Case study of arsenite (As^{3+}) sorption onto goethite with difference pH levels: kinetic and equilibrium sorption

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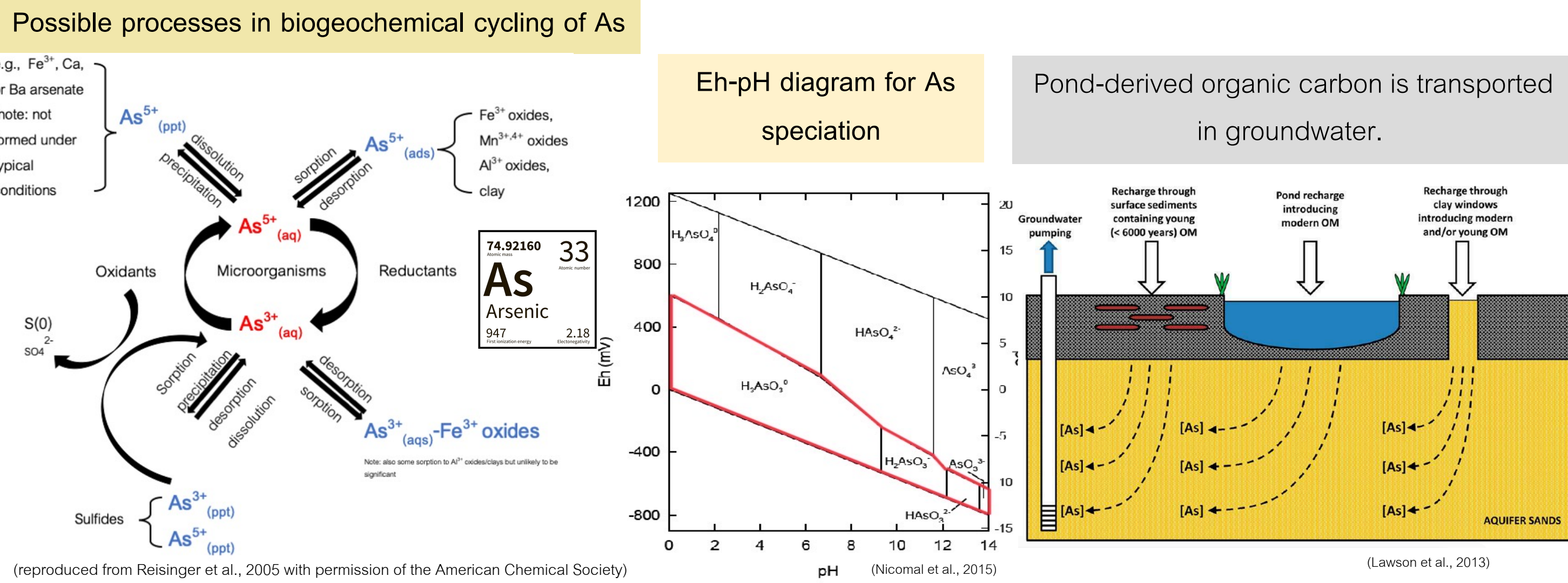
ABSTRACT

Sorption on minerals influences the behavior and movement of arsenic (As) in subsurface environmental systems. Goethite is commonly used to eliminate arsenic in both arsenate (As^{5+}) and arsenite (As^{3+}) forms in iron-containing compounds. In the sorption experiment, different concentrations of As^{3+} and varying pH levels were tested until equilibrium was achieved. In the kinetic experiment, As was sorbed onto goethite at different pH levels and shaken until sorption equilibrium was reached. Physiochemical parameters such as pH, contact time, and initial As^{3+} concentration were assessed using Langmuir and Freundlich isotherms and pseudo-first and pseudo-second-order kinetic models. Results showed the maximum sorption capacity for As^{3+} was 2.17 mg/g at pH 7. The data fit the Freundlich isotherm model better than the Langmuir model across all pH levels (R^2 = 0.99 at pH 7). Although the Langmuir model's separation factor (RL) was between 0-1, indicating a favorable sorption process, the contact time for As^{3+} was observed to be 1,080 minutes for all pH levels. Kinetic data indicated a good fit with the pseudo-second-order model (R^2 = 0.99), with equilibrium rates (k$_2$) of 8.63, 6.08, and 6.48 g/mg·min^{-1} for pH levels 4, 7, and 10, respectively. In conclusion, the study found that a pH level of 7 is effective for the sorption of As^{3+} from aqueous solutions, and goethite could be considered as an As^{3+} sorbent for future investigations in both acidic and alkaline environments.
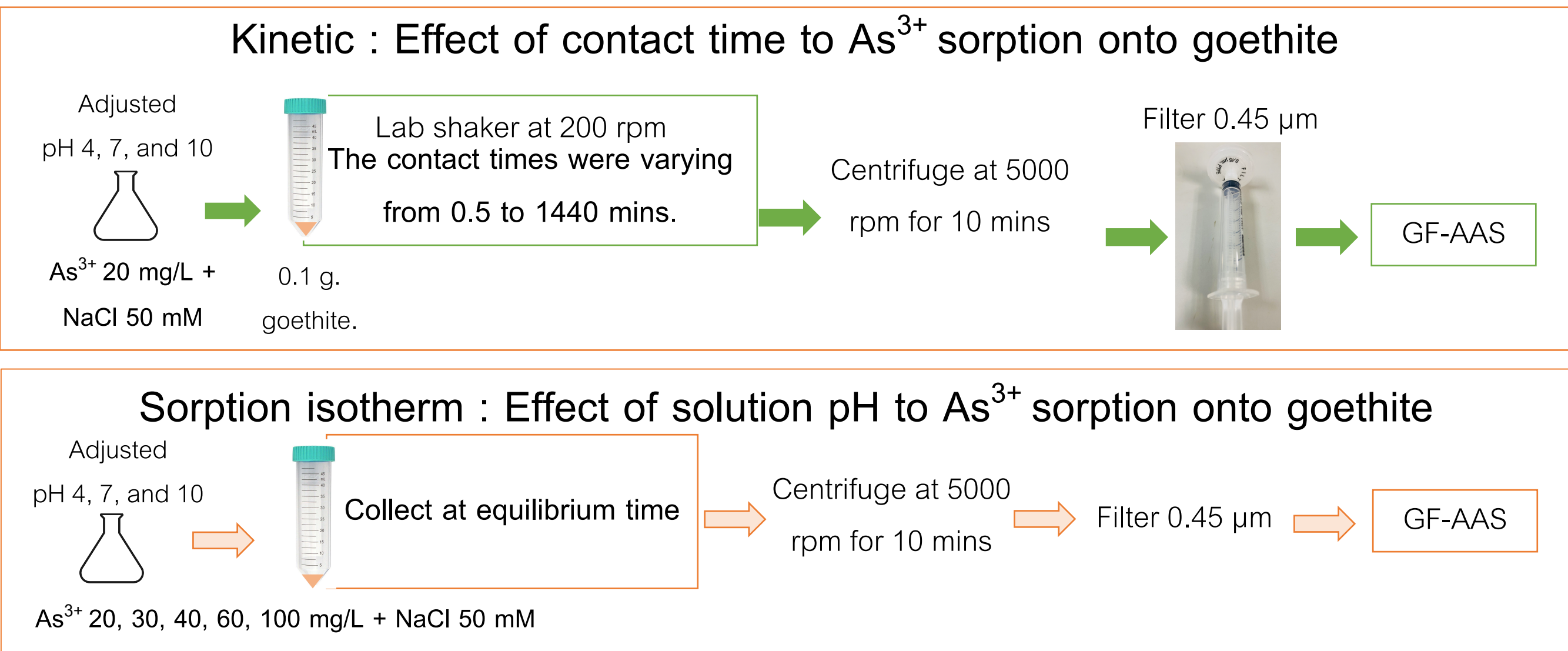
INTRODUCTION

Possible processes in biogeochemical cycling of As

Eh-pH diagram for As speciation

Pond-derived organic carbon is transported in groundwater.

(reproduced from Reisinger et al., 2005 with permission of the American Chemical Society)

(Nicomal et al., 2015)

(Lawson et al., 2013)

OBJECTIVES

1. To investigate the mechanism of As^{3+} transfer to goethite surface under varying pH conditions (4, 7, and 10).
2. To investigate the influence of different pH levels (4, 7, and 10) on the sorption of As^{3+} onto goethite.

METHODOLOGY

Kinetic : Effect of contact time to As^{3+} sorption onto goethite

Adjusted pH 4, 7, and 10

As^{3+} 20 mg/L + NaCl 50 mM

0.1 g. goethite.

Lab shaker at 200 rpm The contact times were varying from 0.5 to 1440 mins.

Centrifuge at 5000 rpm for 10 mins

Filter 0.45 μm

GF-AAS

Sorption isotherm : Effect of solution pH to As^{3+} sorption onto goethite

Adjusted pH 4, 7, and 10

As^{3+} 20, 30, 40, 60, 100 mg/L + NaCl 50 mM

Collect at equilibrium time

Centrifuge at 5000 rpm for 10 mins
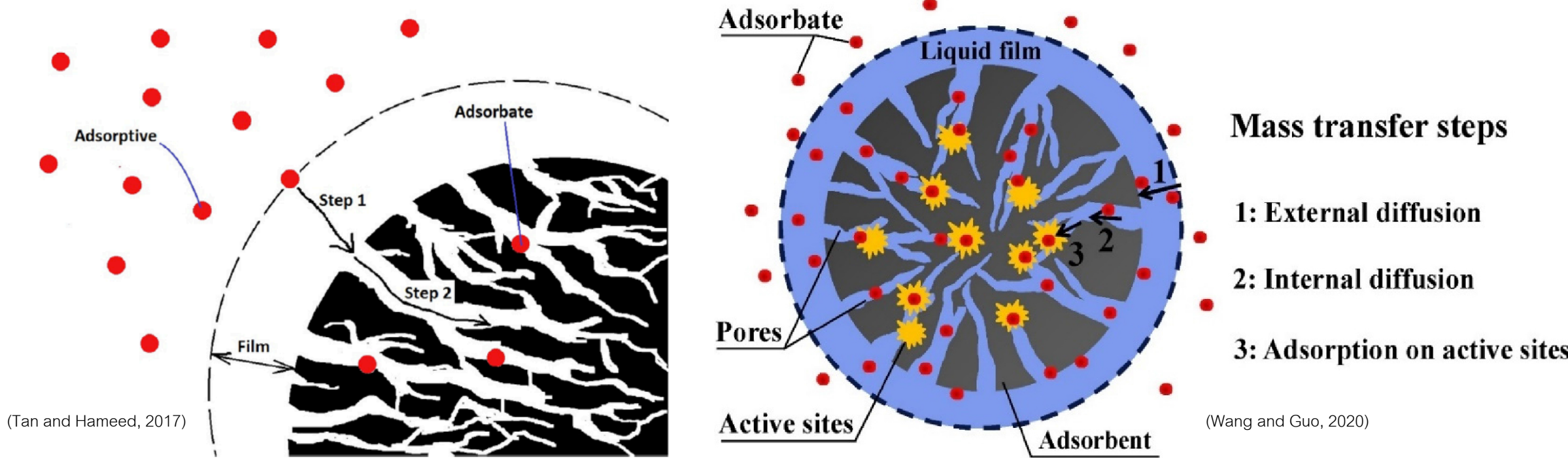
Filter 0.45 μm

GF-AAS

Data analysis

The sorption capacity of As^{3+} concentration sorbed by goethite was calculated by using the following equations 1, 2 : Sorption capacity: $Q_e = \frac{(C_0 - C_e)v}{m}$ % Sorption $= \left(\frac{C_0 - C_e}{C_0}\right)100$

1. Kinetic model

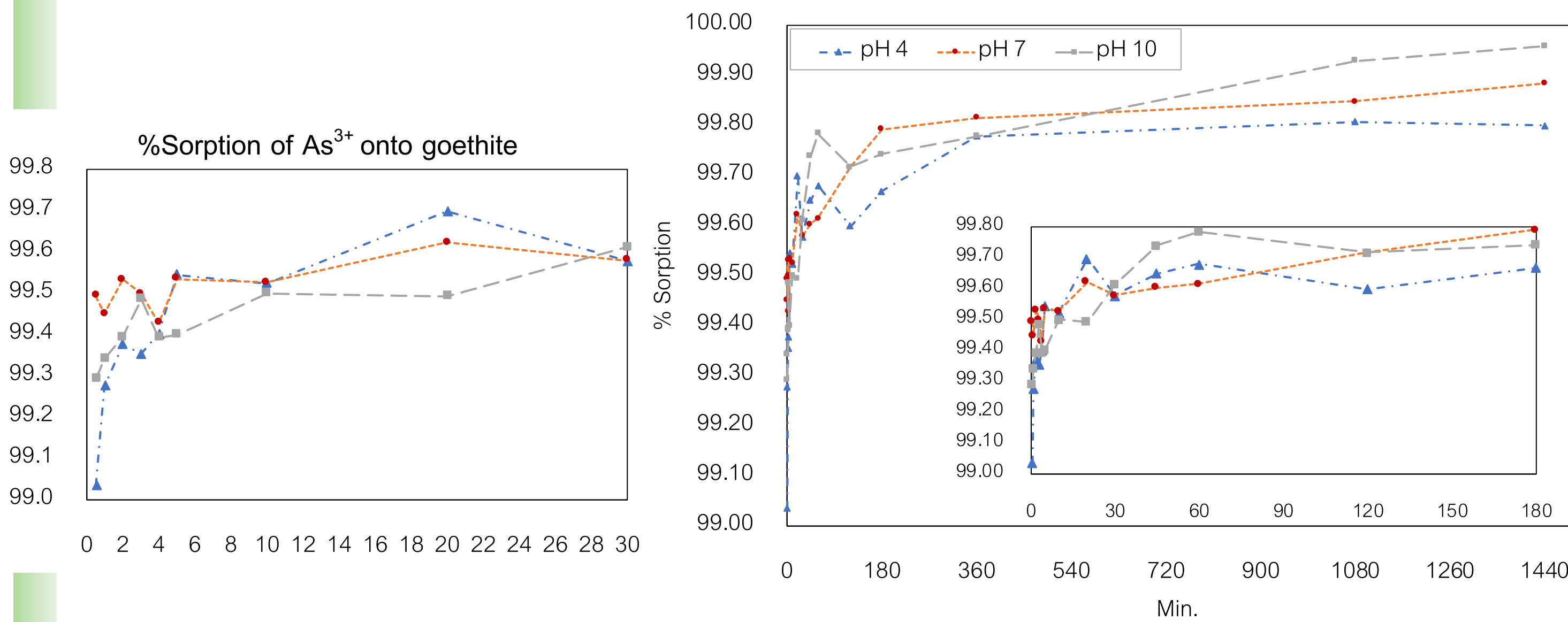| Comparison	Pseudo-first-order model	Pseudo-second-order model
The model assumed	the sorption process results from the electrical attraction between the sorbent surface and sorbate molecules	chemical sorption by the sorbate ions in a liquid solution with exchange electron or valence electron on the sorbent sites
The model equation	$\frac{dq_t}{dt} = k_1(q_e - q_t)$	$\frac{Dq_t}{dt} = k_2(q_e - q_t)^2$
Linear equation	$Log(q_e - q_t) = log q_e - \left(\frac{k_1}{2.303}\right)t$	$\frac{1}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t$

Kinetic model mechanism

Mass transfer steps
1: External diffusion
2: Internal diffusion
3: Adsorption on active sites

(Tan and Hameed, 2017)

(Wang and Guo, 2020)

2. Sorption isotherm

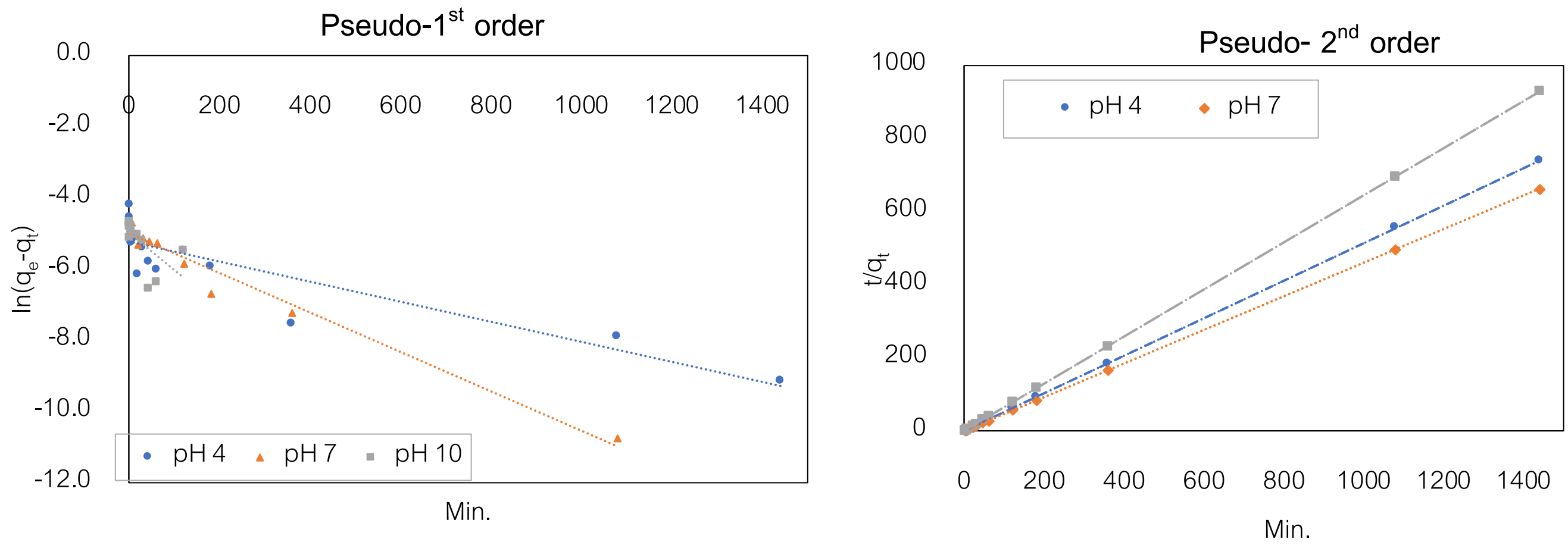| Comparison	Langmuir isotherm	Freundlich isotherm
Sorption site	homogenous	heterogeneous
Sorption layer	mono-layered with a constant energy	multi-layered
Sorbed molecular interaction	✖	✔
Chemical forces	✔	✖
Explanation for chemisorption	✔	✖
The model equation	$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$	$q_e = K_F C_e^{\frac{1}{n}}$
Linear equation	$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m}$	$Log q_e = \frac{1}{n}log C_e + log K_F$

adsorbate

adsorbent
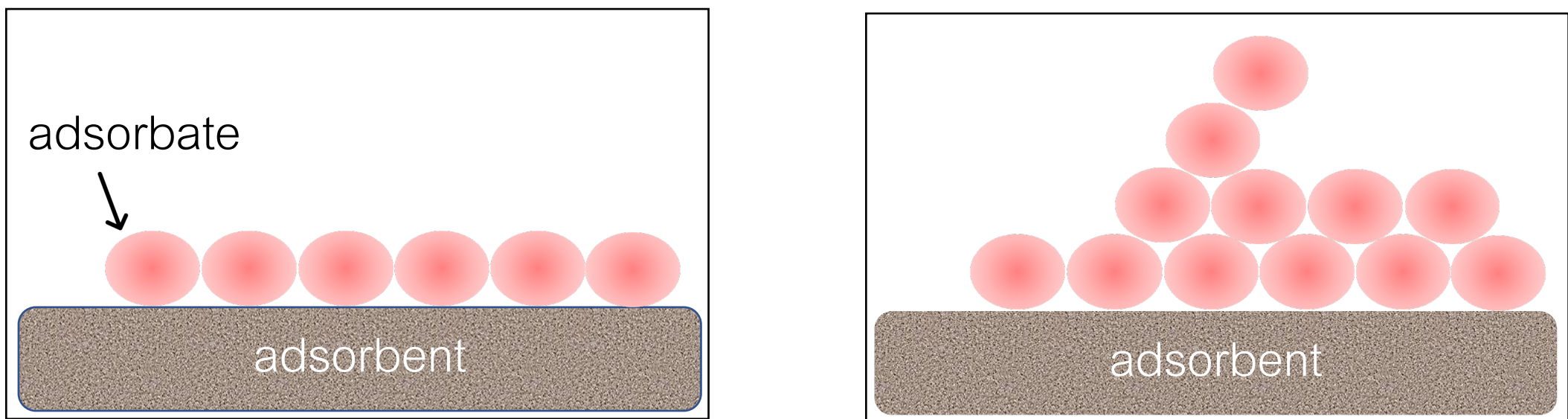
RESULTS

Effect of pH on As^{3+} sorption

%Sorption of As^{3+} onto goethite

Kinetic sorption isotherm

pH	Pseudo-first order			Pseudo-second order		
	Q$_{e(exp)}$ (mg/g)	Q$_{e(cal)}$ (mg/g)	k$_1$ (min^{-1})	R^2	Q$_{e(cal)}$ (mg/g)	k$_2$ (mg/g·min^{-1})	R^2
4	1.9472	5.38×10^{-3}	4.70´10^{-5}	0.8005	1.9547	8.63	0.9999
7	2.1715	6.74×10^{-3}	9.23´10^{-5}	0.9740	2.1721	6.08	0.9999
10	1.5503	6.87×10^{-3}	1.73´10^{-4}	0.3616	1.5508	6.48	0.9999

Pseudo-1st order

Pseudo- 2nd order

Equilibrium sorption As^{3+} onto goethite

Sorption capacity of As^{3+} onto goethite

%Sorption As^{3+} onto goethite
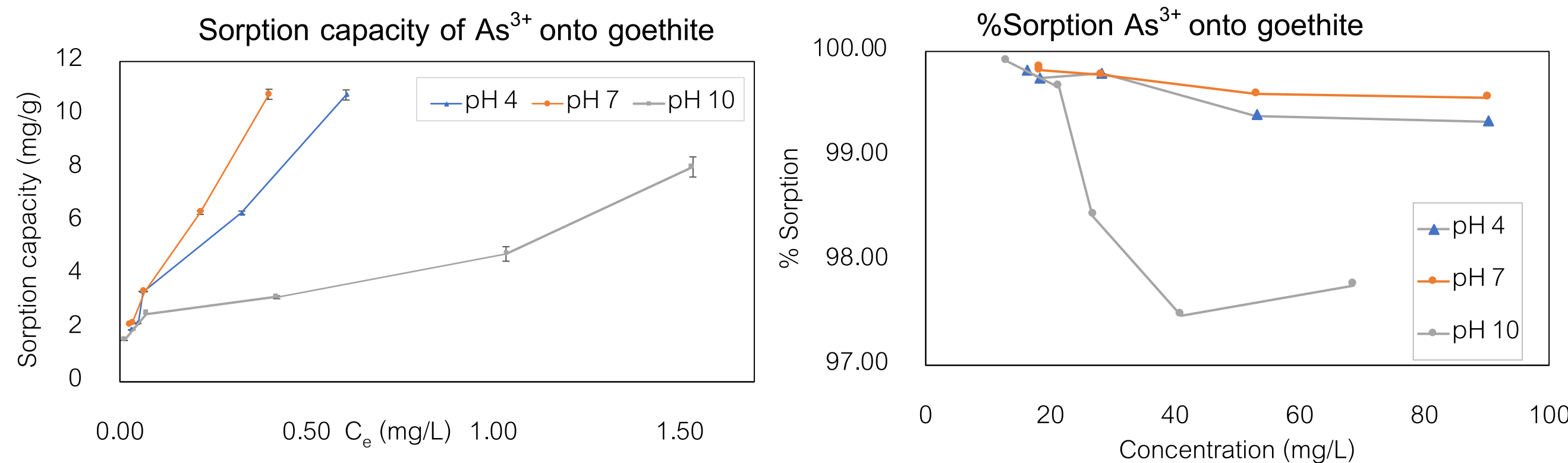
pH	Langmuir isotherm			Freundlich isotherm		
	q$_{m(cal)}$ (mg/g)	K$_L$ (g/L)	R^2	1/n	K$_F$ (g/L)	R^2
4	13.51	4.39	0.89	0.54	13.17	0.97
7	15.17	4.33	0.89	0.59	17.26	0.99
10	7.8	3.54	0.80	0.29	5.32	0.89

Langmuir isotherm

Freudlich isotherm
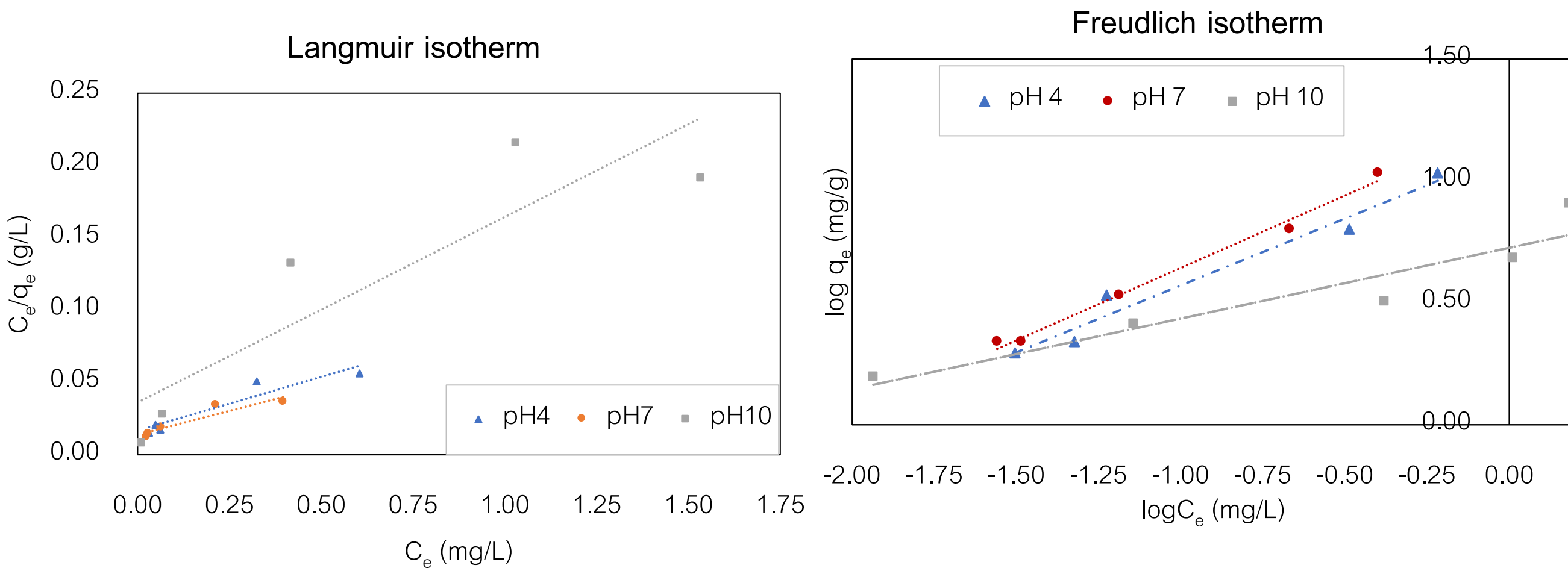
CONCLUSIONS

The rate of As^{3+} ion transport from bulk solution to synthesized goethite varies with different pH levels. The sorption rate is best described by the pseudo-second-order model, indicating that the rate constant (k$_2$) decreases as pH increases. Additionally, the Freundlich isotherm better fits the experimental data compared to the Langmuir isotherm. This characteristic was observed in experiments examining As^{3+} behavior with goethite in natural groundwater. Therefore, pH significantly influences As sorption onto aquifer media and As^{3+}-facilitated goethite colloids in groundwater. Goethite colloids are important for As^{3+} transport, as they can promote As release in groundwater. pH changes also lead to the desorption of As from mineral oxides. These findings provide insight into the pH levels that most affect As^{3+} concentration and suggest treatments to reduce toxicity in groundwater. Further research is needed to assess removal efficiency and material regeneration in water treatment systems.

The physical property of goethite particles	Present study[a]	Literatures	
Chemical composition	α-FeOOH	α-FeOOH	α-FeOOH
pH$_{PZC}$	5.5	6.9±0.2	5.3±0.2
specific surface area (m^2/g)	67	11.61±0.19	8.895
Total pore volume (cm^3/g)	0.21	b	b
Particle size (μm)	1.356	53	74.99

a = Goethite before washed with ultrapure water, b = data not shown

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