

HWRS 561b: Physical Hydrogeology II

Solute transport (Part 4)

Agenda:

1. Equilibrium and non-equilibrium sorption
2. Non-conservative solute transport

Sorption

When solute moves through the pore space, they can interact with the solid through various physical and chemical processes that lead to the solute partition to the solid and leave the aqueous phase. We refer to the net effect of these processes as **sorption**.

Equilibrium sorption vs. kinetic sorption

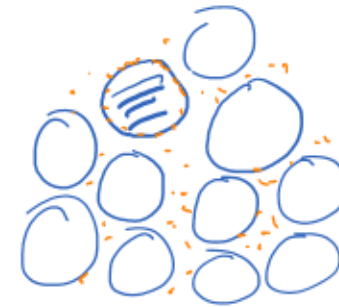
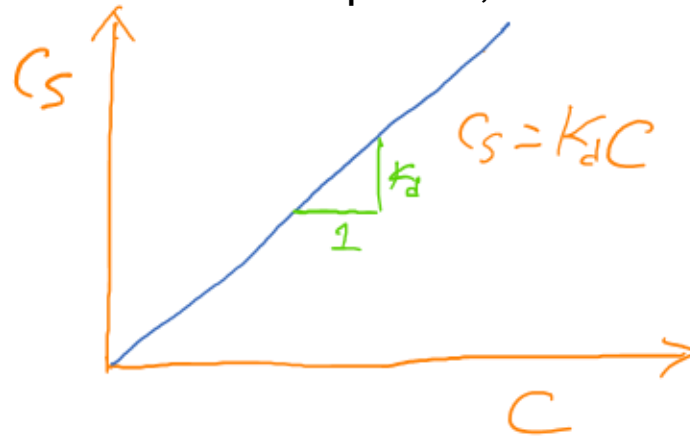
If the sorptive process is rapid compared with the transport, the solute in the aqueous may be assumed in equilibrium condition with the sorbed phase, which is often modeled by an isotherm.

$$C_s = f(C)$$

Linear isotherm

$$C_s = K_d C$$

Handwritten notes: M/M under C_s , M/L^3 under C , and L^3/M next to K_d .



C_s = mass of solute sorbed per dry unit weight of solid (mg/kg)

C = concentration of solute in solution in equilibrium with the mass of solute sorbed onto the solid (mg/L)

K_d = coefficient (L/kg)

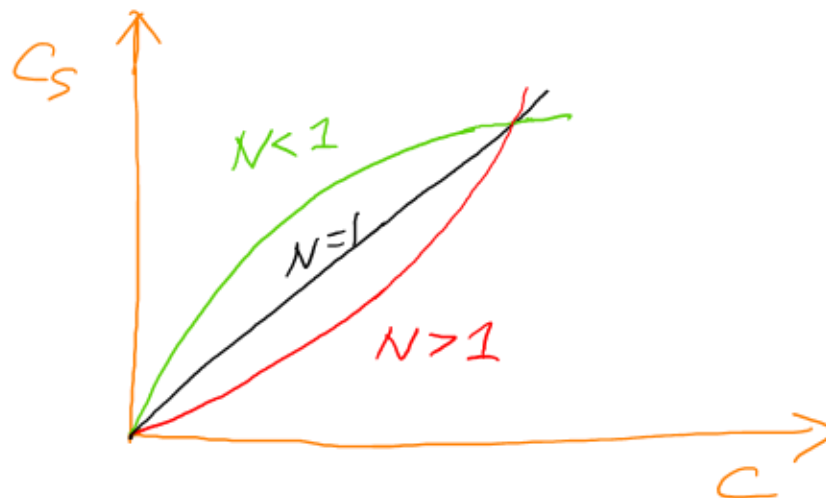
Sorption

Nonlinear isotherm

Freundlich isotherm

$$C_s = K_f C^N$$

K_f and N are fitting parameters to measured isotherms.



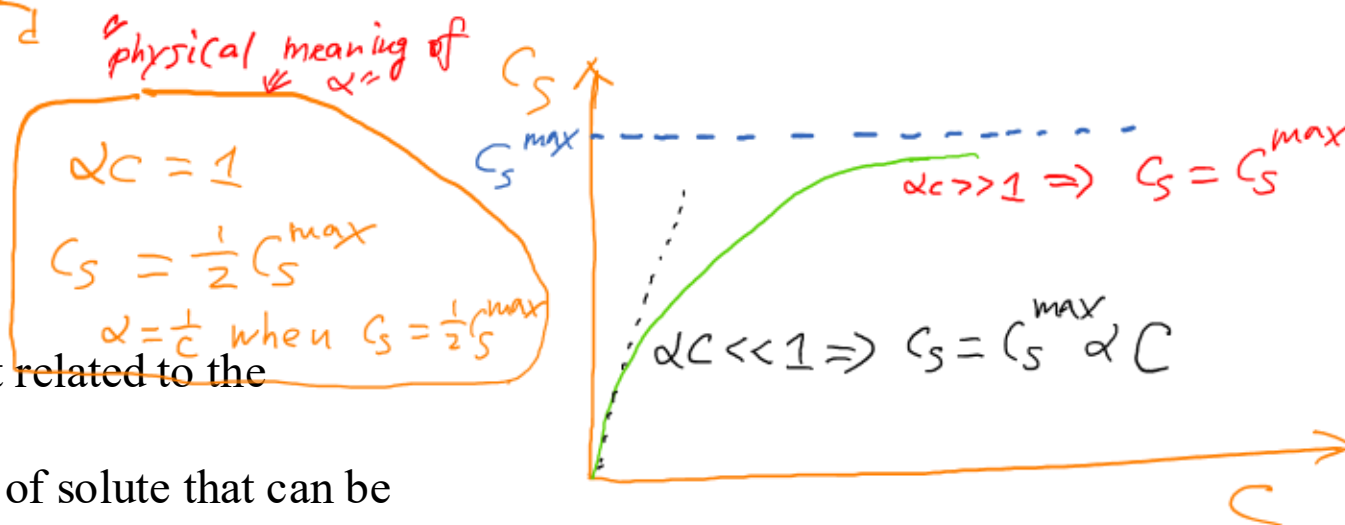
$$C_s = K_f C^{N-1} C$$

Langmuir isotherm

$$C_s = \frac{C_s^{\max} \alpha C}{1 + \alpha C}$$

α is an adsorption constant related to the binding energy (L/mg)

β is the maximum amount of solute that can be absorbed by the solid (mg/kg)



ADE with sorption

$$\phi \frac{\partial C}{\partial t} + \rho_b \frac{\partial C_s}{\partial t} + \phi v \frac{\partial C}{\partial x} - \phi D \frac{\partial^2 C}{\partial x^2} = 0$$

If solid-phase sorption follows a linear isotherm

$$C_s = K_d C$$

We obtain

$$\phi \frac{\partial C}{\partial t} + \rho_b K_d \frac{\partial C}{\partial t} + \phi v \frac{\partial C}{\partial x} - \phi D \frac{\partial^2 C}{\partial x^2} = 0$$

$$\Rightarrow \frac{\partial C}{\partial t} + \frac{\rho_b K_d}{\phi} \frac{\partial C}{\partial t} + v \frac{\partial C}{\partial x} - D \frac{\partial^2 C}{\partial x^2} = 0$$

$$\Rightarrow \left(1 + \frac{\rho_b K_d}{\phi}\right) \frac{\partial C}{\partial t} + v \frac{\partial C}{\partial x} - D \frac{\partial^2 C}{\partial x^2} = 0$$

Define $1 + \frac{\rho_b K_d}{\phi} \equiv R$ Retardation factor

$$\Rightarrow R \frac{\partial C}{\partial t} + v \frac{\partial C}{\partial x} - D \frac{\partial^2 C}{\partial x^2} = 0$$

ADE with sorption

If solid-phase sorption follows a Freundlich isotherm

$$C_s = K_f C^N$$

$$\frac{\partial C}{\partial t} + \frac{\rho_b}{\phi} \frac{\partial C_s}{\partial t} + V \frac{\partial C}{\partial x} - D \frac{\partial^2 C}{\partial x^2} = 0$$

$$\Rightarrow \frac{\partial C}{\partial t} + \frac{\rho_b}{\phi} K_f N C^{N-1} \frac{\partial C}{\partial t} + V \frac{\partial C}{\partial x} - D \frac{\partial^2 C}{\partial x^2} = 0$$

$$R = 1 + \frac{\rho_b}{\phi} K_f N C^{N-1}$$

If solid-phase sorption follows a Langmuir isotherm

$$C_s = \frac{C_s^{\max} \alpha C}{1 + \alpha C}$$

$$\Rightarrow \frac{\partial C}{\partial t} + \frac{\rho_b}{\phi} \frac{C_s^{\max} \alpha}{(1 + \alpha C)^2} \frac{\partial C}{\partial t} + V \frac{\partial C}{\partial x} - D \frac{\partial^2 C}{\partial x^2} = 0$$

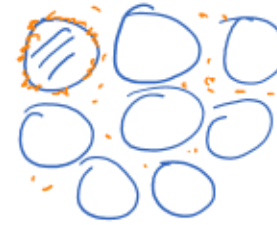
$$R = 1 + \frac{\rho_b}{\phi} \frac{C_s^{\max} \alpha}{(1 + \alpha C)^2}$$

Non-equilibrium (kinetic) sorption

Irreversible first-order kinetic sorption model

$$\begin{cases} \frac{\partial C_s}{\partial t} = k_1 C \\ \frac{\partial C}{\partial t} + \frac{A_b}{\phi} \frac{\partial C_s}{\partial t} + V \frac{\partial C}{\partial x} - D \frac{\partial^2 C}{\partial x^2} = 0 \end{cases}$$

↖ First-order decay rate constant



Reversible linear kinetic sorption model

$$\frac{\partial C_s}{\partial t} = k_2 C - k_3 C_s$$

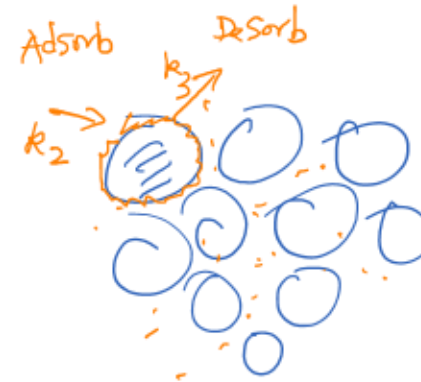
↖ Forward rate constant

↖ Backward rate constant

$$\Rightarrow \frac{\partial C_s}{\partial t} = \gamma (k_4 C - C_s)$$

↖ First-order
rate coefficient

↖ solid-phase adsorption coefficient
(equivalent to K_d)



Non-equilibrium (kinetic) sorption

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Two-site nonequilibrium sorption model

Non-equilibrium (kinetic) sorption

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Two-domain nonequilibrium sorption model