

MATHEMATICAL MODELLING OF THE ADSORPTION OF ENVIRONMENTAL CONTAMINANTS

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INTRODUCTION

In the Paris agreement of 2015, signed by 194 countries as well as the EU, a key long-term goal was to "substantially reduce global greenhouse gas emissions to hold global temperature increase to well below 2°C above pre-industrial levels and pursue efforts to limit it to 1.5°C above pre-industrial levels."

In 2022 annual fossil fuel emissions reached over 37 billion tonnes per year, approximately 6% higher than in 2015. In the period July 2023 to June 2024 the Earth was 1.64°C hotter than in pre-industrial times.

The UN Environment Program states that water pollution (from air, freshwater and ocean contamination) results in an accumulation of toxic chemicals in the food chain while biological and chemical pollutants increase antimicrobial resistance. This environmental contamination significantly contributes to non-infectious diseases such as cancer and respiratory illnesses, causing approximately nine million deaths annually.

The World Health Organization have stated that 1 in 3 people globally do not have access to safe drinking water.

Many international goals can no longer be achieved by emissions reductions alone, there must also be active removal.

Sources: Copernicus: "June 2024 marks 12th month of global temperature reaching 1.5° C above pre-industrial." https://climate.copernicus.eu/copernicusjune-2024-marks-12th-month-globaltemperature-reaching-15degc-above-pre-industrial Copernicus: "New record daily global average temperature reached in July 2024". https://climate.copernicus.eu/new-record-daily-global-average-temperature-reached-july-2024 UR Environment Program, Pollution and health, updated 2024 https://www.unep.org/topics/chemicals-and-pollution-action/pollution-and-health

MOTIVATION I

- Climate change is one of humanity's most critical challenges
- Global warming linked to CO₂ levels



Figure taken from NASA: https://climate.nasa.gov/vital-signs/carbon-dioxide/?intent=121

MOTIVATION II

Luckily we agreed to start cutting emissions in 2015



MOTIVATION III

• **Clean energy: Biogas** is an emerging alternative energy source, but it has impurities (e.g. siloxanes, alkenes)



ΜΟΤΙVATION IV

- Myriad of environmental contaminants e.g. flue gases, car exhaust, household products, pharmaceuticals
- In buildings, **volatile organic compounds (VOCs)** concentrate indoors and have negative effects on the occupant's health.



COLUMN SORPTION

• **Column sorption** is a popular method to remove a pollutant from a contaminated fluid by forcing it through a column that is packed with a porous material onto which the pollutant attaches (adsorption).





COLUMN SORPTION

Typical adsorbents include silica gel, zeolites, MOFs and activated carbonAdsorption \neq AbsorptionPhysisorption & Chemisorption



If 1g of activated carbon is taken and all the pore walls are expanded into a flat surface, this area will reach 1000m2 - Carbofull.org

COLUMN SORPTION



BREAKTHROUGH CURVES

Definition

There are two key experimental measurements: the **breakthrough curve**, which is the concentration of contaminant at the column outlet; the **isotherm** is the relation between the adsorbed mass and the contaminant concentration in the fluid once the system has reached equilibrium.



ISOTHERMS

Definition

The **isotherm** may be calculated by weighing the column before and after the experiment or integrating the lost concentration - check for moisture



- Correctly analyse basic adsorption of trace amounts (remediation of water) don't trust chemists!
- Chemisorption okay, I needed chemists to help here but I was still suspicious
- Capture of large quantities (flue gases, CO2 capture)
- Multiple contaminants (liquid and gas)
- Large adsorbent particles (intra-particle diffusion)
- Scale up from experiments to industrial scale

MATHEMATICAL FORMULATION

FROM EXPERIMENT TO MATHEMATICS



Assumptions:

- 1. The column is regarded as a **circular** cylinder
- 2. Constant void fraction ϕ throughout the column
- 3. (Initially) The fluid velocity field **u** is **constant and unidirectional**
- 4. The walls of the cylinder are impermeable
- 5. The contaminant concentration is **sufficiently low** such that its removal does not affect the flow (see 3, water v. gas)
- 6. The adsorption process is **isothermal**

MATHEMATICAL MODEL

Mass per unit length of contaminant $m_c(x, t)$

$$\frac{\partial m_c}{\partial t} + \frac{\partial}{\partial x} \left(u m_c - D \frac{\partial m_c}{\partial x} \right) = - \frac{\partial m_{ad}}{\partial t} \,,$$

 $q=m_{ad}/m_{at}$ - ratio of adsorbed mass to (constant) adsorbent mass

 $m_c = \phi Ac$ where $c [kg/m^3]$ is the concentration density of contaminant in the carrier fluid, A the cross-sectional area and ϕ the void fraction

$$\frac{\partial}{\partial t}(\phi Ac) + \frac{\partial}{\partial x}(u\phi Ac) = \frac{\partial}{\partial x}\left(D\frac{\partial}{\partial x}(\phi Ac)\right) - m_{at}\frac{\partial q}{\partial t}$$

Leading to the concentration equation

$$\frac{\partial c}{\partial t} + u \frac{\partial c}{\partial x} = D \frac{\partial^2 c}{\partial x^2} - \frac{\rho_b}{\phi} \frac{\partial q}{\partial t} \,,$$

 $ho_b=m_{at}/
m A$ is the bulk density

[Can derive through homogenisation - here we prefer the bleeding obvious route]

Key is the adsorption model ...

Begin with the Langmuir equation

$$\frac{\partial q}{\partial t} = k_{ad} c \left(q_m - q \right) - k_{de} q \,,$$

where

- k_{ad} and k_{de} are rates of adsorption and desorption;
- q_m is the maximum mass that can be captured by the adsorbent (per unit mass of adsorbent)

This is simplest realistic model - problem is that it is nonlinear

Linear Driving Force model

$$\frac{\partial q}{\partial t} = k_{ad} \left(q_m - q \right),$$

leads to negative concentration

NON-DIMENSIONAL MODEL

Non-dimensional quantities are represented with $\hat{\cdot}$:

$$\hat{x} = \frac{x}{L}$$
 $\hat{t} = \frac{t}{\tau}$ $\hat{c} = \frac{c}{c_0}$ $\hat{q} = \frac{q}{q_m}$

Work on reaction time-scale $\tau = 1/(k_{ad}c_0)$, balance advection with adsorption $\Rightarrow L = ($ length flowed over reaction time)

$$Da\frac{\partial \hat{c}}{\partial \hat{t}} + \frac{\partial \hat{c}}{\partial \hat{x}} = Pe^{-1}\frac{\partial^2 \hat{c}}{\partial \hat{x}^2} - \frac{\partial \hat{q}}{\partial \hat{t}}$$
$$\frac{\partial \hat{q}}{\partial \hat{t}} = \hat{c}(1 - \hat{q}) - \kappa \hat{q}$$

 $\text{Da},\text{Pe}^{-1}\ll 1$

- Prove through using experimental values/comparison with numerics of full problem

 $\kappa = k_{de}/(k_{ad}c_0)$

Isotherm $\hat{q}_{\hat{t}} = 0$ leads to $\hat{q}_e = 1/(1+\kappa)$

TRAVELLING WAVE SOLUTION

Numerical simulations show that the solution propagates with a constant shape and velocity, which suggests the existence of a travelling wave.

Introducing the travelling wave coordinate

$$\hat{\eta} = \hat{x} - \hat{\mathsf{s}}(\hat{t}) = \hat{x} - (\hat{v}\hat{t} + \hat{\mathsf{s}}_0), \qquad \hat{c}(\hat{x}, \hat{t}) = \hat{F}(\hat{\eta}), \qquad \hat{q}(\hat{x}, \hat{t}) = \hat{G}(\hat{\eta}).$$

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Leading order equations (neglecting Da, Pe^{-1})

$$\hat{F}' = \hat{v}\hat{G}', \qquad \hat{F} = \hat{v}\hat{G} \qquad -\hat{v}\hat{G}' = \hat{F}\left(1-\hat{G}\right) - \kappa\hat{G} \qquad \hat{v} = 1/\hat{q}_e$$



SINGLE-CONTAMINANT MODEL: SOLUTION

In the end we find

$$\hat{F}(\hat{\eta}) = rac{1}{1 + \mathcal{A} \exp\left(\hat{\eta}/\hat{v}
ight)} \quad \Rightarrow \quad c(L, t) = rac{C_0}{1 + \exp\left(-k_a c_0(t - t_h)
ight)},$$

where c_0 is the concentration entering into the column at the inlet, t_h is the half-time, \hat{v} from far-field condition.

SINGLE-CONTAMINANT MODEL: SOLUTION

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Bohart-Adams solution 1920 equivalent to Thomas model and Bed Depth Service Time model. It's popular!

$$c(L,t) = \frac{c_0}{1 + \exp\left(-k_{BA}c_0(t - \Gamma q_m L)\right)}$$

 $\Gamma = \rho_b/(\phi u c_0)$

Our solution

$$c(L,t) = \frac{1}{1 + \exp(-k_a c_0(t-t_h))},$$

BA model can provide highly inaccurate results!

SINGLE-CONTAMINANT MODEL: BOHART-ADAMS MODEL



Plot of $c(L, t)/c_0$ against time for toluene with a) $c_0 = 0.409 \times 10^{-3} \text{ kg/m}^3$, b) $c_0 = 2.835 \times 10^{-3} \text{ kg/m}^3$. In both cases $k_a \approx 1.2 \text{ m}^3/(\text{kg s})$. BA dotted line, current model solid line

Who can you trust?

ΒA

Our solution

$$c(L,t) = \frac{c_0}{1 + \exp\left(-k_{BA}c_0(t - \Gamma q_m L)\right)}$$

$$c(L,t) = \frac{1}{1 + \exp(-k_a c_0(t-t_h))}$$

BA model can provide highly inaccurate results

Its well-documented success is a result of using known system parameters as unknown fitting parameters, permitting constant values to vary (k_a) , permitting unphysical values (such as negative adsorption sites) and an acceptance of poor fits.

They really needed some maths help

T.G. Myers. Is it time to move on from the Bohart-Adams model for column adsorption? International Communications in Heat and Mass Transfer 159 (2024)

CHEMISORPTION

Having annoyed the adsorption community ... move on to chemisorption With a simple chemical reaction

$$mC + nA \stackrel{k_a}{\underset{k_d}{\longleftrightarrow}} Products$$

In the following we will restrict m, n to be integer. The specific case m = n = 1 may also apply to physisorption = Langmuir model

Corresponding kinetic equation (Sips equation)

$$\frac{\partial q}{\partial t} = k_a c^m (q_m - q)^n - k_d q^n$$

Travelling wave version

$$\hat{F}' = \hat{v}\hat{G}', \qquad -\hat{v}\hat{G}' = \hat{F}^m\left(1-\hat{G}\right)^n - \kappa\hat{G}^n$$

Implicit solutions for breakthrough of form $t - t_h = A\Psi(c)$

CHEMISORPTION

n, m values	Ψ(x)
n = 1, m = 1	$\ln(1-x) - \ln(x)$
n = 2, m = 2	$\frac{1}{(2a-1)x} - \frac{2a}{(2a-1)^2}\ln(x) + \frac{\ln(1-x)}{2(a-1)} - \frac{\ln(2a-1-x)}{2(2a-1)^2(a-1)}$
n = 2, m = 1	$-\frac{1}{a^2}\ln(x) + \frac{1}{a^2 - 1}\ln(1 - x) - \frac{1}{a^2(a^2 - 1)}\ln(a^2 - x)$
n = 3, m = 1	$\alpha_1 \ln(x) + \beta_1 \ln(1-x) + A_1 \ln((x+a_1)^2 + b_1^2) + B_1 \tan^{-1}\left(\frac{x+a_1}{b_1}\right)$
$a \in (1, 4)$	where $a_1 = a^2(a-3)/2$, $b_1^2 = a^3(4-a)(a-1)^2/4$, $\alpha_1 = \frac{-1}{a^3}$, $\beta_1 = \frac{1}{(a-1)^2(2a+1)}$,
	$A_{1} = -\alpha_{1}\beta_{1}(a^{3} - 3a^{2} + 1)/2, B_{1} = -\alpha_{1}\beta_{1}a^{2}(a - 1)(a^{3} - 5a^{2} + 4a + 3)/(2b_{1})$
n = 3, m = 1	$\frac{-1}{a^3}\ln(x) + \frac{\ln(1-x)}{(a-1)^2(2a+1)} + \gamma_1\ln(x-x_1) + \gamma_2\ln(x-x_2)$
$a\in (4,\infty)$	where x_1, x_2 are the negative roots of f
n = 3, m = 1	$-\frac{\ln(x)}{64} + \frac{\ln(1-x)}{81} - \frac{1}{72(x+8)} + \frac{17 \ln(x+8)}{5184}$
a = 4	
n = 3, m = 2	$\alpha_1 \ln(x) + \frac{1}{a^3} \frac{1}{x} + \beta_1 \ln(1-x) + A_1 \ln((x+a_1)^2 + b_1^2) + B_1 \tan^{-1}(\frac{x+a_1}{b_1})$
	where $a_1 = (1 - 3a)/2$, $b_1^2 = (4a^3 - 9a^2 + 6a - 1)/4$, $\alpha_1 = \frac{1 - 3a - a^3}{a^6}$,
	$\beta_1 = \frac{1}{(a-1)^2(a+2)}, A_1 = \frac{\beta_1(a^3 - 9a^2 + 9a - 2)}{2a^6}, B_1 = \frac{-\beta_1(a-1)(9a^3 - 23a^2 + 13a - 2)}{2a^6b_1}$

CHEMISORPTION CO₂ CAPTURE



Linear fitting, $t \sim A\Psi(c)$, of CO₂ capture, (a) m = 1, n = 1 (b) m = 1, n = 2 (c) m = 1, n = 3 (d) m = 2, n = 3

m, *n* determined from chemistry/fitting isotherm/above curves - here see 1, 2

CHEMISORPTION CO₂ CAPTURE



CO₂ capture as c(L, t) First analytical solution (don't count empirical formulae!) for chemisorption!!!

Juicy details in

M. Aguareles, E. Barrabés, T. Myers, A. Valverde. Mathematical analysis of a Sips-based model for column adsorption. Physica D 448 (2023).

Don't always have trace amounts ... Flue gases, exhaust gases

$$\begin{aligned} \frac{\partial c_1}{\partial t} &+ \frac{\partial}{\partial x} (uc_1) = D \frac{\partial^2 c_1}{\partial x^2} - \frac{1 - \phi}{\phi} \rho_a \frac{\partial q}{\partial t} \\ \frac{\partial c_2}{\partial t} &+ \frac{\partial}{\partial x} (uc_2) = D \frac{\partial^2 c_2}{\partial x^2} \\ p &= R_g T(c_1 + c_2) \\ &- \frac{\partial p}{\partial x} = \alpha (M_1 c_1 + M_2 c_2) u^2 + \left(\beta + \frac{(1 - \epsilon)}{\epsilon} \rho_a M_1 \frac{\partial q}{\partial t}\right) u \\ &\frac{\partial q}{\partial t} = \dot{Q} \end{aligned}$$

Now tracking concentration of contaminant and carrier fluid, velocity (Ergun), pressure (ideal gas), and amount adsorbed (equation of your choice)

Non-dimensional form

$$\begin{split} \delta_1 \frac{\partial \hat{c}_1}{\partial \hat{t}} &+ \frac{\partial}{\partial \hat{x}} \left(\hat{u} \hat{c}_1 \right) = \delta_2 \frac{\partial^2 \hat{c}_1}{\partial \hat{x}^2} - \frac{\partial \hat{q}}{\partial \hat{t}} \\ \delta_1 \frac{\partial \hat{c}_2}{\partial \hat{t}} &+ \frac{\partial}{\partial \hat{x}} \left(\hat{u} \hat{c}_2 \right) = \delta_2 \frac{\partial^2 \hat{c}_2}{\partial \hat{x}^2} \\ &1 + \delta_3 \hat{p} = \phi_1 \hat{c}_1 + \phi_2 \hat{c}_2 \\ &- \frac{\partial \hat{p}}{\partial \hat{x}} = \delta_4 \left(\delta_5 \hat{c}_1 + \hat{c}_2 \right) \hat{u}^2 + \left(1 + \delta_6 \frac{\partial \hat{q}}{\partial \hat{t}} \right) \hat{u} \\ &\frac{\partial \hat{q}}{\partial \hat{t}} = \hat{c}_1^m (1 - \hat{q})^n - \delta_7 \hat{q}^n \end{split}$$

$$\phi_i = RTc_{i0}/p_a \qquad \delta_1, \delta_2, \delta_3 \ll 1 \quad \Rightarrow \quad \hat{u} = \frac{1}{\hat{c}_2}, \quad \hat{c}_2 = \frac{1 - \phi_1 c_1}{1 - \phi_1}$$

System now reduced to \hat{c}_1, \hat{q} equations

Define

$$F(\eta) = \frac{1 - \phi_1 \hat{c}_1}{(1 - \phi_1) \hat{c}_1} \qquad G(\eta) = \hat{q}$$

Kinetic equation reduces to

$$-\frac{\mathrm{d}F}{\mathrm{d}\eta} = \left(\frac{F}{1-\phi_1-\phi_1F}\right)^m \left(1-\frac{F}{v}\right)^n - \delta_7 \left(\frac{F}{v}\right)^n$$

Now solve for common m, n combinations

Again m, n could come from chemistry - if known - or fitting to isotherm or breakthrough

If *m*, *n* not integers (i.e when approximating multiple reactions) can still solve KE numerically

Implicit form for general solution: m, n = 1, 1; 1, 2

$$(1 + \delta_7^{1/n})(\hat{t} - \hat{t}_{1/2}) - (\hat{x} - \hat{L}) = \hat{Y}_{mn}(\hat{c}_1)$$

where

$$\begin{split} \hat{Y}_{11}(\hat{c}_{1}) &= \frac{1+\delta_{7}}{1+\phi_{1}\delta_{7}} \left(\ln \left| \frac{\hat{c}_{1}}{1-\hat{c}_{1}} \right| - \phi_{1} \ln \left| \frac{(2-\phi_{1})\hat{c}_{1}}{1-\phi_{1}\hat{c}_{1}} \right| \right) \\ \hat{Y}_{12}(\hat{c}_{1}) &= \frac{1+\sqrt{\delta_{7}}}{\sqrt{\delta_{7}} \left(1+\sqrt{\gamma} \right)} \left(\ln \left| \frac{\hat{c}_{1}}{1-\hat{c}_{1}} \right| - \gamma \ln \left| \frac{(2-\gamma)\hat{c}_{1}}{1-\gamma\hat{c}_{1}} \right| \right) \end{split}$$

and

$$\gamma = \left(\frac{1 + \phi_1 \sqrt{\delta_7}}{1 + \sqrt{\delta_7}}\right)^2$$

Breakthrough - set $\hat{x} = \hat{L}$



Figure 6: Fitting of the model accounting for (m, n) = (1, 1) to the breakthrough data reported by Delgado *et al.* [14] with a range of CO₂ volumetric percentages ϕ_1 at the inlet of the column (runs 10, 12, 13 and 14 in Table 1). The constant velocity model (dashed line) is retrieved when setting $\phi_1 \rightarrow 0$ in Eq. (35a). In each figure, the inset shows the evolution of the flow velocity at the outlet as per Eq. (33a).

- Results reasonably accurate not as good as usual
- \cdot Trace amount result good up to around 50%
- Need more data for comparison/check (i.e. issues with agreement due to bad data, not bad model!!!)

TG Myers, M Calvo-Schwarzwalder, F Font, A Valverde. Modelling large mass removal in adsorption columns. Submitted to ICHMT, Mar. 2024, arXiv preprint arXiv:2404.02939

TG Myers, F FontMass transfer from a fluid flowing through a porous media. International Journal of Heat and Mass Transfer 163, 2020

COMPETITIVE ADSORPTION

The real world can be a scary place



https://www.economist.com/china/2016/07/09/beijing-v-belching-chimneys

COMPETITIVE ADSORPTION

Most fluids contain multiple contaminants, which affects the adsorption behaviour ...

COMPETITIVE ADSORPTION

Most fluids contain multiple contaminants, which affects the adsorption behaviour

We can see very different dynamics when we have more than one contaminant being removed simultaneously



Right hand figure - one contaminant behaves as a single component, the other is displaced => presence of a "dominant" contaminant 32

Work with θ - fractional coverage - rather than q - mass adsorbed, $\theta = q/q_m$

$$\frac{\partial c_i}{\partial t} + \underbrace{u \frac{\partial c_i}{\partial x}}_{advection} = \underbrace{D \frac{\partial^2 c_i}{\partial x^2}}_{dispersion} - \underbrace{\frac{\rho_b q_{i,m}}{\phi} \frac{\partial \theta_i}{\partial t}}_{sink},$$

Question

How do θ_i 's change? We need a **kinetic model**. First, we need to discuss the **adsorption mechanisms**.

ADSORPTION MECHANISMS

We may distinguish between **individual mechanisms** and **interactions** (or **competitive mechanisms**):

$$\frac{\partial \theta_i}{\partial t} = \Phi_i + \Psi_i \,.$$

• Individual mechanisms:

$$C_i + A \xrightarrow[k_{d,i}]{k_{d,i}} C_i A \rightarrow \Phi_i = \underbrace{k_{a,i} C_i \left(1 - \theta_1 - \theta_2\right)}_{adsorption} - \underbrace{k_{d,i} \theta_i}_{desorption}$$

• Competition ($i, j \in \{1, 2\}$):

$$c_i + c_j A \stackrel{k_{r,i}}{\underset{k_{r,j}}{\leftarrow}} c_i A + c_j \rightarrow \Psi_i = k_{r,i} c_i \theta_j - k_{r,j} c_j \theta_j$$

Competition is usually **dominated** by one of the pollutants (species 1) $\Rightarrow k_{r,1} \gg k_{r,2}$.

FINAL MODEL

$$\begin{split} \frac{\partial c_i}{\partial t} &+ u \frac{\partial c_i}{\partial x} = D \frac{\partial^2 c_i}{\partial x^2} - \frac{\rho_b q_{i,m}}{\phi} \frac{\partial \theta_i}{\partial t}, & x \in (0,L), t > 0, \\ \frac{\partial \theta_1}{\partial t} &= k_{a,1} c_1 \left(1 - \theta_1 - \theta_2\right) - k_{d,1} \theta_1 + k_{r,1} c_1 \theta_2 - k_{r,2} c_2 \theta_1, & x \in (0,L), t > 0, \\ \frac{\partial \theta_2}{\partial t} &= k_{a,2} c_2 \left(1 - \theta_1 - \theta_2\right) - k_{d,2} \theta_2 - k_{r,1} c_1 \theta_2 + k_{r,2} c_2 \theta_1, & x \in (0,L), t > 0, \\ D \frac{\partial c_i}{\partial x} &= u \left(c_i - c_{i,0}\right), & x = 0^+, t > 0, \\ \frac{\partial c_i}{\partial x} &= 0, & x \in [0,L], t = 0, \\ c_i &= \theta_i = 0, & x \in [0,L], t = 0. \end{split}$$

Nice dynamical systems problems for static case

REDUCED EQUATIONS

The leading order system reduces to (*choosing zero desorption*, *simply for an easy life*)

$$\begin{split} \frac{\partial \hat{c}_1}{\partial \hat{x}} &= -\frac{\partial \theta_1}{\partial \hat{t}}, & \hat{x} \in \left(0, \hat{L}\right), \hat{t} > 0, \\ \frac{\partial \hat{c}_2}{\partial \hat{x}} &= -\delta \frac{\partial \theta_2}{\partial \hat{t}}, & \hat{x} \in \left(0, \hat{L}\right), \hat{t} > 0, \\ \frac{\partial \theta_1}{\partial \hat{t}} &= \hat{c}_1 \left(1 - \theta_1 - \theta_2\right) + \beta_1 \hat{c}_1 \theta_2, & \hat{x} \in \left(0, \hat{L}\right), \hat{t} > 0, \\ \frac{\partial \theta_2}{\partial \hat{t}} &= \hat{c}_2 \left(1 - \theta_1 - \theta_2\right) - \gamma \beta_1 \hat{c}_1 \theta_2, & \hat{x} \in \left(0, \hat{L}\right), \hat{t} > 0, \\ \hat{c}_i &= 1, & \hat{x} = 0^+, \hat{t} > 0, \\ \frac{\partial \hat{c}_i}{\partial \hat{x}} &= 0, & \hat{x} \in \left[0, \hat{L}\right], \hat{t} = 0, \\ \hat{c}_i &= \theta_i = 0, & \hat{x} \in \left[0, \hat{L}\right], \hat{t} = 0. \end{split}$$

We will construct an **analytical solution** by splitting the column into **two regions** with different dominating mechanisms.

REGION 1: COMPETITION

In this first region we assume adsorbent material almost full, $\Theta = \theta_1 + \theta_2 = 1 - O(\varepsilon)$

$$rac{\partial heta_1}{\partial \hat{t}} = eta_1 \hat{c}_1 heta_2 + \mathcal{O}(arepsilon) \,, \qquad rac{\partial heta_2}{\partial \hat{t}} = -eta_1 \hat{c}_1 heta_2 + \mathcal{O}(arepsilon)$$

change is purely by replacement

We can decouple the leading order problem for the first contaminant

$$\frac{\partial \hat{c}_1}{\partial \hat{x}} = -\frac{\partial \theta_1}{\partial \hat{t}}, \qquad \frac{\partial \theta_1}{\partial \hat{t}} = \beta_1 \hat{c}_1 (1 - \theta_1)$$

(equivalent to single contaminant - but different BCs and rate) **Solution** (Travelling wave):

$$\hat{c}_{1}(\hat{x},\hat{t}) = \frac{1}{1 + \mathcal{A}' \exp\left(\beta_{1}\left(\hat{x} - \hat{t}\right)\right)}, \quad \theta_{1}(\hat{x},\hat{t}) = 1 - \frac{\mathcal{A}' \exp\left(\beta_{1}\left(\hat{x} - \hat{t}\right)\right)}{1 + \mathcal{A}' \exp\left(\beta_{1}\left(\hat{x} - \hat{t}\right)\right)}$$

For the second contaminant we have

$$\hat{c}_2 = 1 + \delta \left(1 - \hat{c}_1 \right) = 1 + \frac{\delta \mathcal{A}' \exp \left(\beta_1 \left(\hat{x} - \hat{t} \right) \right)}{1 + \mathcal{A}' \exp \left(\beta_1 \left(\hat{x} - \hat{t} \right) \right)} \qquad \theta_2 = 1 - \theta_1$$

In the first region we can observe, as $\hat{x} \to \infty$, $\hat{c}_1, \theta_1 \to 0$, but $\hat{c}_2 \to 1 + \delta$ and $\theta_2 \to 1$. This limiting behaviour suggests the existence of a second region with $\hat{c}_1, \theta_1 \approx 0$.

In the first region we can observe, as $\hat{x} \to \infty$, $\hat{c}_1, \theta_1 \to 0$, but $\hat{c}_2 \to 1 + \delta$ and $\theta_2 \to 1$. This limiting behaviour suggests the existence of a second region with $\hat{c}_1, \theta_1 \approx 0$. We introduce $\hat{x} = \hat{z}/\varepsilon$ and obtain

$$\delta_0 \frac{\partial \hat{c}_2}{\partial \hat{z}} = -\mathcal{C} \frac{\partial \theta_2}{\partial \hat{t}}, \qquad \gamma \frac{\partial \theta_2}{\partial \hat{t}} = \hat{c}_2 \left(1 - \theta_2\right) \qquad (\delta = \delta_0 \mathcal{C})$$

Solution:

$$\hat{c}_2(\hat{x},\hat{t}) = \frac{1+\delta}{1+\mathcal{B}'\exp\left[(\delta\hat{x}-(1+\delta)\hat{t})/\gamma\right]}, \quad \theta_2(\hat{x},\hat{t}) = \frac{1}{1+\mathcal{B}'\exp\left[(\delta\hat{x}-(1+\delta)\hat{t})/\gamma\right]}$$

The wave speeds are determined by the matching conditions between the regions

COMPOSITE SOLUTION

A **composite solution** is obtained by adding the solutions in each region and subtracting the overlap value. For example, for \hat{c}_2 :

$$\hat{c}_2 = \hat{c}_2^{(R1)} + \hat{c}_2^{(R2)} - (1+\delta)$$

Proceeding in this way we find

$$\begin{split} \hat{c}_{1}(\hat{x},\hat{t}) &= \frac{1}{1 + \mathcal{A}' \exp\left[\beta_{1}\left(\hat{x} - \hat{t}\right)\right]},\\ \theta_{1}(\hat{x},\hat{t}) &= \frac{1}{1 + \mathcal{A}' \exp\left[\beta_{1}\left(\hat{x} - \hat{t}\right)\right]}.\\ \hat{c}_{2}(\hat{x},\hat{t}) &= \frac{1 + \delta}{1 + \mathcal{B}' \exp\left[\left(\delta\hat{x} - (1 + \delta)\hat{t}\right)/\gamma\right]} - \delta\hat{c}_{1}(\hat{x},\hat{t}),\\ \theta_{2}(\hat{x},\hat{t}) &= \frac{1}{1 + \mathcal{B}' \exp\left[\left(\delta\hat{x} - (1 + \delta)\hat{t}\right)/\gamma\right]} - \theta_{1}(\hat{x},\hat{t}), \end{split}$$

COMPARISON WITH FULL NUMERICAL SOLUTION (MOL)



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ANALYTICAL BREAKTHROUGH CURVES

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If we set $\hat{x} = \hat{L}$, we obtain the breakthrough models. In dimensional formulation, these are

$$\begin{aligned} \frac{c_{1,b}(t)}{c_{1,0}} &= \theta_{1,b}(t) = \frac{1}{1 + \exp(-k_{r,1}c_{1,0}(t - t_{h,1}))}, \\ \frac{c_{2,b}(t)}{c_{2,0}} &= \frac{1 + \delta}{1 + \lambda \exp(-k_{a,2}c_{2,0}(1 + \delta)(t - t_{h,2}))} - \frac{\delta}{1 + \exp(-k_{r,1}c_{1,0}(t - t_{h,1}))}, \\ \theta_{2,b}(t) &= \frac{1}{1 + \lambda \exp(-k_{a,2}c_{2,0}(1 + \delta)(t - t_{h,2}))} - \frac{1}{1 + \exp(-k_{r,1}c_{1,0}(t - t_{h,1}))}, \\ \text{ith} \\ \lambda &= \frac{1 + (1 + 2\delta)\exp(k_{r,1}c_{1,0}(t_{h,1} - t_{h,2}))}{1 + 2\delta + \exp(k_{r,1}c_{1,0}(t_{h,1} - t_{h,2}))}. \end{aligned}$$

We have **two** free parameters: $k_{r,1}, k_{a,2}$; δ is the height of the c_2 peak

Note $k_{a,1}$ does not appear in the solution - beyond the initial transient c_1 only sees occupied sites

VALIDATION AGAINST EXPERIMENTS



Breakthrough model applied to removal of different combinations of siloxanes onto activated carbon. Left panel: D4 (species 1) and L2 (species 2), with the experimental data of LEQUIA . Right panel: D5 (species 1) and D4 (species 2), with the experimental data taken from Santos-Clotas et al. 2020.

WORK IN PROGRESS



Model for two contaminants, where one is fully dominant $\sqrt{}$

- Include desorption perturbation of $k_{de} = 0$?
- Extend to N > 2
- Account for partial dominance (see first figure)
- Chemisorption (for which components?)

Lots of open questions - Who displaces who? Which are dominant interactions? Are there secondary reactions?

CONCLUSIONS

- Where would we be without travelling waves?
- It's getting trickier
- Don't trust anyone
- Work with experimental people!

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MATHEMATICAL MODELLING OF THE ADSORPTION OF ENVIRONMENTAL CONTAMINANTS

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