Multicomponent, nonisothermal VOC adsorption modelling for pharmaceutical emission abatement

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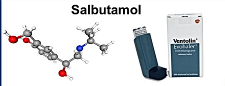
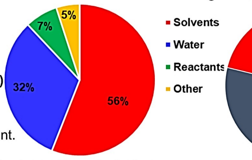
1. *VOCs in the Pharma Industry*

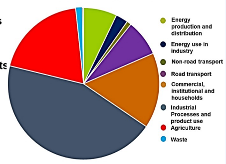
Salbutamol



Materials in API Manufacturing[1]



EU VOC Emission Sectors[2]

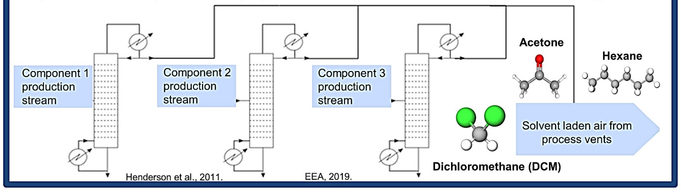


Volatile Organic Compounds (VOC)

- **API manufacturing solvents.**
- Toxic for humans and environment.

VOC Generation in Salbutamol Upstream Manufacturing

- Distillations for solvent separations are the main cause of VOC emissions.
- High environmental repercussions highlight need for efficient, cost-effective VOC control technology.

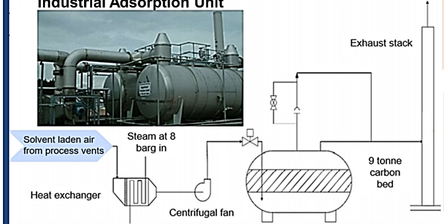


2. *VOC Abatement via Adsorption*

Selective retention of pollutant molecules from waste streams on the surface and pores of porous materials.

Benefits	Challenges
VOC recovery possible, wide range of loading.	Expensive carbon bed regeneration
High efficiency and low energy demand.	Irregular bed saturation due to VOC mixtures
Easy installation/maintenance.	Understudied technoeconomic optimisation.[3]

Industrial Adsorption Unit



Research Gap

- Literature not relevant to reality
- Industrial case studies needed

Modelling & Optimisation

- Improved process efficiency.
- Lower OpEx.
- Lower API manufacturing cost.
- Lower VOC emissions.

AIM: Investigation of effect of column length scale up in multicomponent, nonisothermal VOC adsorption on an activated carbon column, to form a basis towards total process optimisation.

Tzanakopoulou et al., 2023.

3. *Nonisothermal Multicomponent Adsorption Model*

Simulations executed using gPROMS Academic 2.0.0 (CPU: i7 and RAM: 32 GB). gPROMS

Model assumptions

- Radial temperature gradients and concentrations are negligible.
- Wall temperature is constant and equal to surrounding temperature.
- Adsorbent particles and gas phase are in thermal equilibrium.

Energy balance

$$\left(\rho_g C_{pg} + \frac{(1-\varepsilon_b)}{\varepsilon_b}\rho_p C_{pp}\right)\frac{\partial T}{\partial t} = k_{ez}\frac{\partial^2 T}{\partial z^2} - \rho_g C_{pg}\frac{\partial (uT)}{\partial z} + \frac{(1-\varepsilon_b)}{\varepsilon_b}\sum_{i=1}^{n}\Delta H_{ad,i}\frac{\partial q_i}{\partial t} - \frac{2h_o}{\varepsilon_b R_p}(T - T_w)$$

Component mass balance

$$\frac{\partial C_i}{\partial t} = D_{z,i}\frac{\partial^2 C_i}{\partial z^2} - \frac{\partial (uC_i)}{\partial z} - \frac{(1-\varepsilon_b)}{\varepsilon_b}\rho_p\frac{\partial q_i}{\partial t}$$

Extended Langmuir model

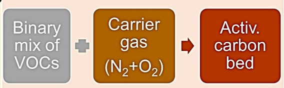
$$q_{e,i} = \sum_{i=1}^{n}\frac{b_i c_i a_i}{1 + (\sum_{i=1}^{k} b_i c_i)}$$

Linear Driving Force model for solid state

$$\frac{\partial q_i}{\partial t} = k_{LDF}(q_{e,i} - q_i)$$

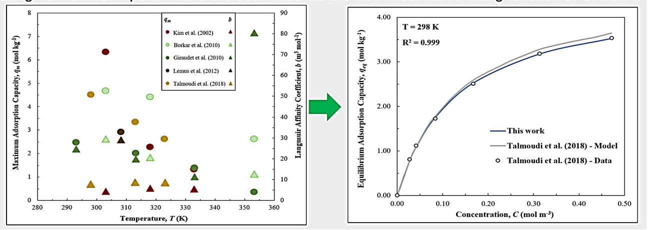
Ergun's Equation

$$-\frac{\partial P}{\partial z} = 150u\mu\frac{(1-\varepsilon_b)^2}{\varepsilon_b^2 d_p^2} + 1.75\rho_g u^2\frac{(1-\varepsilon_b)}{\varepsilon_b d_p}$$



4. *Langmuir Model Parameter Estimation*

Langmuir Isotherm parameters are estimated via the non-linear curve fitting function of ORIGIN.



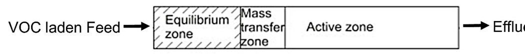
- Use of different isotherms.
- Lack of parameter disclosure in published literature.
- Establishment of VOC Langmuir Isotherm Parameter Database.

OriginPro 2023b The Ultimate Software for Graphing & Analysis

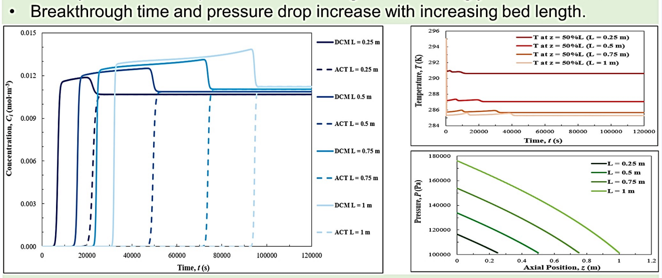
The set of PDEs are solved by:

- Orthogonal collocation on finite elements with varying discretisation points
- Variable order Runge-Kutta formulae and a variable time step

5. *Breakthrough Simulations*



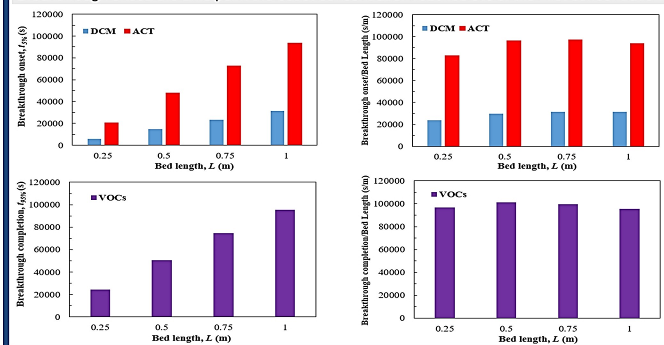
- Weakly adsorbed component breaks through before strongly adsorbed VOC.
- Breakthrough time and pressure drop increase with increasing bed length.



- Temperature peaks signify adsorption taking place (exothermic process).
- Competitive adsorption: outlet concentration exceeds feed conditions (roll-up).

6. *Key VOC Capture Bed Design Metrics*

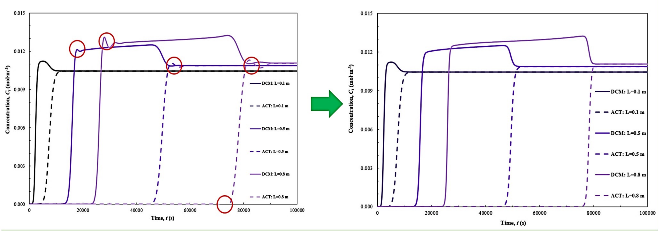
Breakthrough onset: the time point the outlet concentration reaches 5% of the inlet concentration.



- Increasing bed length leads to steeper breakthrough onset increase for acetone.
- Breakthrough onset time changes reach plateau with increasing bed length.

7. *Exponential Grid Transformation*

Spatial grid discretisation optimisation: DCM-Acetone at L = 0.1-0.8 m



Grid with 5 discretisation points vs Grid with 10 points & exponential transformation

Discretisation points	Length (m)	Simulation horizon (s)	CPU time (s)
30	0.5	90000	3.6
90	0.5	90000	9.2
90,Exp(2)	0.5	90000	7.6

8. *Conclusions*

- Simulations of API manufacturing solvent abatement crucial for environmental impact mitigation.
- Lack of published literature on VOC adsorption under industrially relevant conditions.
- **Establishment of** pharma-relevant VOC Langmuir Isotherm **parameter database.**
- **Acetone** demonstrates preferential adsorption over dichloromethane.
- **Larger bed length** leads to longer breakthrough onset times for dichloromethane and acetone.
- **Breakthrough onset increase not analogous to bed length increase** for both VOCs.
- Plateau of change of breakthrough onset with increasing bed length.
- **Exponential spatial grid transformation essential** to reliable industrial-scale simulations.
- **Current efforts** focused on process optimisation via Mixed Integer Linear Programming (MILP).

9. References

1. Henderson et al., **2011**, Expanding GSK's solvent selection guide. *Green Chem.*, **13**(4):854.
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3. Tzanakopoulou & DG, **2023**, Dynamic modelling, simulation and theoretical performance analysis of Volatile Organic Compound (VOC) abatement systems in the pharma industry, *Comput.Chem. Eng.*,**174**,108248.
4. Ruthven, **1984**, Principles of adsorption and adsorption processes, Wiley.
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6. Talmoudi et al., **2018**, Dynamic study of VSA & TSA processes for VOC removal from air, *Int. J. Chem, Eng.*, 2018:1.
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