Adsorbtion of water contaminants - Modelling Camp

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1 Introduction

Tackling environmental challenges is this generation's defining task (EC Green Deal 2020). One of the most common methods for removing contaminants from a fluid is via column adsorption. Adsorption columns are employed in greenhouse gas capture, water treatment and groundwater remediation, biogas cleansing, chromatography and the purification of biopharmaceutical products. Industrial uses include: water providers (removing pollutants, odours, softening hard water and reducing evaporation); the cleansing of flue gases (from power stations, concrete and steel plants, pulp mills, etc); biofuel purification; biotechnology companies; the paint/coating industry (to remove volatile fumes) and many more. Research in these fields is focused on optimising the process, through the use of new adsorbents, configurations and operating regimes.

2 Mathematical analysis of a Sips-based model for column adsorption [1]

Fitting of some data to the Sips models

3 Mathematical model

A fluid passes through a chamber containing solid material at velocity u. The fluid fills the void space in between the solids. Let $m_c(x,t)$ be the mass per unit length of contaminant inside the chamber at time t, and m_{ad} the mass of adsorbed. A mass balance equation gives

$$\frac{\partial m}{\partial t} + \frac{\partial}{\partial x}\left(um_c - D\frac{\partial m_c}{\partial x}\right) = -\frac{\partial m_{ad}}{\partial x} \tag{1}$$

where D is the axial diffusion coefficient for the given void space. The mass of contaminant is given by $m_c = \epsilon A c$, where c [kg/m^3] is the contaminant density, A is the cross sectional area of the chamber, and ϵ is the fraction of the area which is void space. We assume that the void space does not vary in size, and so ϵ and D are assumed to be constant. Moreover, if the adsorbtion is a slow process, or the concentration of adsorbent is small, the fluid velocity is constant. Letting $q = m_{ad}/m_{at}$ (m_{at} is the mass of the adsorbent, which is constant), (1)

$$\frac{\partial c}{\partial t} + u_{in}\frac{\partial c}{\partial x} = D\frac{\partial^2 c}{\partial x^2} - \frac{\rho_c}{\epsilon}\frac{\partial q}{\partial t}, \tag{2}$$

with $\rho_c = \frac{m_{at}}{A}$ the bulk density. This is the advection-diffusion equation with a sink term.

The different models arise from considerations in the sink term. The Langmuir model comes from considering the adsorbent as a surface with distinct sites to which molecules of contaminant can attach. Let q_m be the total number of adsorbtion sites. The rate of adsorbtion is then proportional to $q_m - q$, the number of available sites, and also c. The desorption rate is just proportional to the number of sites filled up. Thus

$$\frac{\partial q}{\partial t} = k_{ad}c(q_m - q) - k_{de}q. \tag{3}$$

The linear version of this model has the c removed.

A more sophisticated model which takes into account the possibility for chemical reactions in the adsorbtion process is the Sips model. In a chemical reaction of the form

$$m \text{ Contaminants} + n \text{ Adsorbate} \iff \text{Products}, \tag{4}$$

the rate of adsorbtion is proportional to number of sites available becomes $(q_m - q)^n$, and the rate of adsorbtion becomes proportional to c^m. Hence the sink term becomes

$$\frac{\partial q}{\partial t} = k_{ad}c^m(q_m - q)^n - k_{de}q^m. \tag{5}$$

On the other hand, if the reaction is unclear or unknown, the value of m may be inferred.

These equations may be solved numerically, however an analytic solution may be obtained using a travelling wave, and these are known to be remarkably similar to the numerical solutions, and can be used to find unknown parameters (adsorbtion and desorbtion rate k_{ad} and k_{de}, and available sites q_m) [2].

3.1 Analytic solution

As previously introduced, we can derive an analytic solution by applying the *travelling wave* [1] formulation to the non-dimensional version of equation (1), Langmuir and the Sips model. We introduce a parameter $s(t)$ measuring the position of the centre of the wave, and set $\eta = x - s(t)$. The speed of the travelling wave is v_0, thus $\eta = x - vt$. Setting $F(\eta) = c(t, x)$ and $G(\eta) = q(x, t)$, reduces (1) to an ODE

$$(1 - \text{Da}v)F' = \text{Pe}^{-1}F'' + vG', \quad -vG' = F^m(1 - G)^n - \delta G^n. \tag{6}$$

Where Pe is the Peclet number, the ratio of reaction to diffusion; in our case this constant is small ($0 < Pe^{-1} << 1$).

4 Results

4.1 Data fitting

The analytical solution of the advection–diffusion equation together with the equation is (3) given explicitly as

$$c(L,t) = \frac{c_{in}}{1 + \exp(k_{\mathrm{ad}} c_{in}(t_{1/2} - t))}. \tag{7}$$

Equation (7) is the breakthrough curve. We then fit equation (7) using experimental data.

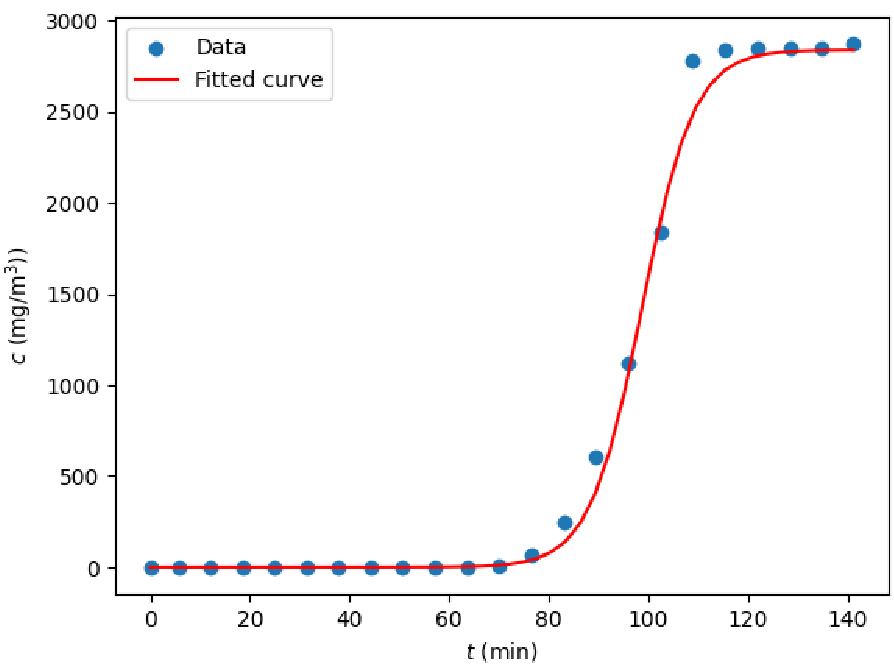

Figure 1: Breakthrough curve

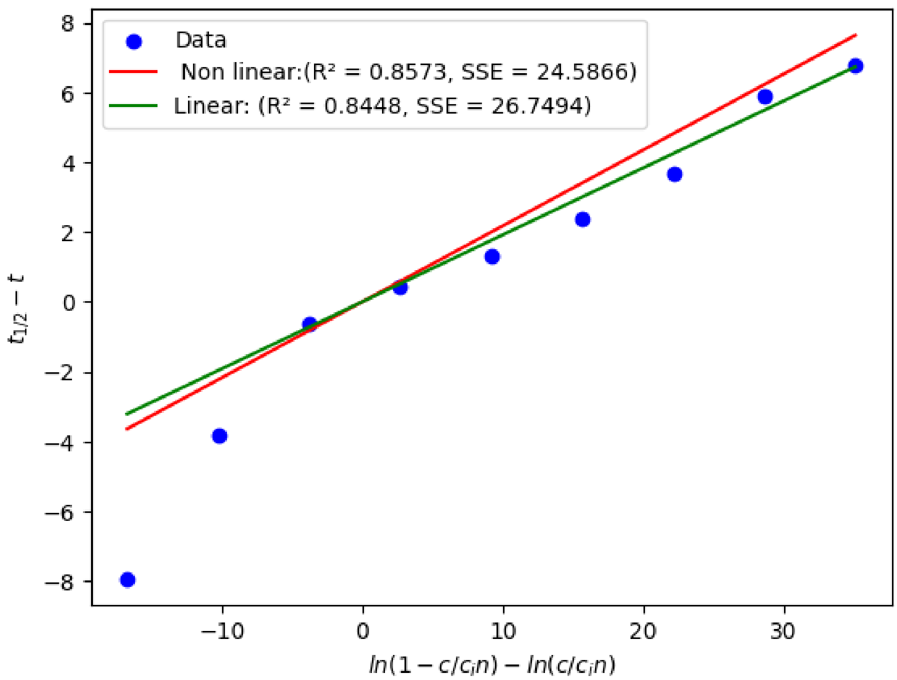

Figure 2: Fitting for $K_{ad} = 0.7656$

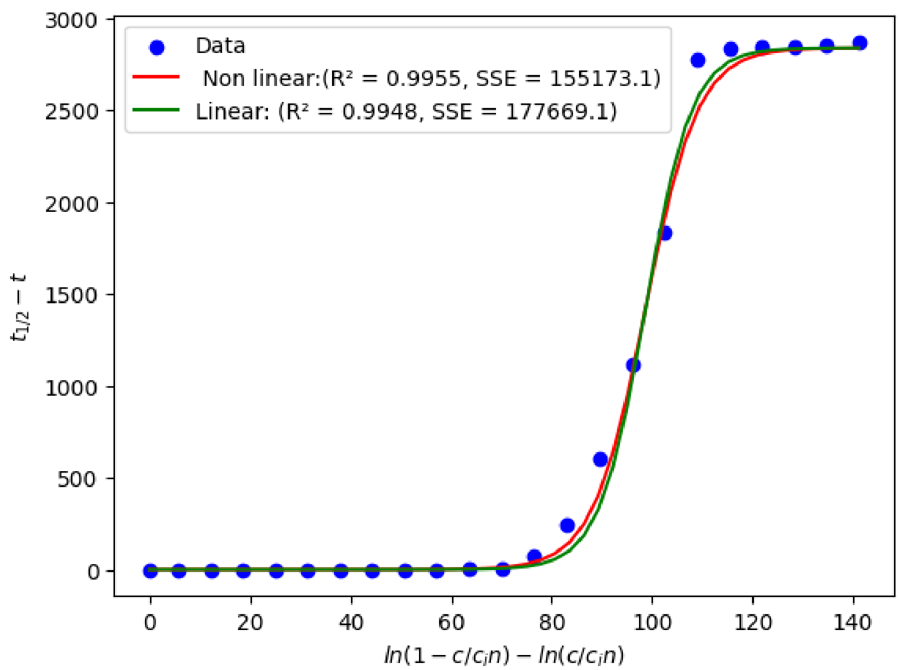

Figure 3: Fitting for $K_{ad} = 0.6752$

References

1. Aguareles, M. *et al.* Mathematical analysis of a Sips-based model for column adsorption. *Physica D: Nonlinear Phenomena* **448,** 133690 (2023).
2. Myers, T. *et al.* Scale Up of Adsorption Column Experiments. *Mathematics in Industry Reports* (2023).