An industrial case study of dynamic adsorption simulation for Volatile Organic Compound (VOC) pharmaceutical emission abatement

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Abstract

Volatile Organic Compound (VOC) emissions have a toxic impact on both environment and human health, so many pharma processes comprise adsorption beds for VOC capture. Optimal management of activated carbon use therein is a key operational and cost issue. This paper presents the application of a validated, non-isothermal adsorption model for an industrially relevant binary (hexane-toluene) mixture under dynamic inlet conditions. Specifically, two VOC inlet concentration patterns are examined in the 100-250 ppm range, emulating industrial VOC generation, revealing preferential adsorption of toluene. Breakthrough times and transitional period durations are also computed and discussed. Longer operation times may be needed for more dilute mixtures, as our results portray. Dynamic models paired with industrial data can deepen our operational insight, enabling extensive technoeconomic VOC mitigation system optimisation towards efficiency maximisation and environmental impact and cost minimisation, towards Industry 4.0.

**Keywords**: Volatile Organic Compound (VOC), dynamic simulation, adsorption.

* 1. Introduction

Global demand for life-saving medicine will steadily increase over the next decades. Primary pharmaceutical manufacturing relies heavily on Volatile Organic Compounds (VOCs) as solvents, but their potential emissions endanger human health and ecosystems alike (DEFRA, 2023). End-of-pipeline methods, such as adsorption (Das et al., 2004) are ideal and widely applied for industrial emissions abatement. However, as gas waste streams from multiple processes are fed to the same unit, frequent and costly adsorbent regeneration is inevitable, as irregular bed saturation hampers process efficiency greatly.

We present here the application of a validated dynamic, nonisothermal adsorption model (Tzanakopoulou et al., 2023) to study a binary mixture (hexane-toluene) under industrial conditions. Adsorption is a profound field of study (Tefera et al., 2014; Knox et al., 2016), but the literature on pharma-relevant VOCs under industrial conditions is rather limited. This study therefore considers two dynamic VOC feed concentration patterns, in order to examine relevant breakthrough trends in an Activated Carbon (AC) adsorption column. The VOC concentration range (100-250 ppm) emulates realistic industrial (multi-unit) feed conditions for both cases, aiming to probe the effect of component/concentration sequencing on bed breakthrough time, cost implications and wider environmental impact.

* 1. Multicomponent, nonisothermal adsorption model development

The validated model we use (Tzanakopoulou et al., 2023) employs the next assumptions:

1. The temperature difference between particles and the gas phase as well as carrier gas adsorption are considered negligible, while the ideal gas law applies (Ruthven, 1984).

2. Equilibrium obeys the Extended Langmuir model for binary mixtures (Ruthven, 1984).

3. Solid phase mass transport is approximated by the LDF model which is characterized as “simple, analytical and physically consistent” (Sircar, 2000).

The equations are derived from these sources, with Eqs. (17-21) from Knox et al. (2016).

The Bosanquet formula, Eq. (12) thus Eq. (5), is verified (Krishna & van Baten, 2012).

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| --- | --- | --- | --- |
|  | (1) |  | (17) |
|  | (2) |  | (18) |
|  | (3) |  | (19) |
|  | (4) |  | (20) |
|  | (5) |  | (21) |
|  | (6) |  | (22) |
|  | (7) |  | (23) |
|  | (8) |  | (24) |
|  | (9) |  | (25) |
|  | (10) |  | (26) |
|  | (11) |  | (27) |
|  | (12) |  | (28) |
|  | (13) |  | (29) |
|  | (14) |  | (30) |
|  | (15) |  | (31) |
|  | (16) |  | (32) |

* 1. Dynamic Model Parameters for Adsorption Systems

The developed model is used to simulate multicomponent VOC adsorption under dynamic inlet concentration. The set of PDEs is solved using RADAU solver and orthogonal collocation on finite elements for space discretization in gPROMS Process 2.0.0. The adsorption of binary hexane – toluene mixture, with air as the carrier, has been examined on beaded activated carbon (Tefera et al., 2014) and a wall temperature of 295 K. The system viscosities are computed from Wilke’s equation for binary mixtures, while Langmuir isotherm parameters are taken from Delage et al., (2000) and Shim et al., (2003) for toluene and hexane respectively. Air is assumed as a binary mixture (N2:O2 = 79:21 % v/v). Table 1 presents the values for the main simulation parameters.

***Table 1. Main model parameter values.***

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | ***Vs***  **(m s–1)** | ***L***  **(m)** | ***R***  **(m)** | ***εb*** | ***x***  **(m)** | ***ρb***  **(kg m-3)** | ***Tin***  **(K)** | ***Tw***  **(K)** |
| HEX | 0.914 | 0.065 | 0.0076 | 0.38 | 0.001 | 606 | 300 | 295 |
| TOL |
|  | ***Cpp***  **(J kg–1 K–1)** | ***kw***  **(W m–1 K–1)** | ***kp***  **(W m–1 K–1)** | ***εp*** | ***b0***  **(m3 mol-1)** | ***ΔHad***  **(J mol-1)** | ***qm***  **(mol kg–1)** | |
| HEX | 706.7 | 14.2 | 0.17 | 0.56 | 2.35∙10-8 | 50,000 | 3.801 | |
| TOL | 4.06∙10-7 | 45,500 | 4.610 | |

Table 2 presents the main dynamic inlet parameter values employed for both patterns.

***Table 2. Pattern 1 and 2 parameter values.***

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **Pattern 1** | ***C0,i***  **(ppmv)** | ***kLDF***  **(s–1)** | ***Dz,i***  **(m2 s–1)** | ***Cpg***  **(J kg–1 K–1)** | ***ho***  **(W m–2 K–1)** | ***kez***  **(W m–1 K–1)** |
| HEX | 200 | 1.88∙10-4 | 1.32∙10-3 | 1,014 | 37.17 | 0.67 |
| TOL | 250 | 5.43∙10-5 | 1.34∙10-3 |
| HEX | 230 | 1.94∙10-4 | 1.32∙10-3 | 1,014 | 37.17 | 0.67 |
| TOL | 250 | 5.50∙10-5 | 1.34∙10-3 |
| HEX | 250 | 1.95∙10-4 | 1.32∙10-3 | 1,014 | 37.17 | 0.67 |
| TOL | 250 | 5.53∙10-5 | 1.34∙10-3 |
| HEX | 165 | 1.82∙10-4 | 1.32∙10-3 | 1,014 | 37.17 | 0.67 |
| TOL | 250 | 5.38∙10-5 | 1.34∙10-3 |
| HEX | 150 | 1.85∙10-4 | 1.32∙10-3 | 1,014 | 37.16 | 0.67 |
| TOL | 250 | 5.33∙10-5 | 1.34∙10-3 |
| HEX | 130 | 1.83∙10-4 | 1.32∙10-3 | 1,014 | 37.16 | 0.67 |
| TOL | 250 | 5.32∙10-5 | 1.34∙10-3 |
| **Pattern 2** | ***C0,i***  **(ppmv)** | ***kLDF***  **(s–1)** | ***Dz,i***  **(m2 s–1)** | ***Cpg***  **(J kg–1 K–1)** | ***ho***  **(W m–2 K–1)** | ***kez***  **(W m–1 K–1)** |
| HEX | 200 | 1.59∙10-4 | 1.32∙10-3 | 1,014 | 37.19 | 0.67 |
| TOL | 100 | 4.63∙10-5 | 1.34∙10-3 |
| HEX | 230 | 1.62∙10-4 | 1.32∙10-3 | 1,014 | 37.19 | 0.67 |
| TOL | 100 | 4.69∙10-5 | 1.34∙10-3 |
| HEX | 250 | 1.65∙10-4 | 1.32∙10-3 | 1,014 | 37.19 | 0.67 |
| TOL | 100 | 4.73∙10-5 | 1.34∙10-3 |
| HEX | 165 | 1.57∙10-4 | 1.32∙10-3 | 1,014 | 37.19 | 0.67 |
| TOL | 100 | 4.58∙10-5 | 1.34∙10-3 |
| HEX | 150 | 1.58∙10-4 | 1.32∙10-3 | 1,014 | 37.19 | 0.67 |
| TOL | 100 | 4.54∙10-5 | 1.34∙10-3 |
| HEX | 130 | 1.52∙10-4 | 1.32∙10-3 | 1,014 | 37.19 | 0.67 |
| TOL | 100 | 4.50∙10-5 | 1.34∙10-3 |

* 1. Results and Discussion

Figure 1 presents the breakthrough curves (outlet concentration vs time) and temperature and pressure variations of the examined binary system (hexane-toluene). In this work the adsorption behaviour of the binary mixture hexane-toluene (with air as the carrier gas) has been examined, for an activated carbon column, under two different dynamic inlet concentration cases (Patterns 1, 2) of industrial relevance. For both scenaria considered, hexane undergoes a series of inlet concentration step changes (as occurring from upstream batch production steps), accompanied by a toluene stream of steady inlet concentration. The latter is fixed at a high (250 ppm) or low (100 ppm) level, for the said Patterns 1-2.

The breakthrough onset time (t5%) is calculated as the time that the component’s outlet concentration reaches 5% of its equilibrium outlet concentration (after all transitions). Breakthrough completion for toluene (t95%) is considered to occur at the time that the outlet concentration of the VOC reaches a 95% fraction of the equilibrium (final) value. For hexane (the weakly adsorbing component), the t105% value is taken to be the breakthrough completion time (as it is approached from higher values after an overshoot). The breakthrough intervals are thus defined as 5-95% for toluene, and 5-105% for hexane.

Fig. 1 (a-b) present the inlet and outlet concentrations for the Pattern 1 case, respectively. Hexane breaks through the column outlet first at t = 1037 s, while toluene breaks through the column second at t = 3190 s. Breakthrough completion comes after the indicative points of t95% = 6769 s for toluene, and t105% = 5200 s for hexane (due to a clear overshoot).

Fig. 1 (c-d) present the inlet and outlet concentrations of pattern two. As observed in pattern one, hexane breakthrough onset precedes toluene’s, at t5% = 1021 s followed by toluene at t5% = 3368 s. Breakthrough completion for toluene is at t95% = 8220 s, which makes it’s duration in pattern 2, 18 % longer than in pattern 1, due to the lower concentration of toluene in the mixture. For hexane, breakthrough completion is t105% = 5038 s, 3 % shorter than in pattern 1. Interestingly, in pattern 2 the breakthrough onset time for hexane is 2 % quicker than in pattern one, despite the lower toluene concentration, while toluene’s breakthrough onset is 5 % larger compared to pattern one, as expected due to the decrease in inlet concentration between the two scenarios.

Fig. 1 (e-f) show temperature and pressure variations for both said Patterns investigated. Continuous dark lines denote Pattern 1, while dashed light lines correspond to Pattern 2. As can be seen in plot (e), adsorption causes a temperature rise when taking place due to its exothermicity. Interestingly, the temperature rise of Pattern 1 leads to a marginally higher temperature rise (Tmax = 299.37 K) compared to Pattern 2 (Tmax = 299.17 K), in which toluene concentration is lower, before stabilising once the mass transfer zone has moved to later parts of the bed. The pressure drop, depicted in panel 1(f), is nearly the same for the two patterns, as expected due to flow conditions and feed concentrations.

Fig. 1 (g-h) present the key metrics of breakthrough, quantifying the transition intervals. All breakthrough time metrics for both cases are summarised in Fig. 1 (g-h) histograms. Breakthrough durations therein are denoted by respective Δt symbols and lighter shading. For Pattern 2, where we have considered toluene at a 60% lower inlet concentration vs. Pattern 1, the breakthrough duration is 74% shorter; for hexane, it is only 4% shorter.

A remarkable observation emerges: though Pattern 1 has a clearly heavier VOC load vs. Pattern 2 (due only to the higher toluene level, as the hexane transient is kept invariant), the adsorption breakthrough duration is shorter for Pattern 1 vs. Pattern 2, for which it is longer. The strongly adsorbing component (toluene) affects the time to reach steady state.

|  |  |
| --- | --- |
|  |  |
| (a) | (b) |
|  |  |
| (c) | (d) |
|  |  |
| (e) | (f) |
|  |  |
| (g) | (h) |

**Figure 1.** Simulation results for dynamic inlet patterns 1 and 2 of the hexane-toluene mixture.

* 1. Conclusions

In an era of global efforts towards sustainable manufacturing, limiting Volatile Organic Compound (VOC) emissions emerges as a priority for the pharma industry, where solvent substitution is not always an option due to the stringent regulatory approval constraints. In tandem to unit operation-specific counter-emission measures, the existence of end-of-pipe adsorption columns safeguards compliance with all environmental protection laws. Nevertheless, feeding adsorption beds with a multitude of VOC-laden gas streams from many process unit vents in batch operation induces irregular activated carbon saturation. Frequent and expensive adsorbent regeneration and changeover thus become inevitable. Despite a vast literature body, industrial VOC adsorption under transient feeds is elusive.

This work presents the application of a validated (Tzanakopoulou et al., 2023), multicomponent, nonisothermal adsorption model to investigate dynamic feed concentration volatile organic compound adsorption. To this end, the mixture of hexane-toluene with air as the carrier gas is studied under inlet conditions informed by industrial data. Two VOC inlet patterns are studied where ehxane undergoes a series of inlet concentration changes and toluene reamins at a constant high (250 ppm) inlet concentration in one scenario and toluene remains at a constant low (100 ppm) inlet concentration in the second scenario. Results reveal a later breakthrough onset time for hexane when in a mixture with a high (250 ppm) toluene inlet concentration, while the opposite happens for toluene. The transient duration is longer for the lower VOC load. Temperature rises in the bed as well as pressure drop increase with increased VOC solvent stream load. This work paves the way for waste stream sequencing efforts, not only under batch, but also future continuous pharmaceutical manufacturing optimisation efforts.

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