Pollutant redistribution in heterogeneous system and data calibration with Semi-Laplace solution

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Introduction

1. Pollutant redistribution in heterogeneous system is ubiquitous in the environment, but traditional numerical solutions are tedious and time-consuming.

2. Semi-Laplace solution is easy to handle and numerical back transformation is very quick and efficient.

3. Three sorption kinetic models (external film diffusion (FD), intraparticle diffusion (IPD) and film-intraparticle diffusion (FIPD)) are applied in Semi-Laplace solution to calibrate the batch test data.

Theory

Mass balance equation:

$$\frac{\partial C_w}{\partial t} + \sum_{i=1}^{n} \beta_i \frac{\partial C_{PE,i}}{\partial t} = 0 \tag{1}$$

Laplace transformation:

$$s\tilde{C}_w - C_w(0) + \sum_{i=1}^{n} \beta_i \left(s\tilde{C}_{PE,i} - C_{PE,i}(0) \right) = 0 \tag{2}$$

Semi-Laplace solution in heterogeneous system:

$$\tilde{C}_{PE,i} = \tilde{g}_i(s) \left(\tilde{C}_w - \frac{C_{PE,i}(0)}{sK_{PE,i}} \right) + \frac{C_{PE,i}(0)}{s} \tag{3}$$

$$\tilde{C}_w = \frac{C_w(0) + \sum_{i=1}^{n} \beta_i \tilde{g}_i(s) \frac{C_{PE,i}(0)}{K_{PE,i}}}{s\left(1 + \sum_{i=1}^{n} \beta_i \tilde{g}_i(s)\right)} \tag{4}$$

$$\tilde{g}_i(s) = \begin{cases} \dfrac{k_i K_{PE,i}}{k_i + \frac{1}{3}\rho_{PE,i} K_{PE,i} R_i s} & \text{FD} \\[2ex] D_{PE,i} K_{PE,i} \left(\sqrt{\dfrac{s}{D_{PE,i}}} \coth\left(R_i \sqrt{\dfrac{s}{D_{PE,i}}} \right) - \dfrac{1}{R_i} \right) \dfrac{3}{R_i s} & \text{IPD} \\[2ex] \dfrac{D_{PE,i} K_{PE,i} \left(\sqrt{\frac{s}{D_{PE,i}}} \coth\left(R_i \sqrt{\frac{s}{D_{PE,i}}} \right) - \frac{1}{R_i} \right) k_i \frac{3}{R_i s}}{k_i + D_{PE,i} K_{PE,i} \rho_{PE,i} \left(\sqrt{\frac{s}{D_{PE,i}}} \coth\left(R_i \sqrt{\frac{s}{D_{PE,i}}} \right) - \frac{1}{R_i} \right)} & \text{FIPD} \end{cases} \tag{5}$$

β_i : solid to liquid ratio of PE particle i ($\beta_i = m_{PE,i}/V_w$) [kg/L]
C_w : solute concentration in aqueous phase [μg/L]
$C_w(0)$: initial solute concentration in aqueous phase [μg/L]
$C_{PE,i}$: solute concentration in PE particle i [μg/kg]
$C_{PE,i}(0)$: initial solute concentration in PE particle i [μg/kg]
s : complex Laplace coordinate [T^{-1}]
$K_{PE,i}$: PE particle i/water partitioning coefficient [μg/kg]
k_i : mass transfer velocity of PE particle i $\left(k_i = \frac{D_{aq,i}}{\delta_i} \right)$ [m/s]
R_i : radius of PE particle i [m]
$\rho_{PE,i}$: density of PE particle i [kg/L]
$D_{PE,i}$: diffusion coefficient in PE particle i [m^2/s]
t : time [s]
$\tilde{g}_i(s)$: specific transform function between $C_{PE,i}$ and C_w in Laplace coordinate

Sherwood numbers to estimate the film thickness δ

$$Sh = \frac{k\,d}{D_{aq}} = \frac{d}{\delta} \Rightarrow \delta = \frac{d}{Sh} \tag{6}$$

(a) Boundary layer theory (mass and momentum balance)

$$\left(\frac{\delta}{\delta_L}\right)^3 \sim \frac{1}{Sc} \quad \text{and} \quad \delta_L \sim \frac{1}{Re^{\alpha}} \quad \text{for } Re < 10^5$$

δ: concentration boundary layer [m]
δ_L: laminar flow boundary layer [m]
Sc: Schmidt number [-]
Re: Reynolds number [-]

(b) Molecular diffusion of spherical particles in stagnant water phase

$$Sh = 2$$

Empirical relationship

$$Sh = 2 + BRe^{\alpha}Sc^{1/3}$$

Application of Kolmogoroff's theory to mass transfer of suspended particles

$$\eta = \left(\frac{v_v^3}{\varepsilon}\right)^{\frac{1}{4}}$$

Macroparticle $d \gg \eta$ $\alpha = 3/4$
Microparticle $d \ll \eta$ $\alpha = 1/2$

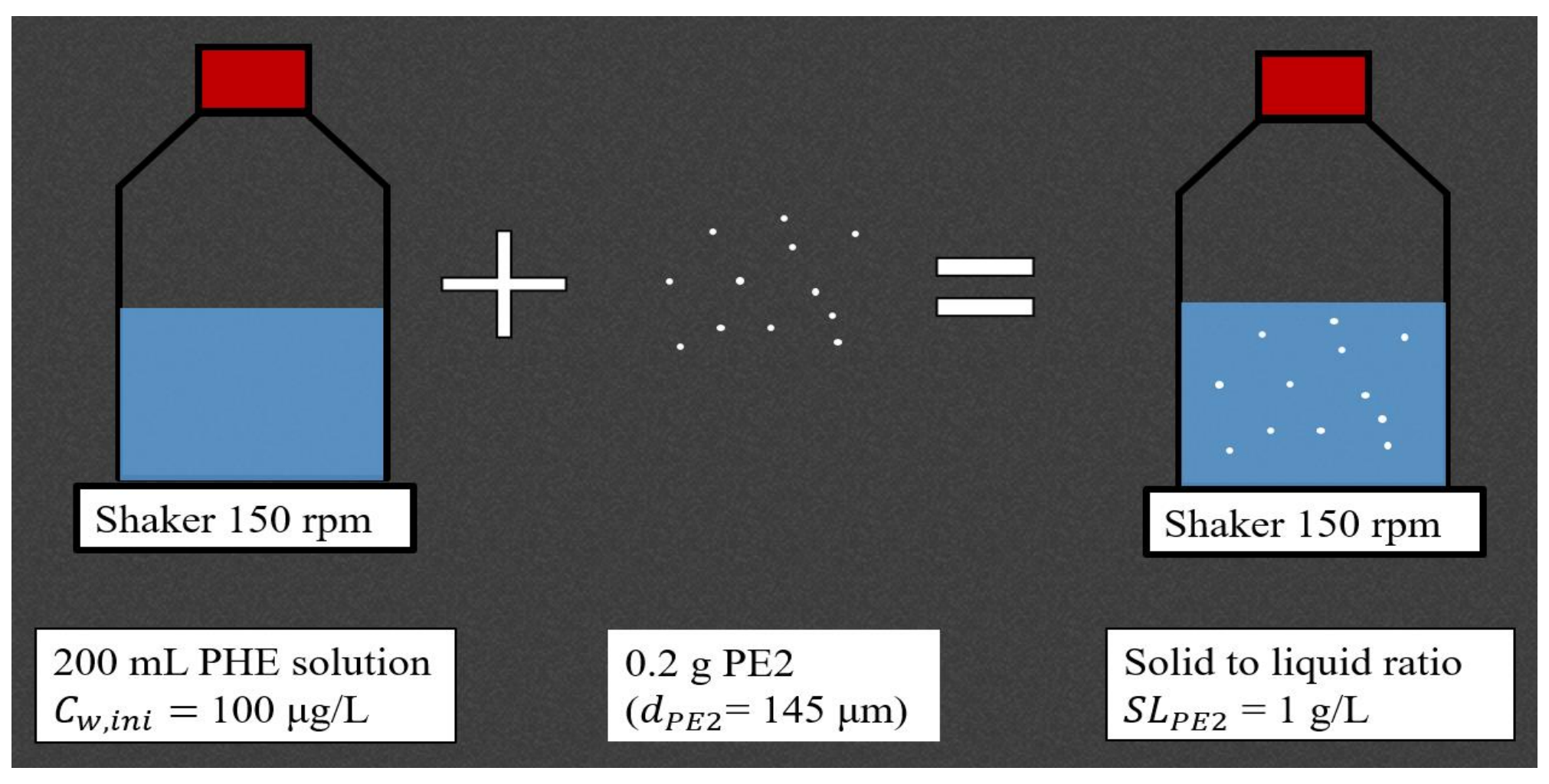
$$Re = \frac{(\varepsilon d)^{1/3} d}{v_v} = \left(\frac{d}{\eta}\right)^{4/3}$$

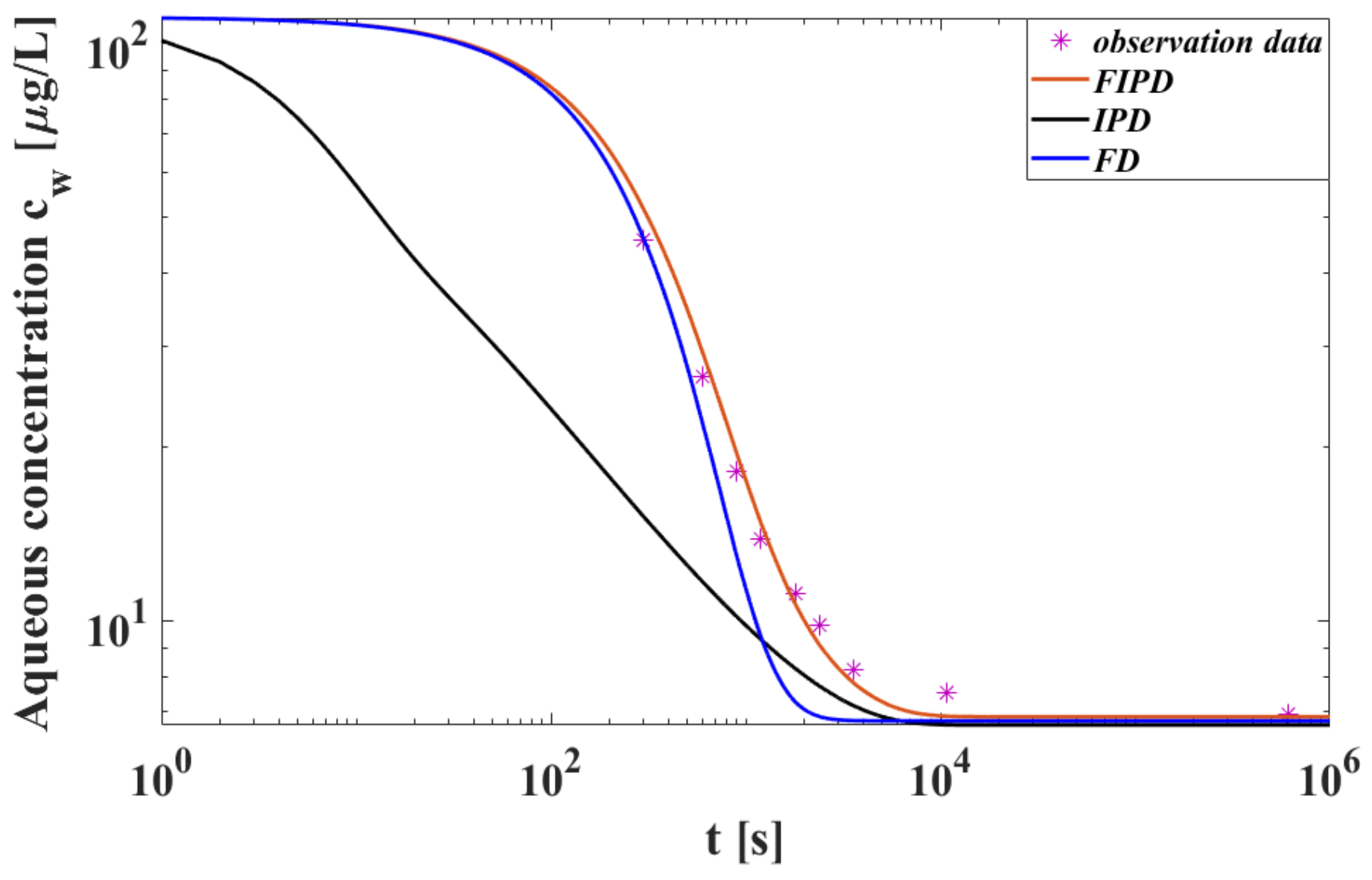
η : Kolmogoroff length scale [m]
ε: energy dissipation rate [W/kg] ($\varepsilon = P/M$)
v_v: kinematic viscosity of the fluid [m²/s]

Results

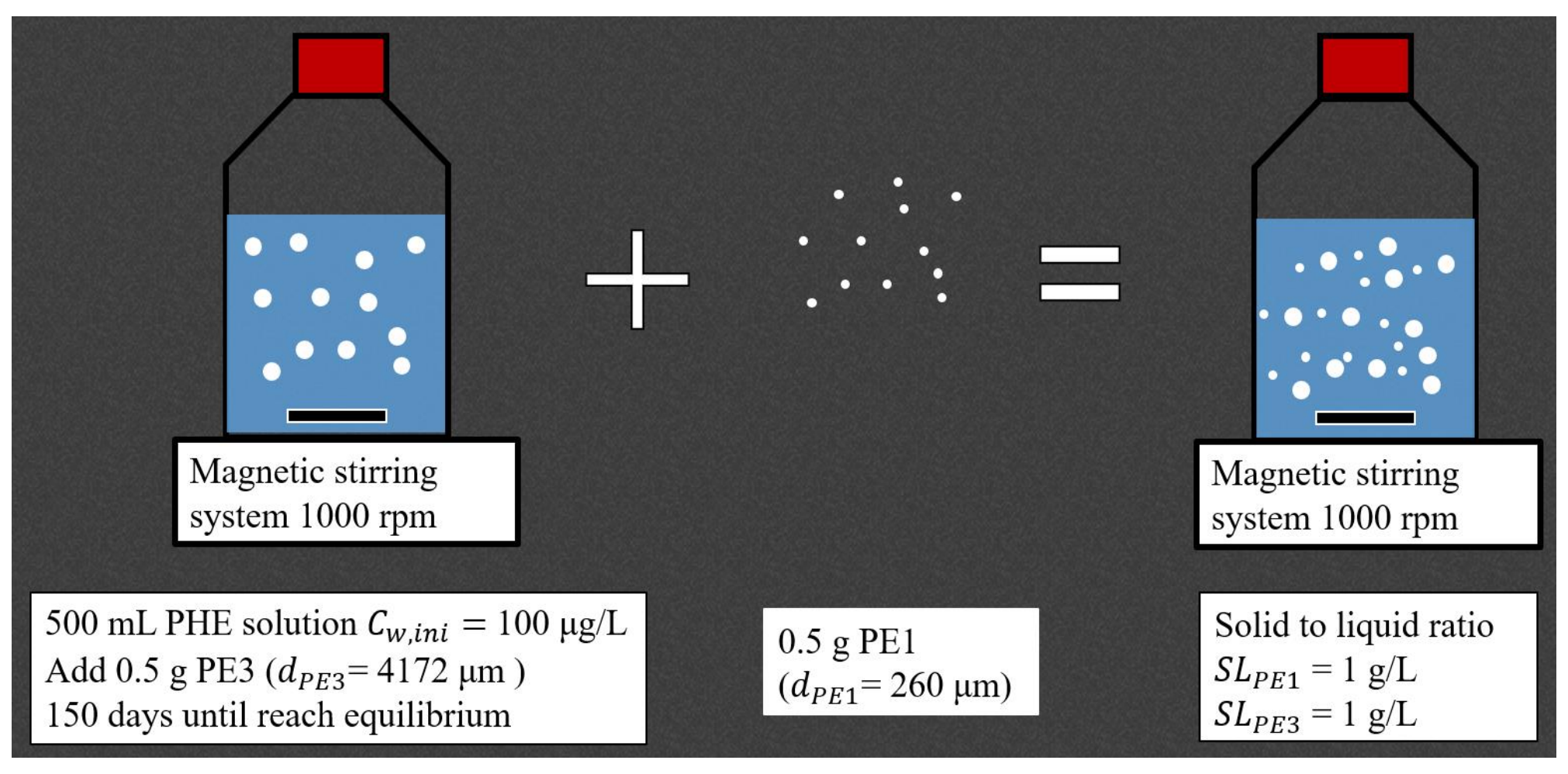
Batch test results:

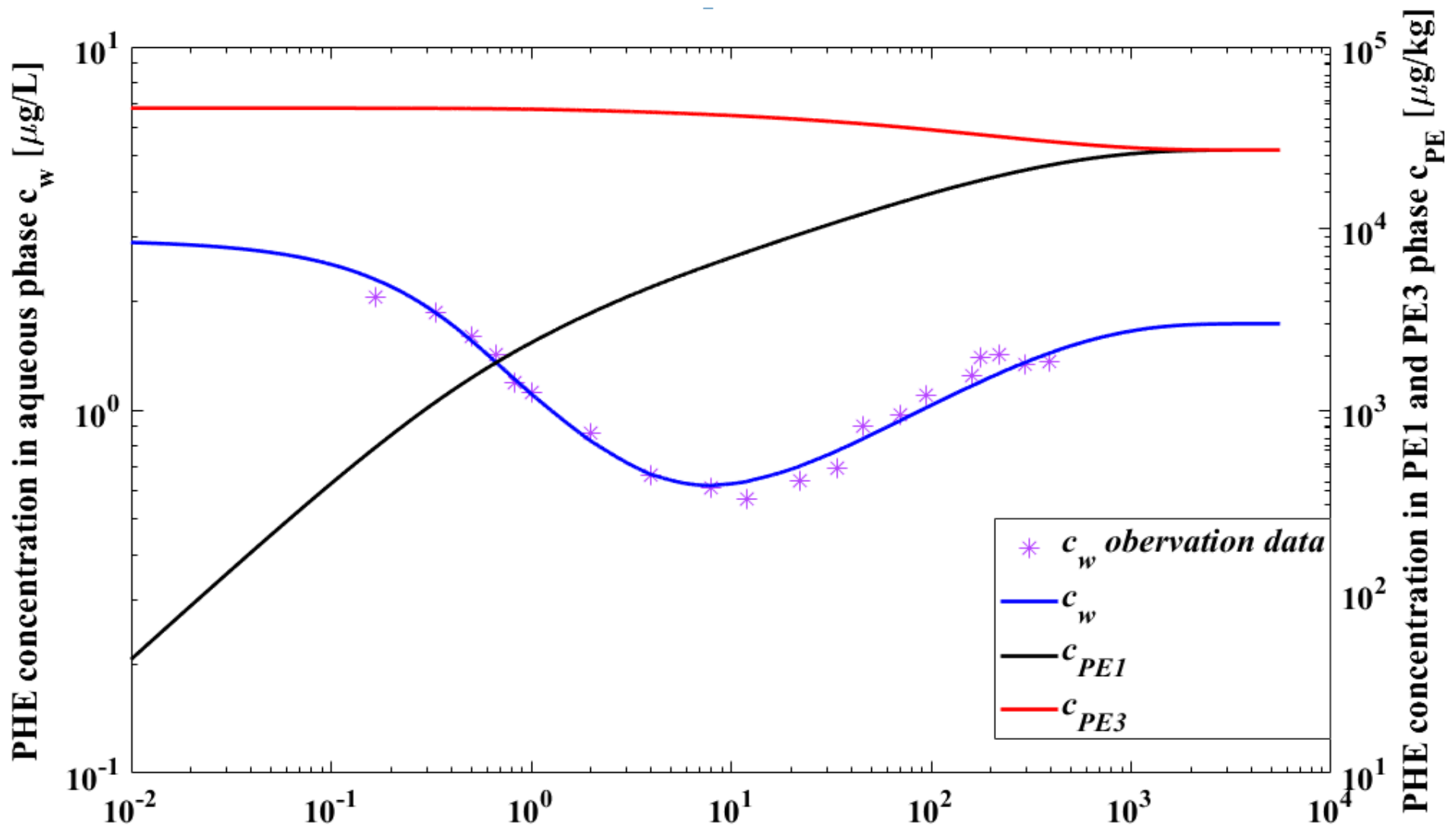
Batch test 1: Sorptive uptake of small PE particles (PE2)



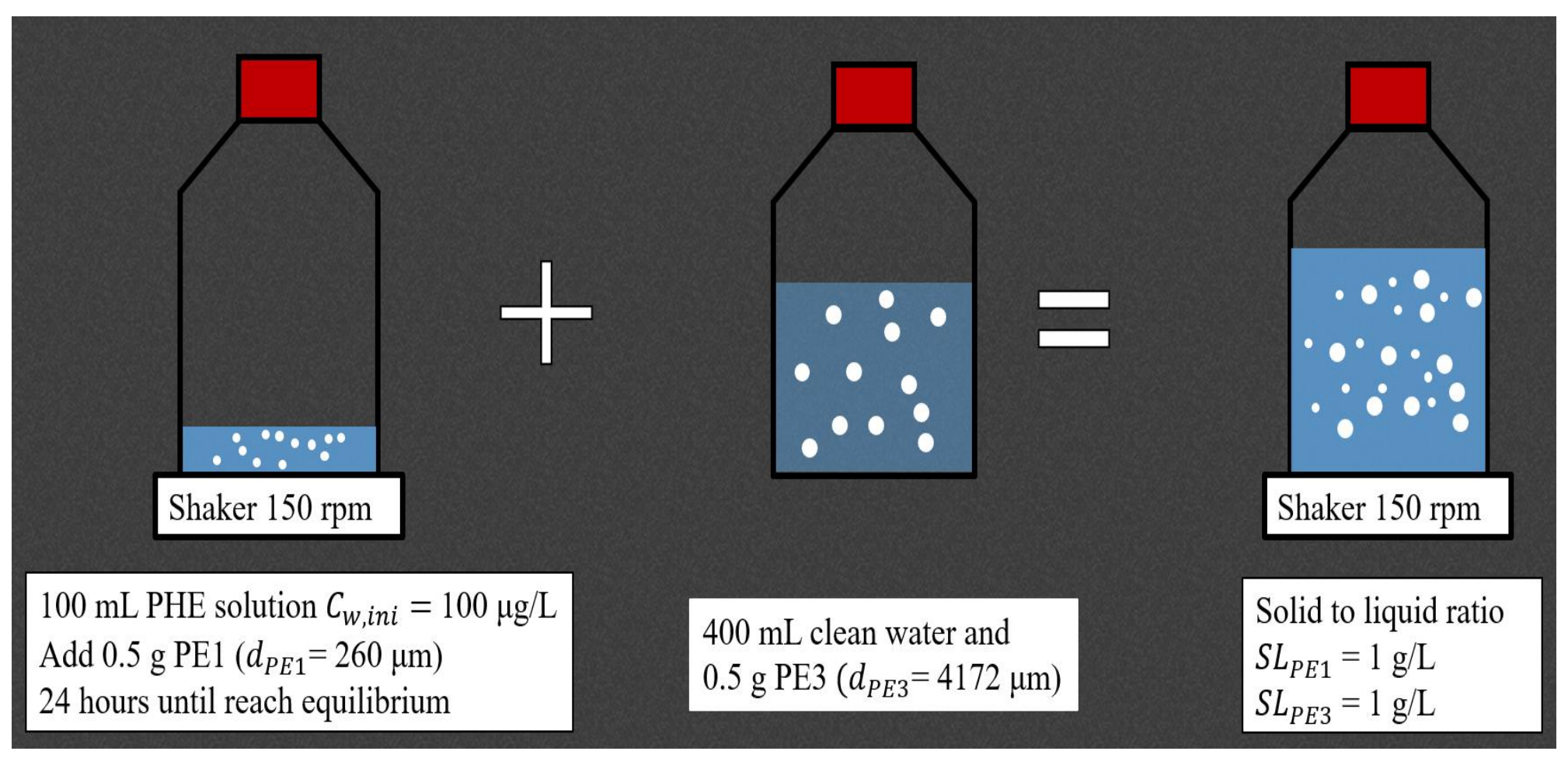


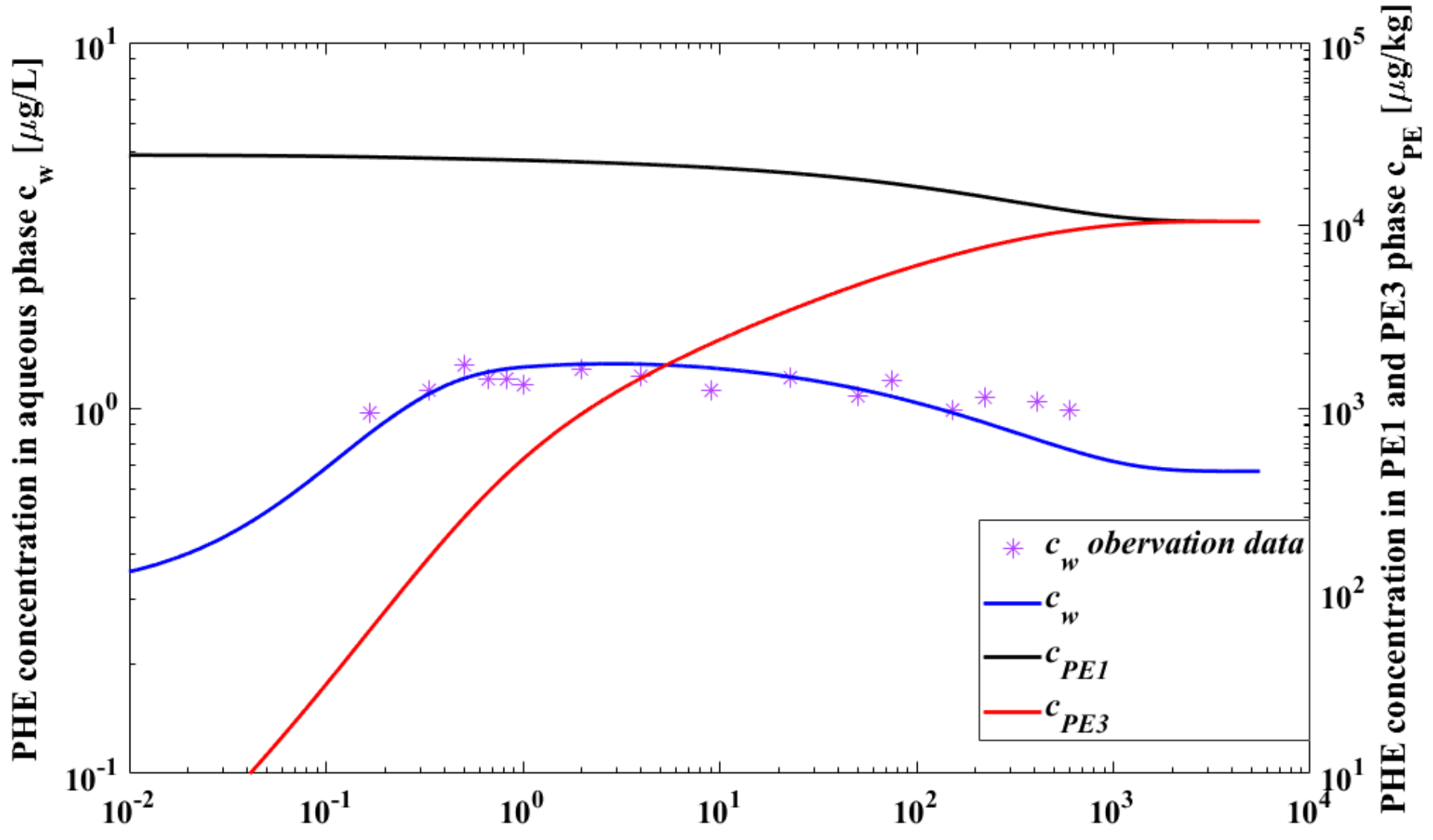
Batch test 2: Preloaded large PE particles (PE3) + clean small PE particles (PE1)



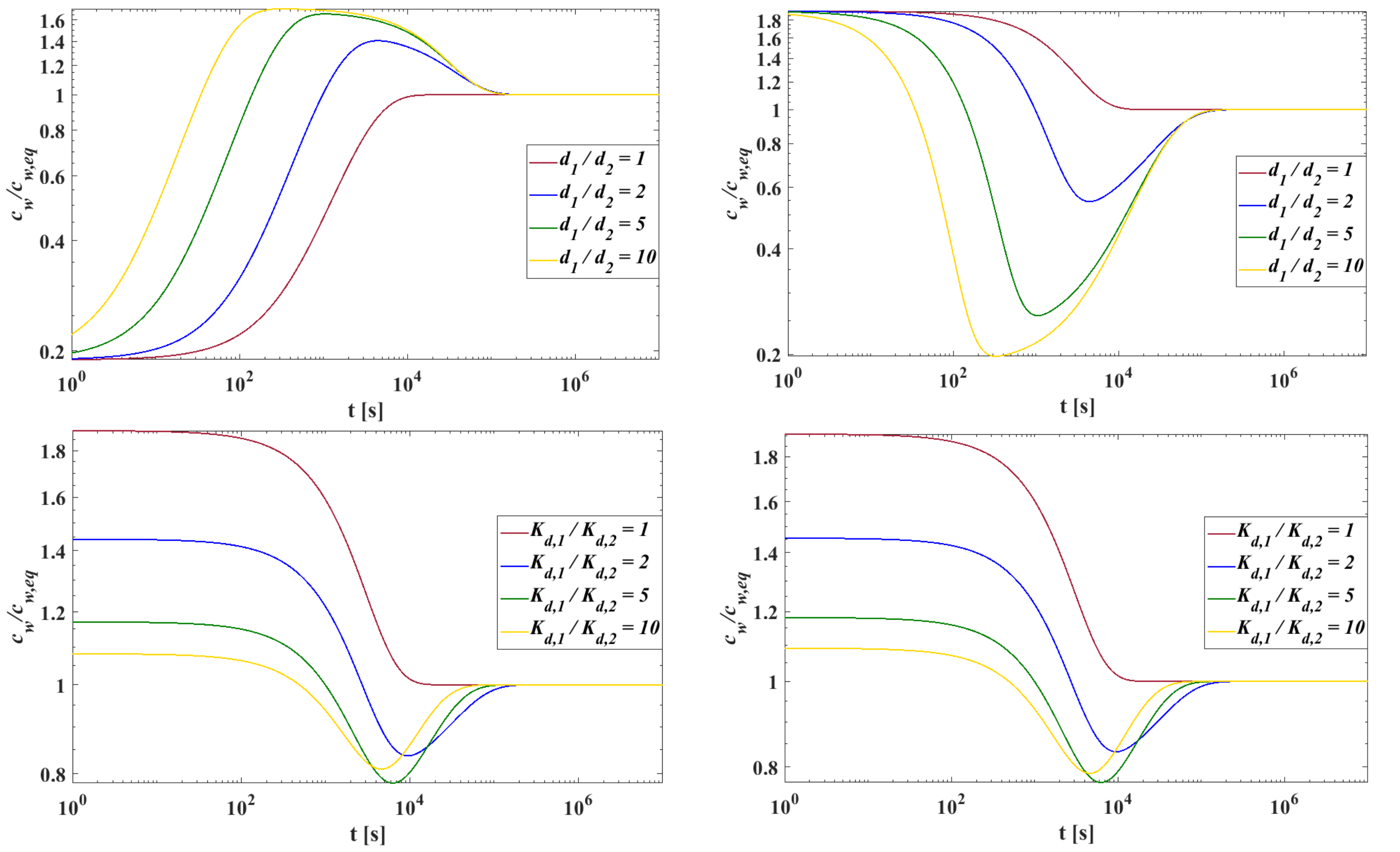


Batch test 3: Preloaded small PE particles (PE1) + clean large PE particles (PE3) with water





Particle size and distribution coefficient influence on pollutant redistribution (FD based curves):



Conclusions

1. The results show mass transfer shift from FD to IPD for small PE particles ($d_{PE1} = 260\mu m$ and $d_{PE2} = 145\mu m$) and large PE particles ($d_{PE3} = 4172\mu m$) only follow the IPD.

2. The energy dissipation rate (ε) of magnetic stirrer system and shaking bed system are $10^{-4.2}$ m²/s³ and $10^{-1.5}$ m²/s³, respectively.

3. Sherwood numbers of PE particles increase with the increase of particle size. The fitting Sherwood numbers show good consistence to the Kolmogoroff's theory based empirical Sherwood number relationships ($Sh = 2 + 0.6Re^{\alpha}Sc^{1/3}, \alpha\epsilon[0.5, 0.75]$).

4. The distribution coefficient (K_{PE}) of PE/water is around 15000 L/kg.

5. A transient overshooting concentration in aqueous phase occurs due to different sorption kinetics of particles. The greater the sorption kinetics difference, the higher the overshooting concentration.

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