Mathematical modelling of mass transport equations in fixed-bed absorbers

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Summary. This work presents a dimensionless analysis of mass transport equations in fixed-bed absorbers. Focus is centered in isothermal and incompressible problems, with special attention to nonlinear adsorption and desorption processes that take place at absorbent particles. The general differential–algebraic equation system is expressed in dimensionless form, and the model is particularized into four different formulations. The model is analyzed and used to simulate a standard industrial test efficiently. Formulations are selected depending on the relative importance of the different physical phenomena involved in each part of test.

Key words: dimensionless analysis, activated carbon filter, convection – diffusion – reaction equation, numerical simulation, mass conservation, adaptive modelling.

1 Introduction

Modelling adsorption and desorption in fixed–bed absorbers is of high interest in several industrial applications and consequently it has been widely studied (see [1, 2, 3] among many others). In the automotive sector, activated carbon filters called *canisters* are used to reduce the emission of hydrocarbons (HC) from the fuel tank. The production of these filters requires the verification of several quality and efficiency indicators. One of them is provided by the Working Capacity test (WC). This test measures the mass of butane that can be adsorbed by a canister at a prescribed loading – unloading sequence (imposed flows of a butane mixture and clean air respectively).

The transport of HC along the filter and the adsorption – desorption in the activated carbon particles requires accurate description of two spatial scales: the macro scale, for the canister itself with characteristic lengths of decimeters, and the micro scale (two orders of magnitude smaller, in the order of millimeters) for the activated carbon pellets. A model with two phases for each scale

is considered here. The conservation mass of a single-solute is imposed at both scales. The spatial coordinates are averaged in a representative elementary volume [4] and equations of both scales are expressed in dimensionless form. After that, the micro scale equation is transformed into a system of two ordinary differential equations by imposing a spatial discretization of its weak form, which is defined in assumed spherical particles and incorporates appropriate boundary conditions (see [1] for a description of the related Homogeneous Surface Diffusion Model). The resulting algebraic–differential equation system is integrated numerically by an stabilized fractional step method in realistic finite element simulations.

2 Dimensionless model

Dimensionless form of mass balance equations is expressed in terms of the following variables: $\boldsymbol{x} = \boldsymbol{x}'/L$, $\mathrm{t} = V\mathrm{t}'/L$ and $\boldsymbol{v} = \boldsymbol{v}'/V$, where L and V are reference values for length and velocity, and $\boldsymbol{x}'$, t' and $\boldsymbol{v}'$ represent dimensional spatial coordinates, time and interparticle velocity respectively. Mass transport equations depend on the unknowns $\mathrm{c}(\boldsymbol{x},\mathrm{t}) = \mathrm{c}'(\boldsymbol{x}',\mathrm{t}')/c_{\mathrm{ref}}$, $\bar{\mathrm{q}}(\boldsymbol{x},\mathrm{t}) = \bar{\mathrm{q}}'(\boldsymbol{x}',\mathrm{t}')/q_{\mathrm{ref}}$, and $\mathrm{q}_{\mathrm{R}}(\boldsymbol{x},\mathrm{t}) = \mathrm{q}'_{\mathrm{R}}(\boldsymbol{x}',\mathrm{t}')/q_{\mathrm{ref}}$, where q_{ref} and c_{ref} are reference values, and c', $\bar{\mathrm{q}}'$ and q'_{R} are equal to the interparticle concentration, the mean value (in the particle) of the mass adsorbed by unit of clean carbon mass, and the same magnitude but in the external surface of the particles.

On one hand, transport in the macro scale is given by the following dimensionless equation:

$$\frac{\partial \mathrm{c}}{\partial \mathrm{t}} + \boldsymbol{v} \cdot \boldsymbol{\nabla}\mathrm{c} = \boldsymbol{\nabla} \cdot \left(\frac{\boldsymbol{\nabla}\mathrm{c}}{P_{\mathrm{e}}}\right) - \left(\frac{S_{\mathrm{t}}}{B_{\mathrm{i}}E_{\mathrm{d}}} + \mathrm{r}_{\varepsilon_{\mathrm{p}}}\frac{\partial \mathrm{L}(\bar{\mathrm{q}})}{\partial \bar{\mathrm{q}}}\right)\frac{\partial \bar{\mathrm{q}}}{\partial \mathrm{t}} \qquad (1)$$

where $\boldsymbol{\nabla}$ is the gradient operator with respect to $\boldsymbol{x}$, and the following dimensionless numbers are used: Peclet, P_{e}, Biot, B_{i}, and Staton, S_{t}. The surface diffusion modulus is denoted by E_{d}, the porosity ratio by $\mathrm{r}_{\varepsilon_{\mathrm{p}}}$, and the dimensionless Fredulich isotherm by $\mathrm{L}(\bar{\mathrm{q}})$. The parameters are defined as

$$P_{\mathrm{e}} = \frac{VL}{D}, \quad B_{\mathrm{i}} = \frac{k_{\mathrm{f}}c_{\mathrm{ref}}R}{D_{\mathrm{s}}q_{\mathrm{ref}}\rho_{\mathrm{s}}(1-\varepsilon_{\mathrm{p}})}, \quad S_{\mathrm{t}} = \frac{k_{\mathrm{f}}L(1-\varepsilon_{\mathrm{f}})}{VR\varepsilon_{\mathrm{f}}}, \quad E_{\mathrm{d}} = \frac{LD_{\mathrm{s}}}{VR^2},$$
$$\mathrm{r}_{\varepsilon_{\mathrm{p}}} = \frac{1-\varepsilon_{\mathrm{f}}}{\varepsilon_{\mathrm{f}}}\varepsilon_{\mathrm{p}}, \quad \mathrm{L}(\bar{\mathrm{q}}) = \frac{1}{A^{1/n}}\bar{\mathrm{q}}'^{1/n}, \quad A = A'\frac{c_{\mathrm{ref}}^n}{q_{\mathrm{ref}}}, \qquad (2)$$

where D is fluid diffusion, k_{f} the film mass transfer coefficient, R the particle radius, D_{s} the surface diffusion, ρ_{s} the clean carbon density, ε_{f} and ε_{p} the interparticle and the intraparticle porosities, and A' and n the isotherm coefficients.

On the other hand, the dimensionless transport equations at the micro scale are found from the spatial discretization of the surface diffusion equation at particle level complemented with Robin boundary conditions:

$$\frac{\partial \bar{q}}{\partial t} = 3\, B_i\, E_d\, (c - L(q_R))$$
$$\frac{\partial q_R}{\partial t} = 10\, B_i\, E_d\, (c - L(q_R)) + 35\, E_d\, (\bar{q} - q_R). \tag{3}$$

Note that diffusion of the intraparticle fluid phase is neglected, both to keep the model simple and because it is not relevant in gas absorbtion modelling [3]. The formulation of the model corresponding to equations (1) and (3) is called the *three Variables Formulation* (3VF). A first simplification of the model follows from $S_t/(B_i E_d) \gg r_{\varepsilon_p} \frac{\partial L(\bar{q})}{\partial \bar{q}}$, which is verified with reference values given in table 1. However, note that the reaction term in equation (1) remains nonlinear due to the coupling with equations (3). A linear model is found only with linear isotherms (i.e., $n = 1$).

Apart from this obvious simplification three options can be developed, first assuming that diffusion inside particles, D_s, is large enough to consider $\bar{q} = q_R$. This case is referred as the first *two Variables Formulation* (2VF–A), and its reaction term depends on the film mass transfer coefficient, k_f, but it does not on D_s. The second approach in characterized by the hypothesis $c = L(q_R)$, which corresponds to the assumption that k_f is large enough to consider Dirichlet conditions at the particle external surface. This formulation will be referred as 2VF–B and it depends on S_t/B_i and therefore on D_s, but it does not on k_f. Finally the third formulation imposes simultaneously the hypothesis of 2VF–A and 2VF–B: $\bar{q} = q_R = L^{-1}(c)$. The model is then independent of k_f and D_s. It will be referred as 1VF because it only depends on one variable. In this case, two equivalent formulations can be used, one in terms of c and the other in terms of $\bar{q}$. Both can be further simplified using the isotherm relationship presented in equation (2), assuming that P_e is large and the following inequalities:

$$\frac{S_t}{B_i E_d} \gg (1 + r_{\varepsilon_p}) \left(\frac{\partial L^{-1}(c)}{\partial c} \right)^{-1} \quad \text{and} \quad \frac{S_t}{B_i E_d} \gg (1 + r_{\varepsilon_p}) \frac{\partial L(\bar{q})}{\partial \bar{q}}, \tag{4}$$

which are true for reference values, see table 1. Then, typical nonlinear first–order hyperbolic equations are obtained.

The solutions of these equations may present shocks when a high value of the unknowns precedes lower ones along the characteristics. In a one dimensional problem, with zero initial conditions and a boundary condition equal to c^{in}, or equivalently $\bar{q}^{in} = A(c^{in})^n$, chocks with the following velocities are found for each 1VF formulation:

$$v_{sh}^c = \frac{B_i E_d}{S_t} \frac{(c^{in})^{1-n}}{A\, n(2-n)} \quad \text{and} \quad v_{sh}^{\bar{q}} = \frac{B_i E_d}{S_t} \frac{(\bar{q}^{in})^{\frac{1}{n} - 1}}{A^{\frac{1}{n}}}. \tag{5}$$

Note that these two velocities are in general not equal (except for $n = 1$). In order to determine which formulation is preferable, a global mass balance criterium is used: *In a one-dimensional problem, for any of time, the accumulated flow–in through the boundary should be equal to the mass inside the domain,*

Table 1. Dimensionless parameters for loading (left) and unloading (right)

P_e	E_d	A	n	r_{ε_p}	P_e	E_d	A	n	r_{ε_p}
10^5	2.1	0.8	0.31	1.36	10^7	0.021	1.04	0.31	1.36
S_t	B_i	S_t/B_i	B_iE_d	$S_t/(B_iE_d)$	S_t	B_i	S_t/B_i	B_iE_d	$S_t/(B_iE_d)$
50.3	0.083	603.3	0.17	292	0.51	0.084	6.03	0.002	292

i.e. between the boundary and the position of the shock front. This condition can be expressed as $v_{sh}\mathcal{M}(\bar{q}^{in}) = L(\bar{q}^{in})$, where $\mathcal{M}(\bar{q}) = S_t/(B_iE_d)\bar{q}$ is the approximation to the mass by unit of volume in dimensionless form under hypothesis of equations (4); the general expression is given by $\mathcal{M}(c,\bar{q}) = c + r_{\varepsilon_p}L(\bar{q}) + S_t/(B_iE_d)\bar{q}$. The c–based 1VF formulation verifies the condition only for $n = 1$, instead, the $\bar{q}$–based verifies the global mass balance for all n. Thus, the adequate 1VF is the $\bar{q}$–based formulation.

2.1 Dimensionless analysis

In this subsection, three relevant considerations about the dimensionless structure of the model are highlighted. First, note that hypothesis of equations (4), which have been used for 1VF analysis, allows to simplify also 2VF and 3VF formulations (although, as commented before, they remain nonlinear except for $n = 1$). Moreover, as $S_t/(B_iE_d)$ indicates the relative importance of the mass adsorbed with respect to the mass present in the interparticle fluid fase, hypothesis of equations (4) are expected to apply to all usual absorbent media. Recall that this ratio of dimensionless numbers is independent of reference velocity, V.

Second, the Biot number, B_i, which is also independent of V, indicates the relative importance of k_f with respect to D_s. Previous works, see [1], present the following classification: high dependence on k_f for $B_i << 1$, high dependence on D_s for $B_i >> 100$, and relevance of both effects for $B_i \in [0; 100]$. In the model presented here, first case, $B_i << 1$, corresponds to 2VF–A formulation, which is governed by S_t, B_iE_d and the other parameters of equations (2). Second case, $B_i >> 100$, corresponds to 2VF–B formulation, which depends on S_t/B_i, E_d and the other parameters. And third case, $B_i \in [0; 100]$, to the general 3VF, which depend on all dimensionless parameters defined in equations (2).

Finally, note that the influence of reference velocity is restricted to P_e, S_t and E_d. Low velocities imply small P_e and large S_t and E_d. As large S_t and E_d are also found with large k_f and D_s, the 1VF formulation is expected to be the most appropriated for low velocities. Note that in this case the model depends basically on $S_t/(B_iE_d)$, and on P_e, for velocities in the order of L/D or smaller.

3 Application: Working Capacity test

The model presented in previous section has been used to simulate the WC test. Each regime of the test (loading and unloading) is modelled with a different formulation. The representative dimensionless numbers for each regime are summarized in table 1. Note that, on one hand, $S_t/(B_i E_d)$ verifies hypothesis of equations (4), thus simplified formulations can be considered. Moreover, note that in both cases $B_i << 1$ thus 2VF–A or 1VF are expected. And finally, remark that 1VF is more likely to be appropriate for loading than 2VF–A, because of the low velocities, at least compared with those of unloading. On the other hand, P_e^{-1} is much smaller than one (and therefore than $S_t/(B_i E_d)$), therefore interparticle diffusion is expected to be not relevant in any of both regimens, except, locally, in regions with very low velocities. It has been verified that the results obtained with calibrated parameters and real 3D–canisters, and using the same formulation throughout the domain (1VF for loading and 2VF–A for unloading) are satisfactory.

4 Conclusions

A mathematical model for transport and adsorption – desorption of hydrocarbons in activated carbon has been presented and analyzed. The model has been apply to the numerical simulation of the Working Capacity test with canisters (automotive filters for hydrocarbons in gas phase). Different formulations of the model are proposed for each part of the test, obtaining realistic results with complex tridimensional geometries.

References

1. S. Baup, C. Jaffre, D. Wolbert, and A.Laplanche. Adsorption of pesticides onto granular activated carbon: determination of surface diffusivities using simple batch experiments. *Adsorption*, 6:219–228, 2000.
2. M. A. Hossain and D. R. Yonge. Finite Element Modeling of Single Solute Activated Carbon Adsorption. *J. of Environmental Engrg.*, 118(2):238–252, 1992.
3. P. C. Wankat. *Rate–Controlled Separations*. Blackie Academic and Professional, Glasgow, 1994.
4. S. Whitaker. *The method of volume averaging*. Kluwer academic publishers, 1999.