

Mathcol: Exploiting mathematics to aid in the design of adsorption columns

Abel Valverde¹, Maria Aguares², Esther Barrabés², Alba Cabrera-Codony³, Francesc Font⁴, Harvey M. Thompson⁵, Timothy G. Myers⁶

¹ Universitat Politècnica de Catalunya, Departament d'Enginyeria Química, C/ Colom, 1-11, 08222 Terrassa, Spain

² Universitat de Girona, Department of Computer Science, Applied Mathematics and Statistics, Campus de Montilivi, 17071 Girona, Catalonia, Spain

³ LEQUIA, Institute of the Environment, Universitat de Girona, 17003 Girona, Catalonia, Spain

⁴ Universitat Politècnica de Catalunya, Department of Fluid Mechanics, 08019 Barcelona, Spain

⁵ University of Leeds, School of Mechanical Engineering, Leeds LS2 9JT, United Kingdom

⁶ Centre de Recerca Matemàtica, Campus de Bellaterra, Edifici C, 08193 Bellaterra, Barcelona, Spain

1. Project description

Tackling environmental challenges is this generation's defining task (EC Green Deal 2020). The climate conference in Paris (COP21, November 2015) and the following conferences reaffirmed the consensus that we cannot achieve the CO₂ reductions required to maintain the global temperature rise to well below 2°C without the extraction of atmospheric greenhouse gases in tandem with emission reductions and a range of other measures. To achieve even 2°C scenarios by 2050, almost 6 billion tonnes of CO₂ should be captured and stored each year across all sectors. Similarly, the UN Sustainable Goal of a toxic free environment requires the removal of a multitude of existing contaminants.

Column sorption is perhaps the most popular practical sorption method, used for a wide range of processes such as the removal of emerging contaminants, Volatile Organic Compounds (VOCs), pharmaceuticals, dyes and salts from fluids, but also to treat waste water, exhaust gases and greenhouse gases. It may be applied to both liquids and gases. Sorption is regarded as efficient and relatively easy to incorporate into an industrial production chain. However, this is offset by an increase in cost which makes the technology less attractive. For example, in the case of carbon capture from power plant CO₂ emissions are typically reduced by 90% but at an increase of between 45-70% in energy costs.

During the final stages of the project 'MTM2017-82317-P Mathematics in nanotechnology and industry', a mathematical model was developed to describe the removal of contaminants from a fluid using an adsorption column. Using a variety of mathematical techniques, the model was simplified to a state where an approximate analytical solution was possible. The analytical solution as well as a preliminary numerical solution were compared with three experimental data sets: for

the removal of CO₂ from gas and amoxicillin and congo red dye from water. Excellent agreement was demonstrated. MATHCOL's motivation is to further the understanding of the column adsorption process, starting from the model developed during MTM2017-82317-P, in order to improve the design of future equipment and increase its effectiveness while reducing costs.

2. Modelling of adsorption mechanisms

2.1 Concentration dependent kinetic models and adsorption isotherms

Adsorption isotherms represent the equilibrium behaviour of a system, plotting the adsorbed mass against a given concentration. In column adsorption the equilibrium concentration may be identified as the inlet value (provided this is constant). **Figure 1** shows the classification of different isotherms reported by McCabe *et al.* [1] and Recasens [2]. The simplest isotherm is the irreversible or rectangular isotherm which states that the mass adsorbed at equilibrium is independent of the contaminant concentration. Strongly favourable and favourable may be related to the Langmuir isotherm or the Freundlich isotherm with $n > 1$ (see §2.1.1 and §2.1.2, respectively). These show that the adsorbed mass increases rapidly with a small increase of contaminant and therefore indicate a good adsorbent. On the other hand, an unfavourable adsorbent may adsorb small quantities for large amounts of contaminant, these may be related to Freundlich with $n < 1$. Freundlich with $n=1$ and the Henry isotherm both cover the linear case (see §2.1.2 and §2.1.7, respectively). Favourable, unfavourable, rectangular and linear may all be covered the Sips isotherm (discussed in §2.1.3).

Isotherms may often be considered as the steady-state of a differential equation (the kinetic equation) describing the attachment rate in terms of the concentration of the contaminant and available attachment sites. Since adsorption refers to mass being captured at the adsorbent surface, the kinetic equation may also be referred to as the sink term. In the following section we provide the sink term related to each of the discussed adsorption isotherms, with the exception of the Dubinin-Radushkevich isotherm, which is based on the Polanyi potential adsorption theory. We employ partial derivatives in the equations to clarify that they may be applied for column adsorption, where the adsorbed fraction also depends on the position inside the column (in batch experiments time may be the only variable).

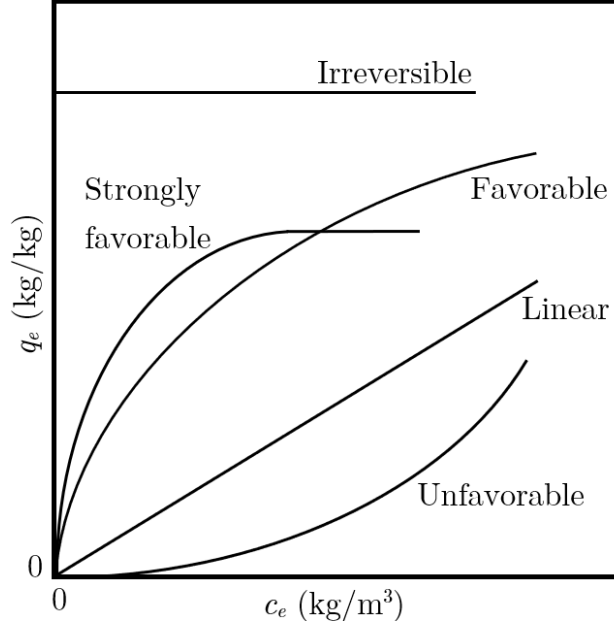


Figure 1. Different types of adsorption isotherms. Adapted from McCabe et al. [1]

2.1.1 Langmuir

The isotherm proposed by Langmuir [3] is based on the assumption that the contaminant molecules create a monolayer of adsorbate upon the adsorbent surface, which is energetically homogeneous and accounts for a maximum number of available adsorption sites. Thus, the adsorption rate at the surface is proportional to both the remaining sites and the pressure due to free contaminant molecules in the fluid. Desorption is only proportional to the already occupied sites in the surface. This may be written

$$\frac{\partial \theta}{\partial t} = k'_{ad}p(1 - \theta) - k_{de}\theta, \quad (1)$$

where θ is the fractional coverage of the adsorbent sites. Using the ideal gas law, we may write $p = cRT$, where c represents the free contaminant concentration. Expressing the coverage in terms of the adsorbed mass, q (kg/kg), such that $\theta = q/q_m$, where the maximum adsorbed mass is denoted q_m (kg/kg), we obtain

$$\frac{\partial q}{\partial t} = k_{ad}c(q_m - q) - k_{de}q, \quad (2)$$

where $k_{ad} = k'_{ad}RT$.

Equation (2) will be referred to from now on as the Langmuir sink or Langmuir kinetic equation. In this form the rate of adsorption may be viewed as proportional to the available sites and

concentration of contaminant throughout the column. Thus it implies purely physical adsorbate-adsorbent interactions[4–7] however, mathematically, it could equally well represent a first order chemical reaction.

When equilibrium is reached, $\partial q/\partial t = 0$, rearranging Eq. (2) leads to the Langmuir isotherm

$$q_e = \frac{q_m K_L c_e}{1 + K_L c_e}, \quad (3)$$

where q_e (kg/kg) is the adsorbed fraction at equilibrium and $K_L = k_{ad}/k_{de}$ is Langmuir's equilibrium constant.

2.1.2 Freundlich isotherm

Freundlich [8] suggested an empirically based isotherm of the form

$$q_e = K_F c_e^{1/n}, \quad (4)$$

which corresponds to the equilibrium state of the kinetic equation

$$\frac{\partial q}{\partial t} = k_{ad} c^{1/n} - k_{de} q. \quad (5)$$

The nonlinear dependence on concentration is typically attributed to an energetically heterogeneous surface of the adsorbent or an order of reaction different to 1 [9]. Despite having no theoretical basis, the Freundlich isotherm does provide a good fit to certain data. However, since q_e increases proportional to $c_e^{1/n}$ there is no limit on its value, i.e. it provides no maximum for the amount adsorbed q_m . Consequently Freundlich is best employed far from this maximum.

2.1.3 Sips isotherm

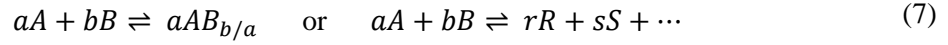
The main objection to the Freundlich isotherm is that there is no limit to the amount that may be adsorbed as the concentration increases. The contribution of Sips [10] was another empirically based isotherm that limited the adsorption

$$q_e = \frac{q_m K_S c_e^m}{1 + K_S c_e^m}. \quad (6)$$

This isotherm is the most general so far and can reproduce all of the forms shown in **Figure 1**. In the limit $K_S c_e^m \rightarrow \infty$ the rectangular isotherm is retrieved, $K_S c_e^m \ll 1$ results in the Freundlich

isotherm (and then $m = 1$ is linear). The Langmuir isotherm corresponds to $m = 1, m < 1$ is favourable, $m > 1$ unfavourable.

The Sips isotherm may be retrieved by applying the law of mass action to a reaction of the form



where $r + s + \dots = a$. A is the adsorbent with stoichiometric coefficient a , B is the contaminant with stoichiometric coefficient b , and $AB_{b/a}$ or R and S are adsorbates. The Sips isotherm corresponds to a kinetic equation of the form

$$\frac{\partial q}{\partial t} = k_{ad}c^b(q_m - q)^a - k_{de}q^a, \quad (8)$$

where $m = b/a$ and $K_S = (k_{ad}/k_{de})^{1/a}$.

2.1.4 Tóth isotherm

The Tóth isotherm is a semi-empirical relation based on the analysis of hundreds of a certain type of isotherm

$$q_e = \frac{q_m K_{T_0} c_e}{(1 + (K_{T_0} c_e)^l)^{1/l}}. \quad (9)$$

This is based on monolayer adsorption on a heterogeneous surface [11]. Its similarity to the Sips model leads the Tóth isotherm to be associated with chemical sorption. However, while the Sips model may be inferred from a chemical reaction the Tóth isotherm cannot. It has an associated kinetic equation

$$\frac{\partial q}{\partial t} = k_{ad}c^l(q_m^l - q^l) - k_{de}q^l. \quad (10)$$

2.1.5 Temkin isotherm

The Temkin isotherm [12] is analogous to the Langmuir sink, equation (2), but assuming that both the adsorption and the desorption terms vary exponentially with the adsorbed fraction,

$$\frac{\partial q}{\partial t} = k_{Tad}e^{-\frac{a_T}{RT}q}c - k_{Tde}e^{\frac{b_T}{RT}q}. \quad (11)$$

At equilibrium we obtain

$$q_e = \frac{RT}{a_T + b_T} \ln(k_{Tad}c_e/k_{Tde}). \quad (12)$$

The Temkin isotherm doesn't capture the correct behaviour of the equilibrium data at low concentrations or close to saturation. Hence, it is mainly useful in the intermediate part of the isotherm.

Brunauer *et al.* [13] derive the Temkin isotherm from the Langmuir isotherm but assuming a heterogeneous adsorbent surface, where the enthalpy changes linearly over the surface. Their isotherm expression is

$$q_e = \frac{RT}{a_T + b_T} \ln\left(\frac{1 + K_{T0}c_e}{1 + K_{T1}c_e}\right), \quad (13)$$

where $K_{T0} = k_{Tad}/k_{Tde}$, $K_{T1} = K_{T0}\exp(-(a_T + b_T)/RT)$. This reduces to the original Temkin isotherm in the limit $K_{T0}c_e \gg 1, K_{T1}c_e \ll 1$. Almost forty years later Temkin derived the same equation [41,42].

2.1.6 Dubinin-Radushkevich isotherm

The Dubinin-Radushkevich isotherm [14],

$$q_e = q_m \exp(-\beta \varepsilon^2), \quad (14)$$

where β is a constant related to the adsorption energy, and ε is the adsorption potential. It is based on an assumption that adsorption occurs in the micropores of an irregular adsorbent surface, where the overlapping of the pore walls leads to an increase of the adsorption potential, so hindering the process [14]. Thus, the coverage of the adsorbent surface at equilibrium is represented by a Gaussian distribution. The parameter ε corresponds to the Polanyi adsorption potential, $\varepsilon = RT\ln(c_s/c_e)$, where c_s is the saturation concentration of the contaminant in the fluid. Polanyi proposed that the molecules of contaminant feel a potential that isothermally compresses them to the surface of the adsorbent. The molecules of adsorbate condense due to this compression, forming a thick layer on the adsorbent surface. The adsorption potential is obtained by defining that the chemical potential over the surface of the liquid layer in contact with the fluid must be equal to that at a large distance. The above expression for ε is used in the original paper by Dubinin [14], but the Polanyi potential can be frequently seen with $1 + c_s/c_e$ as the argument instead of c_s/c_e . As Hu *et al* [15] point out, this is an error that has perpetuated in the literature.

2.1.7 Henry isotherm

The Henry isotherm applies to dilute systems

$$q_e = K_H c_e, \quad (15)$$

where K_H is the Henry constant [2]. The corresponding kinetic equation is

$$\frac{\partial q}{\partial t} = k_{ad}c - k_{de}q. \quad (16)$$

The Henry isotherm may be viewed as an approximation to the Langmuir isotherm in the limit $K_L c_e \ll 1$. The kinetic equations coincide in the limit $q_m \gg q_e$ (such that the Henry adsorption coefficient k_{ad} is equal to the Langmuir coefficients $k_{ad}q_m$).

The Henry constant corresponds to the distribution coefficient. The terms distribution and partition coefficients are often used interchangeably [16]. Kopinke *et al* [17] point out that the term ‘partitioning’ is most frequently used for solute distribution between two volume phases rather than for surface adsorption.

2.1.8 Modified Langmuir isotherm

The Langmuir model has no mechanism to reduce the desorption rate as the fluid becomes saturated. This may be rectified by altering the desorption term

$$\frac{\partial q}{\partial t} = k_{ad}c(q_m - q) - k'_{de}(c_s - c)q, \quad (17)$$

which leads to the modified Langmuir isotherm,

$$q_e = \frac{q_m K_{ML} c_e}{c_s + c_e (K_{ML} - 1)}. \quad (18)$$

The Langmuir sink is retrieved in the limit $K_{ML} \gg 1$ (and $K_{ML} = c_s K_L$). Note that, unlike the Langmuir coefficient, K_L , the coefficient in the modified model, K_{ML} , is non-dimensional. This is practical when the constant is used in thermodynamic relations, since no definition of a standard state is needed.

2.2 Concentration independent kinetic models

We now focus on kinetic equations which neglect the effect of the contaminant concentration. These all suffer from the drawback that they indicate adsorption occurs even when there is no material to adsorb. The first three correspond to the rectangular/irreversible isotherm, that is the equilibrium value of q is constant. The fourth relation, the Elovich equation, has no isotherm. However, all are often used inconsistently by applying an isotherm obtained through a different kinetic relation to determine the actual equilibrium value. These models are more commonly employed in studies of batch experiments.

Since flow is negligible in a batch experiment the model may be solved in a straightforward manner by integrating the kinetic equation (which now involves a total rather than partial derivative), consequently batch experiments provide a simple mechanism to analyse the equilibrium behaviour. The solutions obtained in this manner are not valid for column experiments, where the “initial condition” is space dependent. Specifically, if initially there is no adsorbed material in the column $q(x, 0) = 0$, this will continue to hold for different times along the column: at the inlet we may apply $q(0, 0) = 0$ but at some point along the column $x = x_1 > 0$ the contaminant will only reach that point at time $t_1 > 0$, such that the initial condition there is $q(x_1, t_1) = 0$. This problem is discussed and resolved by Myers *et al.* [18–20] by applying a travelling wave solution.

2.2.1 Pseudo-first order model

The so-called pseudo-first order model, also known as the linear sink or linear kinetic equation [18–20], was first proposed by Lagergren in 1898 [21]. It is based on the assumption that the adsorption rate is proportional to the difference between the values of the equilibrium and current adsorbed fraction,

$$\frac{dq}{dt} = k_L(q_e - q), \quad (19)$$

where k_L is the kinetic coefficient. The steady-state corresponds to the rectangular isotherm $q = q_e$.

Integrating the pseudo-first order equation determines the amount adsorbed during a batch process as a function of time

$$q = q_e(1 - \exp(-k_L t)). \quad (20)$$

2.2.2 Pseudo-second order model

It is well-known that chemisorption may be the controlling mechanism for the adsorption reaction, a number of authors have related this to the so-called "pseudo-second order model", see [22–25]. The pseudo-second order model was first proposed by Blanchard *et al* [26] in an attempt to create a chemically-based model capable of explaining the adsorption of any divalent metallic ion (M^{2+}) onto ammonium impregnated zeolite. They considered a reaction similar to the one in (7), but assuming that it is irreversible, where A is M^{2+} and B represents the adsorption sites. Thus, defining the stoichiometric factors as $a = 1$, $b = 2$, the law of mass action [27] provides the sink term

$$\frac{dq}{dt} = k_{ps0}(q_e - q)^2, \quad (21)$$

where k_{ps0} is the pseudo-second order kinetic constant. Again this demonstrates a rectangular isotherm, $q = q_e$.

Integrating leads to

$$q = \frac{q_e^2 k_{ps0} t}{1 + q_e k_{ps0} t} . \quad (22)$$

2.2.3 Avrami's fractional-order kinetic model

Avrami's kinetic model [28], also known as Avrami fractional-order model, was originally developed to describe a multi-step mechanism of crystallization based on nucleation and growth. It has received attention by its relation with adsorption due to chemical reaction processes [29,30].

The Avrami sink term may be written

$$\frac{dq}{dt} = q_e \exp(-(k_{av} t)^\omega) \omega k_{av}^\omega t^{\omega-1} = (q_e - q) \omega k_{av}^\omega t^{\omega-1} . \quad (23)$$

where k_{av} is the Avrami kinetic constant and ω is the Avrami exponent. Contrary to the equation reported by certain authors, see [30,31], it is important to highlight that the negative sign in the exponential is not affected by the exponent ω [28,32]. This equation is often quoted by defining $k'_{av} = \omega^{1/\omega} k_{av}$ [33] and has a constant isotherm. The corresponding solution is

$$q = q_e [1 - \exp(-(k_{av} t)^\omega)] . \quad (24)$$

Although Avrami's kinetic model is widely used in the literature when fitting results obtained from batch studies, its application has been questioned for solid-fluid adsorption systems due to the lack of physical meaning, and its use in adsorption problems based on unrelated phenomena [34].

2.2.4 Elovich kinetic equation

The Elovich equation was first proposed by Roginsky and Zeldovich [35] in 1934. It reads

$$\frac{dq}{dt} = a_E \exp(-b_E q) , \quad (25)$$

where a_E and b_E are constants.

In batch systems we can directly integrate equation (25) with the initial condition $q(0) = 0$, to get

$$q = \frac{1}{b_E} \left(\ln \left(\frac{t}{t_0} + 1 \right) \right) , \quad (26)$$

where $t_0 = 1/(a_E b_E)$.

The standard procedure to determine the parameters in the Elovich equation is to adjust t_0 such that the experimental data appears on a straight line when plotted as q against $\ln\left(\frac{t}{t_0} + 1\right)$, and then b_E comes from the slope. It is often assumed that $t \gg t_0$ and thus equation (26) may be written as

$$q = \frac{1}{b_E} \left(\ln \frac{t}{t_0} \right). \quad (27)$$

There is debate about the physical meaning of t_0 and b_E , since they seem to be more a mathematical artefact rather than a physical quantity [36,37]. McLintock [36] provides new insight into the interpretation of the value t_0 by suggesting that this is the time when the Elovich law starts to apply in systems where there are different stages: a first linear stage followed by a chemisorption stage. The Elovich equation has frequently been associated with chemisorption, although the sink term is not related to any chemical reaction law.

2.2.5 Intra-particle diffusion equation

In 1963 Weber and Morris [38] proposed a kinetic equation for batch adsorption where the limiting mechanism is intra-particle diffusion,

$$q = k_{int} t^{1/2} + C_{int}, \quad (28)$$

where k_{int} is the intraparticle diffusion rate and C_{int} a constant.

Equation (28) may be thought of as a small time solution of Fick's law for spherical particles [39–41]. Nevertheless, there are serious drawbacks to this model:

- The theoretical derivation of equation (28) is based on Fick's law without any sink term. This indicates that the equation is only valid in batch adsorption at very small times [41], when adsorption hasn't yet occurred and the fluid is simply diffusing into the particles. Consequently k_{int} is not strictly a reaction rate but a parameter that characterizes the intraparticle diffusion [42].
- The addition of the constant C_{int} is experimentally based. McKay *et al.* [42] relate this value to the resistance in the boundary layer.

3. Breakthrough models

Perhaps the most useful piece of experimental data for quantifying column adsorption is the breakthrough curve. Consequently there exist a large number of formulae to describe breakthrough subject to different operating conditions.

3.1 Langmuir sink related models

By far the most common representation of the breakthrough curve takes the form

$$\frac{c(L, t)}{c_{in}} = \frac{1}{1 + \exp(A - Bt)}, \quad (29)$$

where A, B are constant. This general form covers the Bohart-Adams (BA) mode [44] (as well as Amundson's extension [45], Bed Depth Service Time (BDST) [46,47] and Yoon-Nelson [48]. The form of the mass sink and model assumptions defines A, B . Bohart and Adams derived eq. (29) from a balance between advection and the mass sink, where the mass sink takes a Langmuir form with zero desorption. Amundson's derivation follows is based on the same assumptions but using a co-ordinate moving with the carrier fluid. The shift in co-ordinate system is generally negligible [20]. The BDST is simply a rearranged Bohart-Adams form and so easily reverts to eq. (29). The Yoon-Nelson model is based on the probability of molecules escaping at the outlet, The models and derivations are discussed in [20] where it is shown that eq. (29) is generally only accurate if the physical meaning of A, B is neglected and they are instead used as fitting parameters. In particular it is shown that the method used to develop the BA solution requires unphysical assumptions and incorrect initial conditions which then determine A, B in terms of the operating conditions. Since the BA model (and hence Amundson) neglects desorption this affects the contaminant wave speed. Neglecting the definitions of A, B allows the model to fit data but when the correct definition is applied the comparison against data can be extremely poor. This non-physical approach becomes clear in that the derivation is based on a constant adsorption coefficient (with respect to concentration and amount adsorbed) yet in practice when A, B are calculated the adsorption coefficient varies with inlet concentration, thus invalidating the solution.

The "so-called" Thomas model is simply a form of the BA solution (see [20]), and it is often attributed to a Thomas's 1944 paper [49]. In fact it is presented in his 1948 work [50] as a particular limit of the previous solution. The 1944 Thomas model provides a complex expression for concentration in terms of Bessel functions and an infinite series. The limit provided in the 1948 model reduces exactly to the Amundson correction to BA, once Thomas's co-ordinate system is shifted back to the standard form [20,49,50]. Thomas receives more credit than he deserves.

Using a rigorous mathematical derivation and applying a travelling wave form the following equation is developed in Myers *et al* [20]

$$\frac{c(L, t)}{c_{in}} = \frac{1}{1 + \exp\left(k_{ad}c_{in}(t_{1/2} - t)\right)}. \quad (30)$$

Although identical in form to eq. (29) it has a mathematically consistent derivation and contains a single unknown, the adsorption coefficient k_{ad} , which was shown to remain constant for a range of experimental data.

3.2 Linear sink model

The derivation of the breakthrough model is simplified by using a linear sink such as eq. (19) (where, since q now depends on space and time, the total derivative in (19) becomes a partial derivative). The objection that the linear sink suggests adsorption in the absence of material still holds.

With a linear sink and following the travelling wave route mentioned above the concentration may be found everywhere, leading to a breakthrough form

$$\frac{c(L, t)}{c_{in}} = 1 - \frac{1}{2} \exp\left(k_L(t_{1/2} - t)\right), \quad (31)$$

see [51].

3.3 Models for low concentration regions

The Wolborska [52] and Clark [53] models tackle the modelling of adsorption columns by coupling the advection-diffusion-reaction (or only advection-reaction) equation in steady-state with a linear mass transfer rate at the surface of the adsorbent

$$\frac{\partial c^*}{\partial t} = k_m(c - c_i), \quad (32)$$

where $\partial c^*/\partial t$ represents the boundary condition at the surface of the adsorbent, c_i is the average concentration of adsorbate in the adsorbent and k_m is the mass transfer coefficient (1/s).

Wolborska [52] obtained a solution by considering a situation where the adsorbent is far from being saturated, *i.e.* $c \gg c_i$. Thus, the sink term reads

$$\frac{\partial c^*}{\partial t} = k_W c. \quad (33)$$

where k_W is the mass transfer coefficient. The corresponding breakthrough may be found after neglecting diffusion in the mass balance of contaminant,

$$\frac{c(L, t)}{c_{in}} = \exp\left[-\frac{k_W}{u}L + \frac{k_W c_{in}}{q_e}t\right]. \quad (34)$$

This may be obtained from equation (29) by taking a small time limit. It is quite clear that the form $c(L, t) \propto \exp(A t)$ indicates exponential growth in the outlet concentration, so the Wolborska model must be viewed strictly as a small time approximation, i.e. only applicable to describe the first part of the breakthrough curve.

Clark [53] took a similar approach but assuming that the adsorbent is always in equilibrium, and represented by the Freundlich isotherm, i.e. $c_i = c_e = (1/K_F)^n q^n$. The concentration c was taken to be proportional to the adsorbed fraction q , $c_{in} q = q_e c$. The resultant breakthrough curve is

$$\frac{c(L, t)}{c_{in}} = \frac{1}{\left[1 + \left(\left(\frac{c_{in}}{c_b} \right)^{n-1} - 1 \right) \exp \left(\frac{(n-1)k_m}{u} v(t_b - t) \right) \right]^{1/(n-1)}}, \quad (35)$$

where v is the velocity of the adsorption zone (m/s), and c_b (kg/m³) and t_b (s) are a concentration and time at breakthrough, respectively. These final parameters are difficult to determine, effectively being taken as the first measurement after breakthrough. This use of a single experimental point in the breakthrough expression is also used [20] (see discussion below), but they take the time when the concentration is half the initial value which is a much more accurate measurement.

Note that since v and k_m are unknown and c_b is hard to determine accurately, Clark chose to write his equation in the form

$$\frac{c(L, t)}{c_{in}} = \frac{1}{\left[1 + A' \exp(r(t_b - t)) \right]^{1/(n-1)}}, \quad (36)$$

where A' and r are constant fitting parameters [53]. The model is therefore based on fitting with two parameters and with the adsorbent in an equilibrium state (described by the Freundlich equation). It has various inconsistencies/weaknesses: Freundlich only applies away from the maximum adsorbed amount, where $c \ll c_e$ hence the Clark model can also only apply to this region; in equilibrium $c \propto q^n$ but everywhere else $c \propto q$.

3.4 Sips sink model

The Sips sink, eq. (8), does not have the restriction on concentration of the Freundlich model and generalises the Langmuir sink to include different orders of reaction. Myers *et al.* [20] first proposed a model using a Sips sink (8) but based on the isotherm in (6) with $m = b/a \leq 1$, equivalent to the $1/n$ exponent in Freundlich sink. With the adsorption term proportional to c^m , where m is determined from the isotherm (not by fitting to the breakthrough curve), they obtained the following expression

$$\frac{c}{c_{in}} = \frac{mq_e + 2(1 - m) - (1 - m)\exp[(mq_e + 1 - m)k_{ad}c_{in}^m(t_{1/2} - t)/q_e]}{mq_e + 2(1 - m) + mq_e\exp[(mq_e + 1 - m)k_{ad}c_{in}^m(t_{1/2} - t)/q_e]}, \quad (37)$$

where $q_e = 1/(1 + k_{de}/(k_{ad}c_{in}^m))$ and k_{ad} is the Sips adsorption coefficient. In the limit $m \rightarrow 1$ the symmetric curve, equation (30), is retrieved, as $m \rightarrow 0$ equation (31) is retrieved.

As an alternative, Aguares *et al.* [54] reported different breakthrough models based on Sips sink (8) with a and b integers. They related these exponents to the partial orders of the chemical reaction occurring in a chemisorption process. Solutions were provided for combinations where $b \leq a$, with $a = 1,2,3$ and $b = 1,2$. To demonstrate the accuracy they showed excellent agreement between experimental data of CO₂ adsorption on PEI (polyethylenimine) and the breakthrough model with $a = 2$ and $b = 1$ (which they related to the partial orders of reaction of the reaction between CO₂ and the NH₂ radicals on the adsorbent surface). This 2,1 model, rearranged and simplified, reads

$$t = t_{1/2} - \frac{q_m}{k_a c_{in} ((q_m/q_e)^2 - 1)} \left[(q_m/q_e)^2 \ln(c/(c_{in} - c)) + \ln \left(\frac{(q_m/q_e)^2 c_{in} - c}{c(2(q_m/q_e)^2 - 1)^2} \right) \right], \quad (38)$$

where $q_m/q_e > 1$.

3.5 Large mass loss

Myers *et al.* [18] developed a model to deal with significant mass loss, for example with flue gases which may contain of the order 70% greenhouse gases. The loss of such a significant quantity affects both the pressure and velocity results. Their model then requires an extra β , where $\beta = R_g T c_{in} / (\mathcal{M} p)$, R_g [J/(Kmol)] is the ideal gas constant, T [K] the temperature of the column, c_{in} [kg/m³] the inlet concentration of adsorbate, \mathcal{M} [kg/mol] the molecular mass of the adsorbate and p [Pa] the pressure at the outlet of the column. The breakthrough curve is given by

$$\frac{c(L, t)}{c_{in}} = \frac{2 - \beta - \exp(k_L(t_{1/2} - t))}{2 - \beta - \beta \exp(k_L(t_{1/2} - t))}. \quad (39)$$

Note, the earlier claim that the adsorption coefficient is independent of the inlet concentration no longer holds, since k_L is affected by pressure: a large inlet concentration which is then removed will lead to a rapid drop in pressure and hence a drop in the adsorption rate. Consequently we may only state the adsorption coefficient is independent of concentration for the removal of trace amounts.

3.6 Intra-particle diffusion models

Valverde *et al.* [43] have proposed a model accounting for finite speed diffusion from the fluid to the inside of the particles, where subsequently adsorption occurs (following the Langmuir model). They obtain a breakthrough model explicit in time,

$$t = t_{1/2} + \frac{\tau}{\beta} \left[\ln(2) + (1 + k + \beta) \ln\left(\frac{c}{c_{in} - c}\right) + \ln\left(1 - \frac{c}{c_{in}}\right) \right], \quad (40)$$

where $\tau = 1/(k_{ad}c_{in})$, $\beta = 3k_p/(R_p\rho_a q_e k_{ad})$ and $k = k_{de}/(k_{ad}c_{in})$.

This model has been verified against experimental data for the adsorption of distillery spent wash using bagasse fly ash [55], as well as toluene and D4 siloxane onto activated carbon [43]. The size effect was assessed, indicating a better performance of equation (40) than the non-intraparticle model (30) when the slow intra-particle diffusion was the controlling mechanism. The key parameter that distinguishes this situation is β : large values of β allow the model to reduce to equation (30).

4. Types of breakthrough curves

In the following we will classify the different forms of breakthrough curve for single contaminant removal into four groups. The different forms are illustrated through a variety of breakthrough data shown in **Figure 2**.

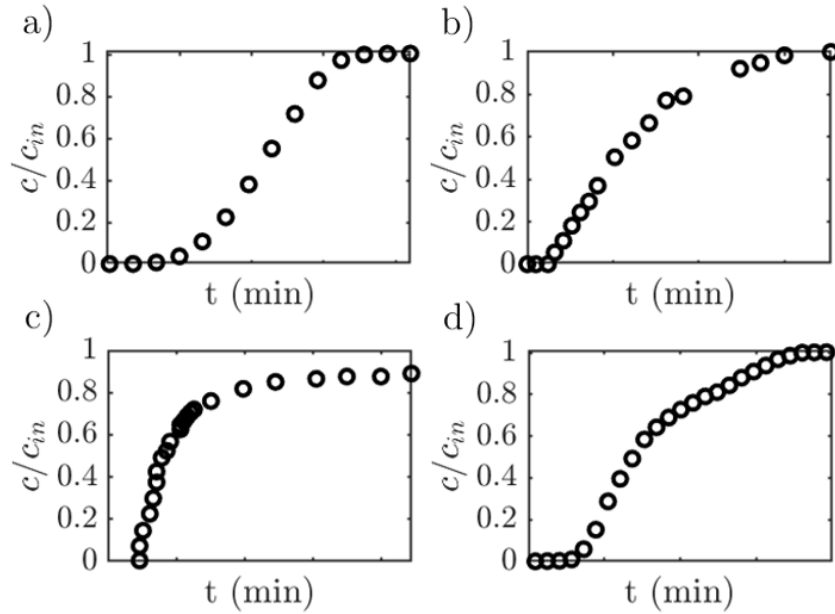


Figure 2. Breakthrough curve types: a) Symmetric (S), b) Asymmetric with sharp initial rise and rapid decay (ARD), c) Asymmetric with sharp initial rise and slow decay (ASD), d) Asymmetric piece-wise with non-smooth transition (APW).

4.1 Symmetric curve (S)

This classification (**Figure 2a**) is the classic S-shaped curve, which is symmetric (or close to symmetric) under a rotation of 180° about the point $(t_{1/2}, c_{1/2})$ where $t_{1/2}$ is the time when the outlet concentration is half the inlet value $c = c_{1/2}$.

All equations related to the Langmuir sink, *i.e.* of the form (29), produce a symmetric curve about $(1/2, t_{1/2})$ and so may be successful in reproducing the S-shaped curves of **Figure 2a**, although as pointed out in [20] only equation (30) by Myers *et al.* is consistent with the model assumptions and the physical meaning of the constants.

The data plotted in **Figure 2a** comes from an experiment for the adsorption of toluene on steam activated carbon, with adsorbent particles in the range 212-425 μm , see [20].

4.2 Asymmetric with a sharp initial rise and a rapid final decay (ARD)

This form of curve (**Figure 2b**) has the highest gradient $\partial c/\partial t$, at first breakthrough and a final rapid approach as $c/c_{in} \rightarrow 1$ (in fact if we zoom in sufficiently close to the first breakthrough region it may be possible to observe a very brief low gradient region). The data shown relates to the adsorption of Cr(III) on NaX zeolite taken from Barros *et al* [56].

Comparison of the linear model (31) with data for Cr(III) adsorption on zeolite [20] shows that it appears to accurately capture results with an initial sharp rise of the form shown in **Figure 2b**. However, it is then shown that with increasing concentrations, and all other conditions fixed, it may appear accurate but requires a variable k_L , so breaking the model assumptions. Hence, although the form (31) can replicate the correct shape it should not be employed on ARD-type data.

The Cr(III) data was analysed in [20] using the Sips isotherm. The isotherm data suggested $m \approx 0.5$ and matching to breakthrough data provided excellent agreement and a constant adsorption coefficient. The same data was analysed in [54] for different values of a and b . The best match to data was found with $b = 1, a = 2$, corresponding to equation (38) (note these values indicate $m = 0.5$). They were also able to relate these values of a and b to the chemical reaction that occurs during the chemisorption process

4.3 Asymmetric with a sharp initial rise and very slow decay (ASD)

The data shown in **Figure 2c** corresponds to the adsorption of amoxicillin on activated carbon, taken from de Franco *et al* [57]. The asymmetric form and slow final decay may be approximated by a linear sink breakthrough or the variable velocity equation (39).

In [58] it is shown that equation (39) can match the amoxicillin breakthrough data but only when β is used as a fitting parameter and its physical definition is neglected. This inconsistency fits with the fact that the model was derived for a large mass loss while the data of **Figure 2c)** relates to the removal of trace amounts, suggesting that while the equation may be able to reproduce the shape it does not correctly describe the physical behaviour.

4.4 Asymmetric piece-wise with a non-smooth transition between regions (APW)

In **Figure 2d)** there are distinct regions with a noticeable change between them. The example in the figure shows a convex form: an initial sharp rise followed by a region with a lower gradient. The data shown relates to the adsorption of toluene on steam activated carbon, but with large adsorbent particles in the range 425-600 μm , taken from [59].

To our knowledge at present no mathematical solution exists which captures this form of breakthrough curve. The switch in behaviour suggests that more than one mechanism is at work. Consequently, researchers have attempted to fit such data with intra-particle diffusion models. The idea being that with larger particles the process has two time-scales: the first associated with rapid attachment to the outside of the particle and the second a slower, diffusion controlled capture on the inside. When outside sites are all occupied the diffusion dominated process takes control and the form of breakthrough changes. This is consistent with the fact **Figure 2a), d)** relate to the same experimental conditions but the former has particle sizes in the range 212-425 μm while in the latter in the range is 425-600 μm .

Mondal *et al* [60] carry out a numerical study of a model which incorporates radial fluid flow and intra-particle diffusion. Their agreement with experimental data shows varying degrees of accuracy but certain results do exhibit piece-wise behaviour.

Alternative possible explanations for the switch include blocking of the pores by large molecules (pharmaceutical molecules are often large compared to the adsorbent pores) or the presence of a range of adsorbent particle sizes, small ones with rapid intra-particle diffusion large ones with a much slower rate.

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