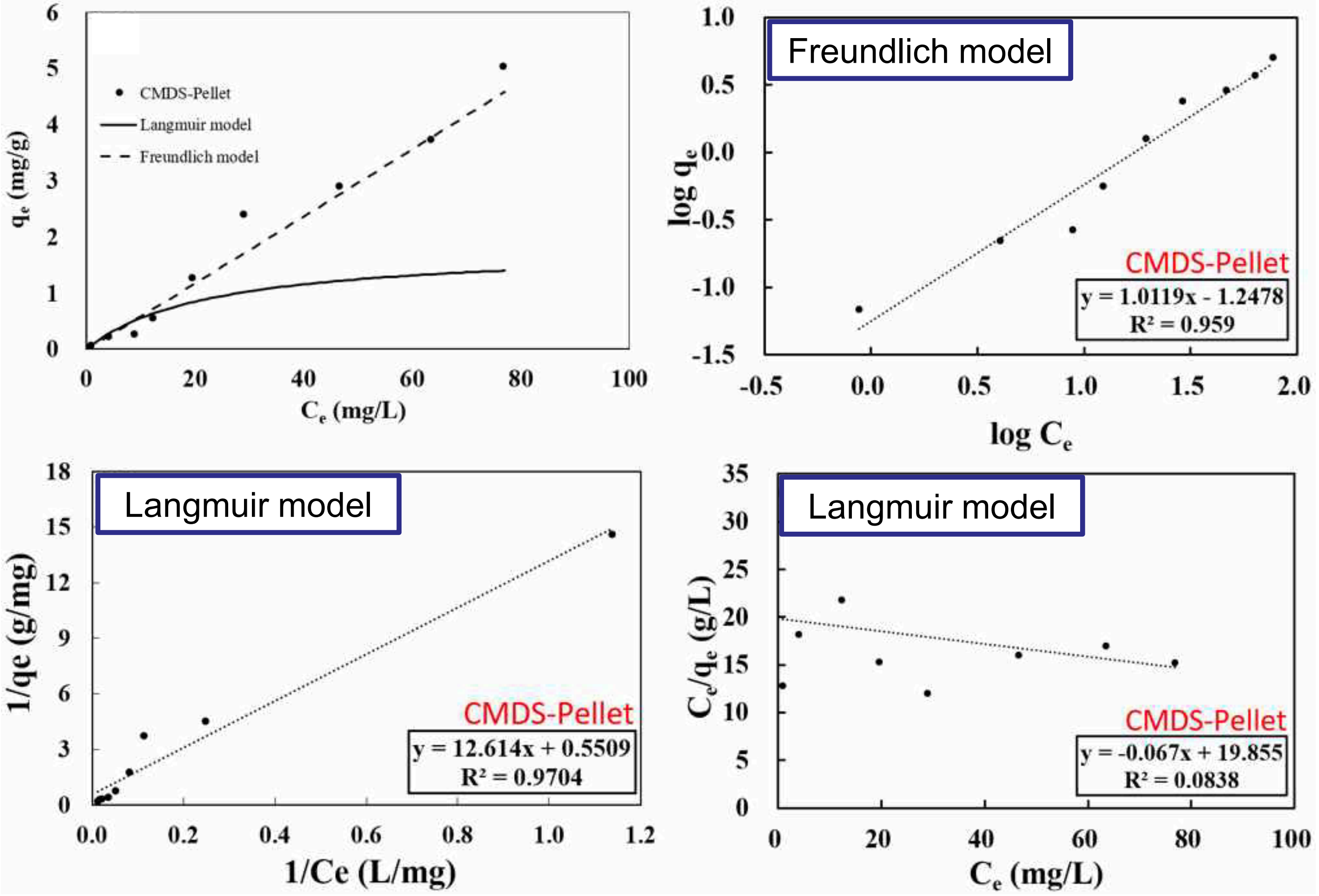
Results & discussion

✓ **Results for adsorption isotherm experiment (CMDS-Pellet)**

- **3 days**

- A **higher R^2** of 0.9704 was observed with the **Langmuir model**
- **K_L : 0.0437 L/mg**
- **Q_{max} : 1.8153 mg/g**

Arsenic Concentration	Adsorption Rate
1 mg/L	12.2 %
80 mg/L	20.8 %
100 mg/L	23.3 %



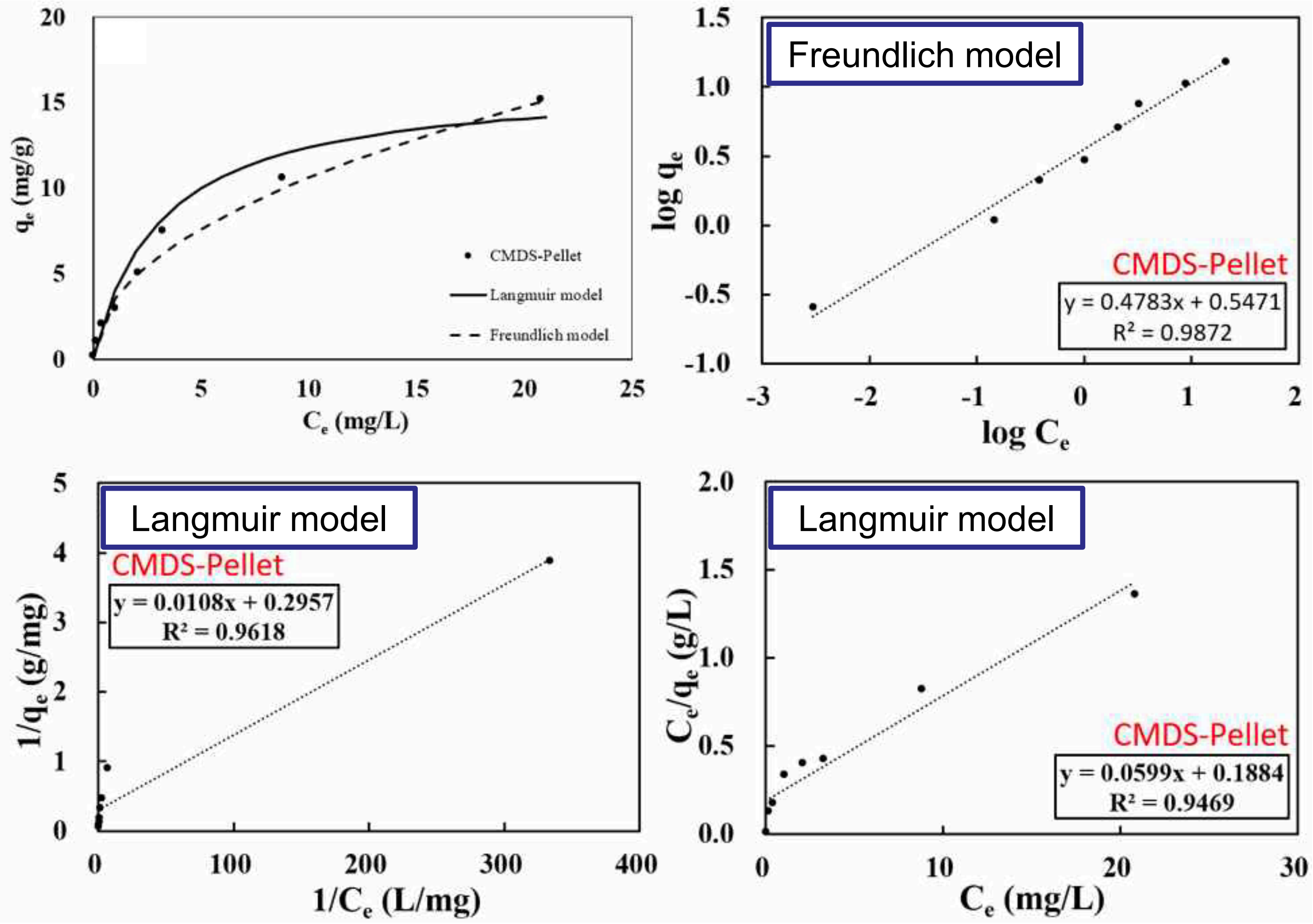
Results & discussion

✓ **Results for adsorption isotherm experiment (CMDS-Pellet)**

- **30 days**

- Although the Freundlich model exhibited a higher R^2, the Langmuir model also showed a significant R^2
- **Q_{max} : 16.7054 mg/g**

Arsenic Concentration	Adsorption Rate
1 mg/L	100 %
60 mg/L	85.4 %
100 mg/L	79.2 %



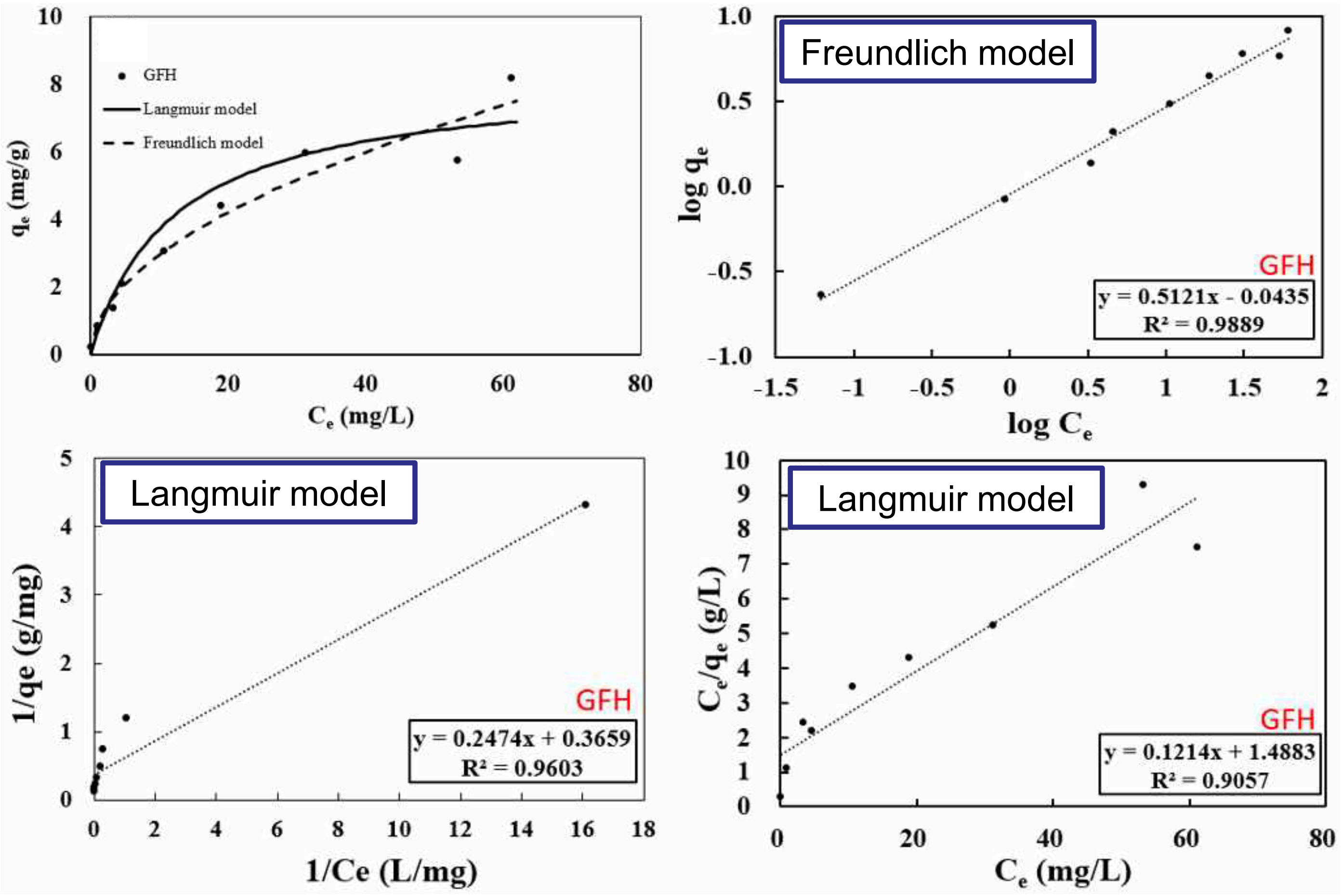
Results & discussion

✓ **Results for adsorption isotherm experiment (GFH)**

- **3 days**

- The Langmuir model had a high R^2, but a **higher R^2 of 0.9889** was observed in the **Freundlich model**
- **K_L : 0.0437 L/mg**
- **K_F : 0.9047 (mg/g) $(L/mg)^{1/n}$**
- **Q_{max} : 2.7331 mg/g**

Arsenic Concentration	Adsorption Rate
1 mg/L	93.8 %
80 mg/L	33.4 %
100 mg/L	38.9 %



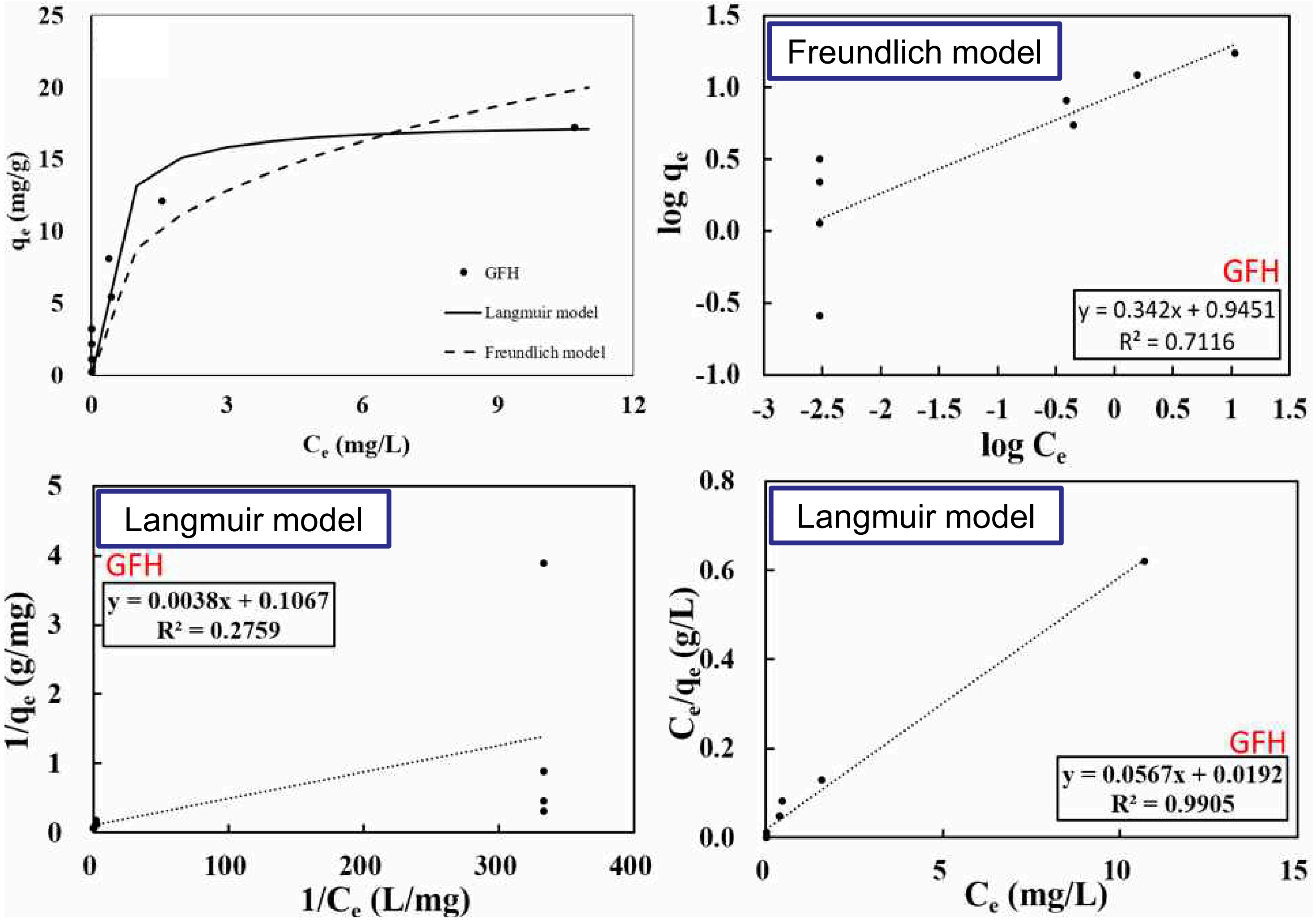
Results & discussion

✓ **Results for adsorption isotherm experiment (GFH)**

- **30 days**

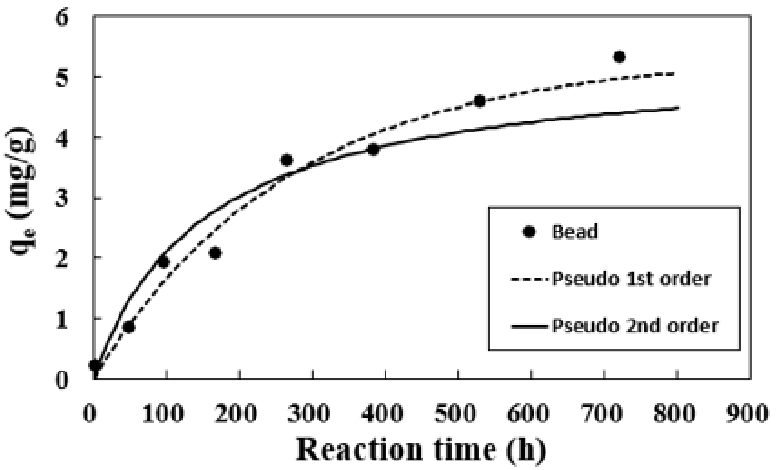
- A **higher R^2** of 0.9905 was observed in the **Langmuir model**
- **K_L : 2.9518 L/mg**
- **Q_{max} : 17.6 mg/g**

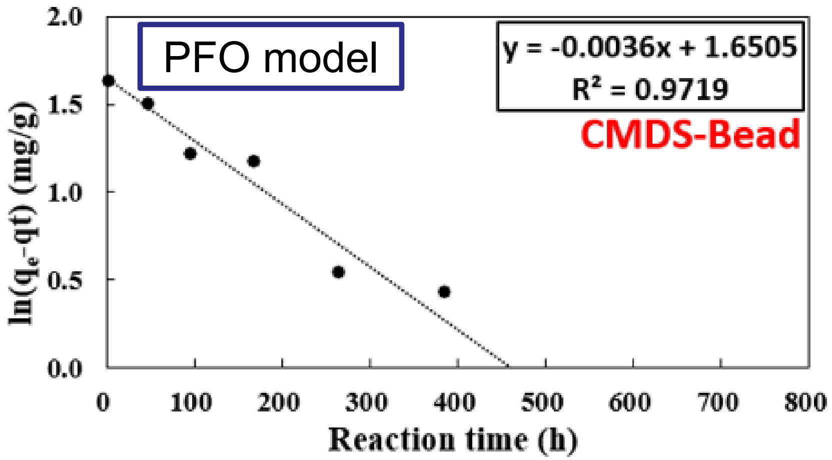
Arsenic Concentration	Adsorption Rate
1, 5, 10, 15 mg/L	100 %
60 mg/L	97.4 %
100 mg/L	89.3 %

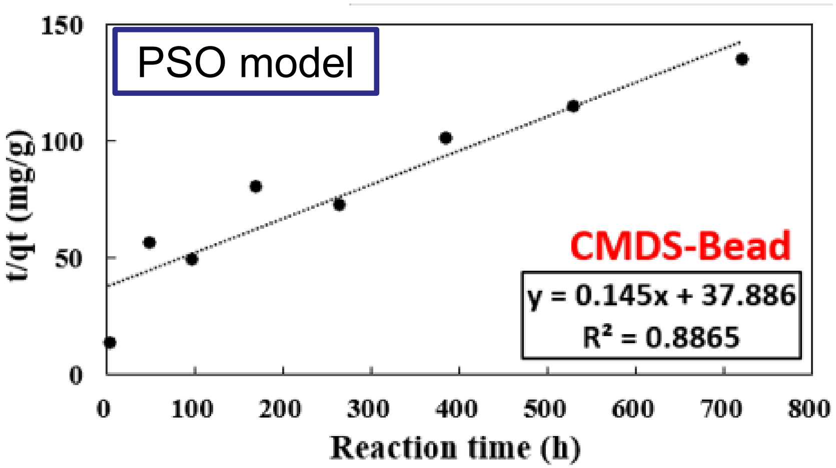


Results & discussion

✓ **Results for adsorption kinetic experiments (CMDS-Bead)** ❖ Initial arsenic concentration of 29.49 mg/L





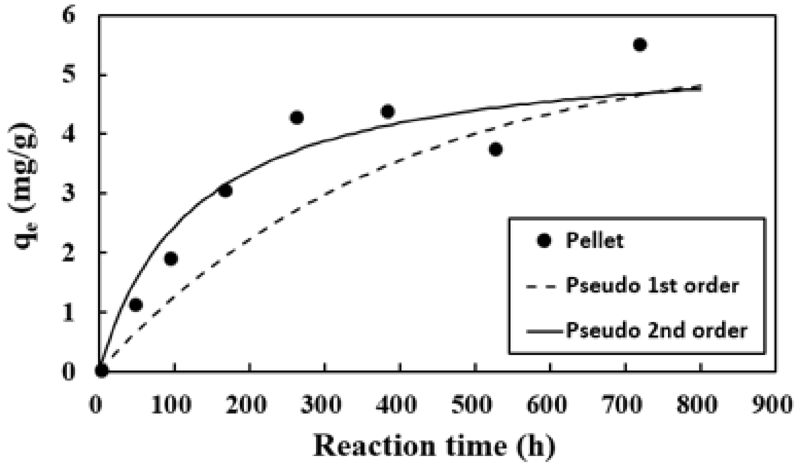


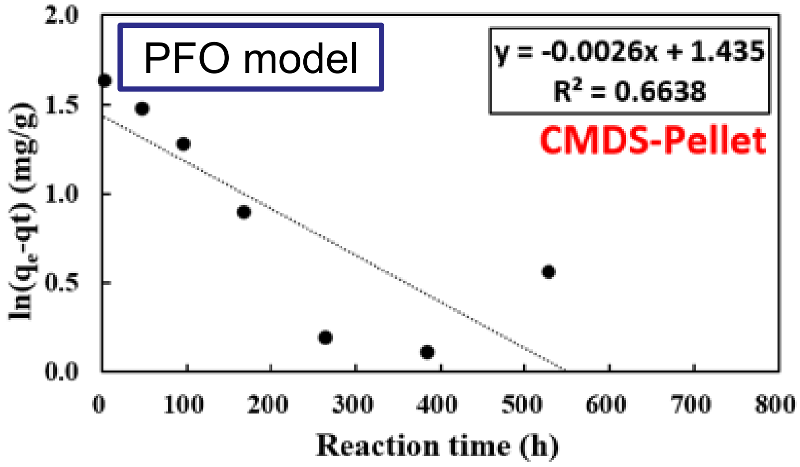
- **No adsorption equilibrium was observed**
- The **PFO** kinetic model exhibited a relatively **higher R^2** value of 0.9719

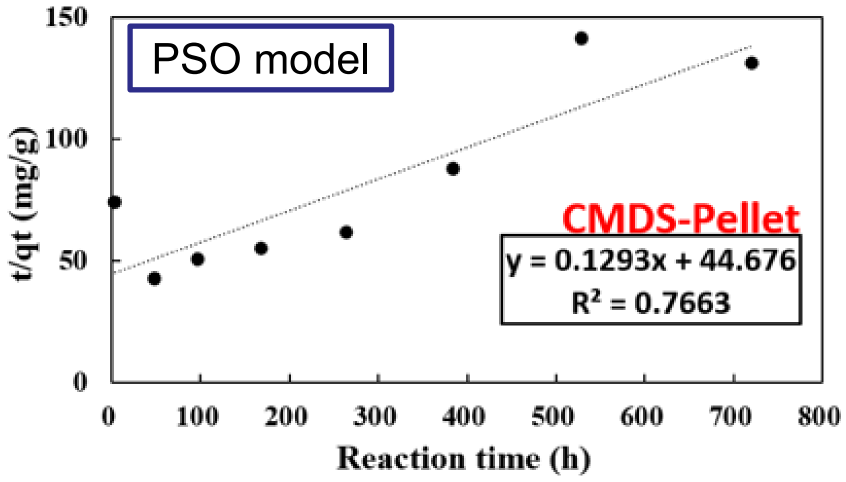
Results & discussion

✓ **Results for adsorption kinetic experiments (CMDS-Pellet)**

❖ Initial arsenic concentration of 29.49 mg/L





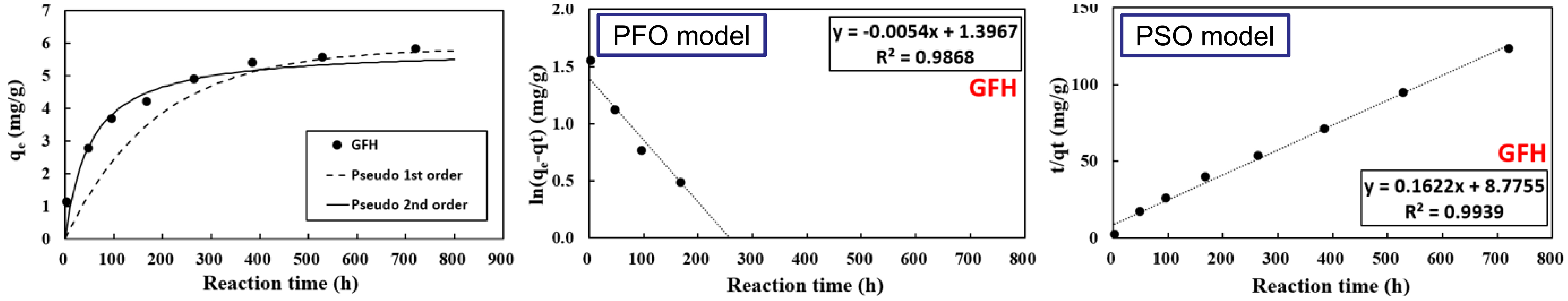


- This demonstrates a trend of increasing adsorption rate over time
- **No adsorption equilibrium was noted**
- A **higher R^2** value of 0.7663 was seen in the **PSO** model compared to the PFO kinetic model

Results & discussion

✓ Results for adsorption kinetic experiments (GFH)

❖ Initial arsenic concentration of 29.49 mg/L



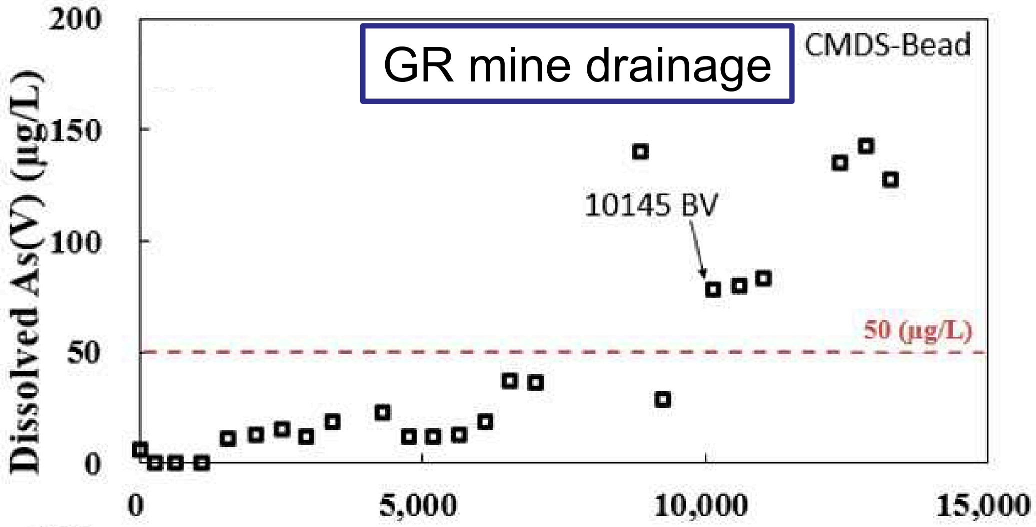
- **The adsorption appeared to approach equilibrium between 15 and 30 days**
- A **higher R^2** value of 0.9939 was observed in the **PSO** kinetic model compared to the PFO kinetic model

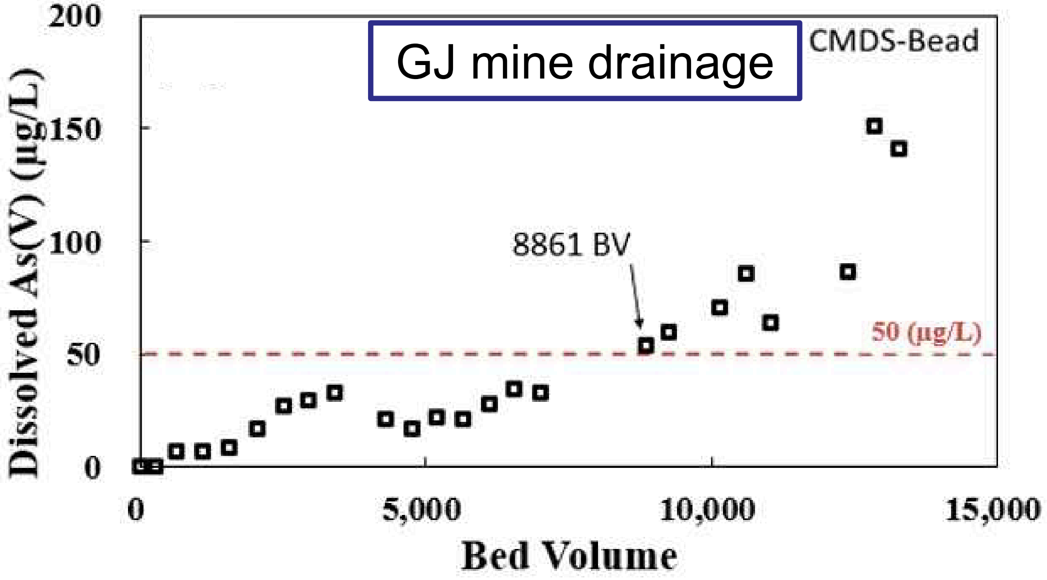
❖ For GFH, similar results aligning with the PSO kinetic model were also reported by Kumar et al. (2020)

Results & discussion

✓ **Arsenic in effluent of column & breakthrough**

- **CMDS-Bead**





Mine drainage	Breakthrough point
GR Mine	10,145 BV
GJ Mine	8,861 BV

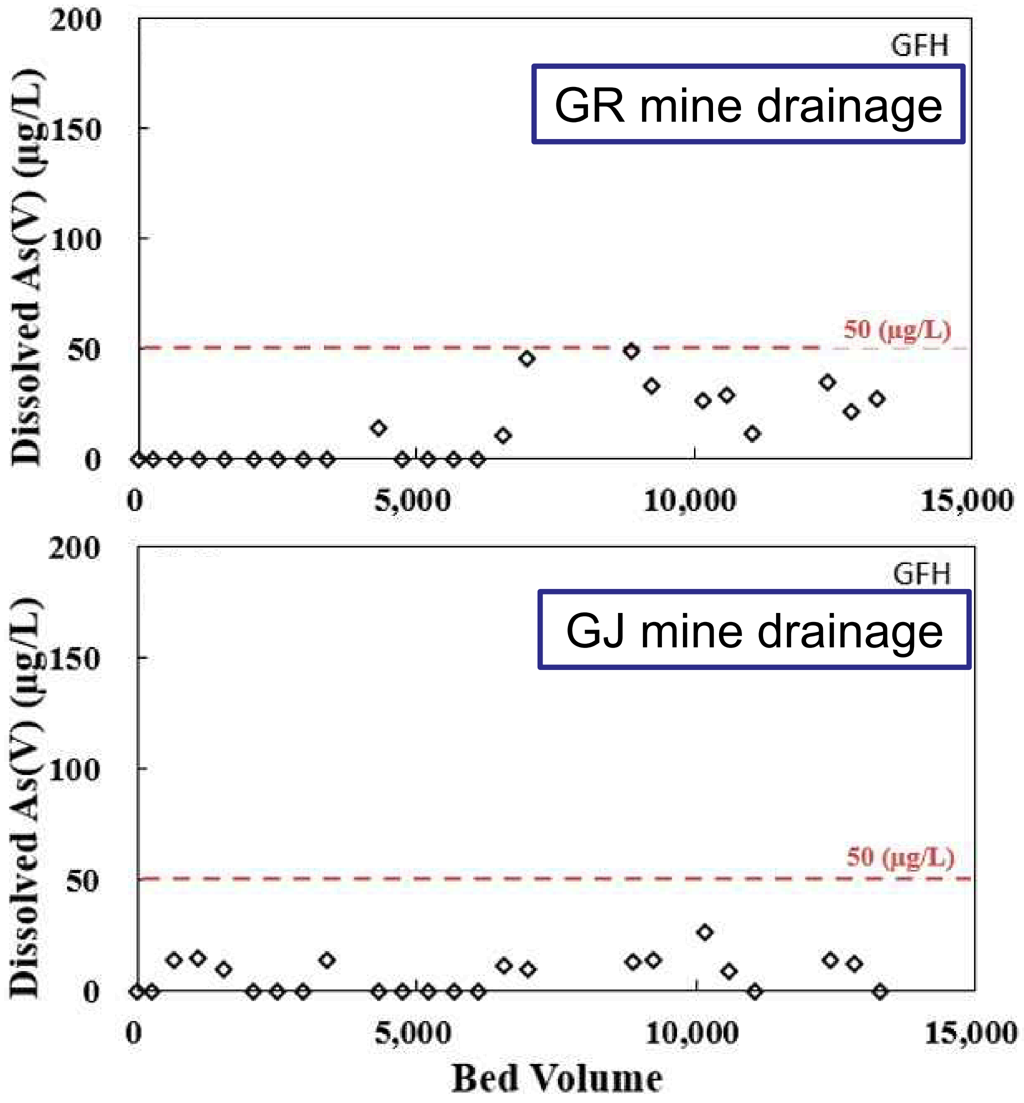
❖ Arsenic discharge standard in the South Korea (0.05 mg L^{-1})

Results & discussion

✓ **Arsenic in effluent of column & breakthrough**

- **GFH**

- **No breakthrough time** observed after 13,291 BV



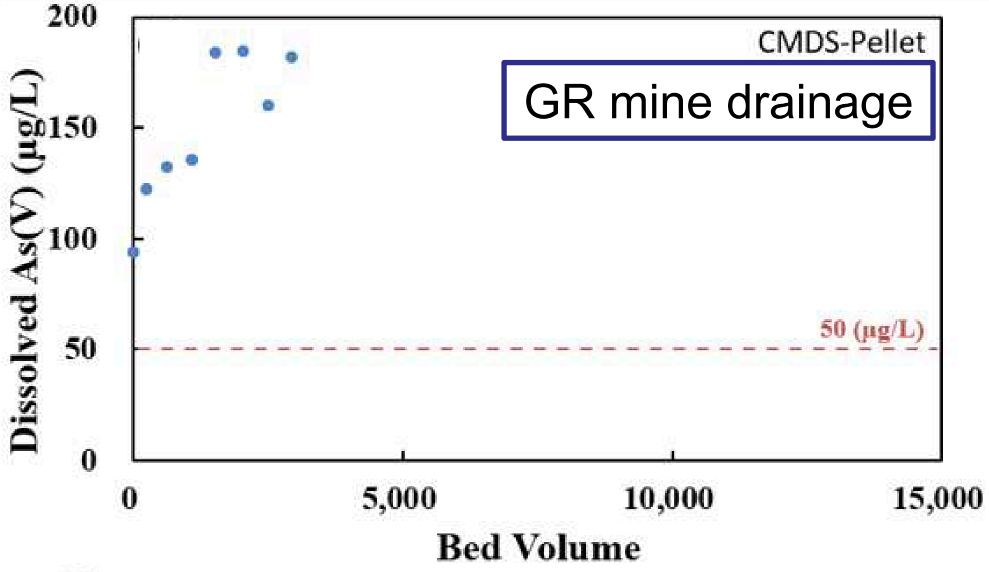
❖ Arsenic discharge standard in the South Korea (0.05 mg L^{-1})

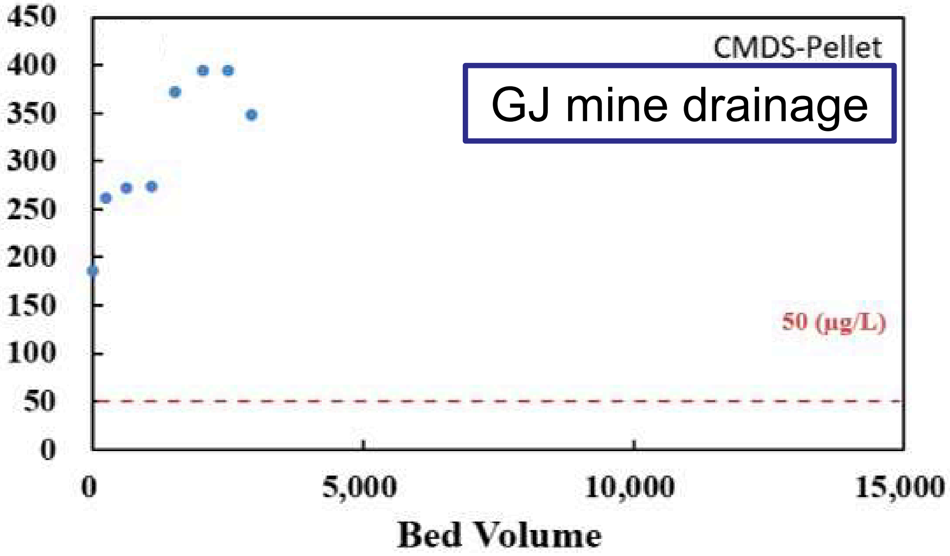
Results & discussion

✓ **Arsenic in effluent of column & breakthrough**

- **CMDS-Pellet**

- The assessment showed that from the beginning, the discharge did not meet the allowed standards





❖ Arsenic discharge standard in the South Korea (0.05 mg L^{-1})

Results & discussion

✓ **Results for column experiments**

- **Calculated hydraulic conductivities**

- The adsorbent repair conductivity is evaluated based on the modified Darcy's law equation

$$K = \frac{Q \cdot L}{A \cdot h \cdot t} \ (cm/sec)$$

(K : hydraulic conductivity [cm/sec], Q : flow rate [cm^3/s], *A* : sample cross-sectional area [cm^2], L : adsorbent length [cm], *t* : permeation time [sec], h : head difference [cm])

Adsorbent	Hydraulic conductivity (cm/sec)	Comparison
CMDS-Bead	5.32×10^{-2}	classified as homogeneous sand
CMDS-Pellet	9.51×10^{-2}	similar to homogeneous gravel or sand
GFH	1.49×10^{-2}	classified as homogeneous sand

Conclusion

- **Adsorption isotherm experiments**
  - CMDS-Bead & Pellet: Langmuir & Freundlich models
  - GFH: Langmuir model
  - Longer experiment (30 d > 3 d) tended to have Langmuir isotherm

Adsorbents	Q_{max} (mg/g)
CMDS-Bead	**16.2**
CMDS-Pellet	**16.7**
GFH	**17.6**

- **Adsorption kinetic experiments**
  - GFH and CMDS-Pellet: PSO model
  - CMDS-Bead: PFO model (may require longer-period assessment)
- **Column experiments (Breakthrough point)**
  - CMDS-Bead: 10,145 BV (GR) / 8,861 BV (GJ)
  - GFH: >13,291 BV

➢ Overall, **CMDS-Bead,** which repurposes waste materials while also being cost-effective, has demonstrated a **high adsorption capacity** similar to that of GFH → **environment-friendly and alternative arsenic adsorbent**

THANK YOU
for
your attention