MODELING THE ADSORPTION OF VOLATILE ORGANIC COMPOUNDS ONTO ACTIVATED CARBONS

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Introduction

The adsorption on fixed activated carbon beds is a common industrial process; especially for the recovery of volatile organic compounds (VOCs). Its high efficiency and relatively low cost is interesting for air treatment units [1]. However, the adsorption of VOCs onto activated carbon is highly exothermic and ignition risks arise when high levels of pollutants are to be treated [2]. Indeed, accidents were reported for industrial processes when unusual peaks of VOC concentrations occurred at the inlet of the adsorber.

The objective of this study was to set up a numerical model able to predict the coupled mass and heat transfers in the fixed bed during the adsorption of VOCs. Thereby, the simulation determines the efficiency of the process while ensuring its safety.

Such a model is, most often, based on adsorption equilibria, which constitutes the thermodynamic limit of adsorption [3]. Therefore, accurate isotherm models are required. Since temperatures will be rising inside the adsorber during the removal of VOCs, these models should give the amounts of adsorbed compounds over a wide range of temperatures. Our previous work did focus on this aspect and compared common models (Langmuir, Freundlich, etc.) for a selection of VOC between 20 and 80°C [4].

In addition, taking into account the heat transfers requires the heat of adsorption that is the energy released by the adsorption of the VOC onto the activated carbon. This characteristic could be predicted from the type of adsorbent as well as the nature of the organic compound [5].

Experimental

Breakthrough curves and temperature profiles were measured along the fixed bed using a gas chromatograph equipped with a flammable ionization detector and thermocouples, respectively. A schematic diagram describes the experimental unit on Fig. 1.

Three VOCs were studied: acetone, ethyl formate and dichloromethane. These organic compounds were chosen from different chemical species and because they exhibit various heats of adsorption on activated carbons. Furthermore, five activated carbons were chosen thanks to the type of activation, the ratio of mesoporous and microporous volumes and the distribution of micropore sizes.

Finally, some operating conditions were investigated. On the one hand, inlet concentrations of VOCs were ranging from 50 to 100 $g.m^{-3}$. On the other hand, the flow rate of the gas phase was varying from 0.14 to 0.28 $m.s^{-1}$.

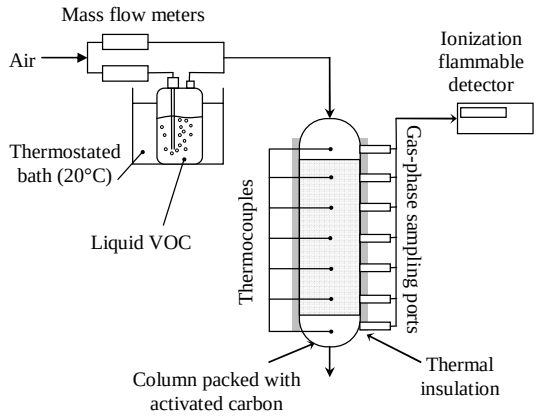

Fig. 1 Schematic of the adsorption column

Theoretical

A theoretical model was developed taking into account the mass and heat balances as well as the adsorption kinetics (linear driving force) and equilibria (temperature-dependent form of the Langmuir model). It ended up with a set of four partial differential equations with respect to one space axial dimension and time.

Numerical

Various numerical methods were used in order to solve this set of partial differential equations. From the comparison, the numerical method of lines with an adaptive spatial meshing procedure was the quickest and the most accurate method. Indeed, other methods such as finite volume methods were exhibiting false diffusion or large oscillations in the narrow mass transfer zone.

Results and Discussion

The temperature profiles and breakthrough curves measured in a lab-scale adsorption column were compared to simulation. The model was adjusted to the experimental data via the adsorption rate in the equation of the linear driving force model. The influence of the temperature on this parameter was taken into account [6].

An example of modeling results is presented on Fig. 2 and 3 for the adsorption of ethyl formate onto the Pica NC60 activated carbon.

Breakthrough times and maximum temperature rises were computed with a coefficient of determination of 0.988 (Fig. 4) and 0.901, respectively. From the comparison of simulation and experimental results, the advantage of accounting for

dispersions of heat and mass was shown and the importance of the temperature on the adsorption equilibria was enlightened.

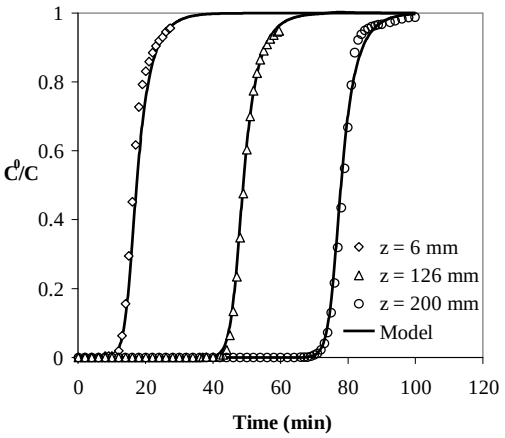

Fig. 2 Modeling breakthrough curves along the adsorber

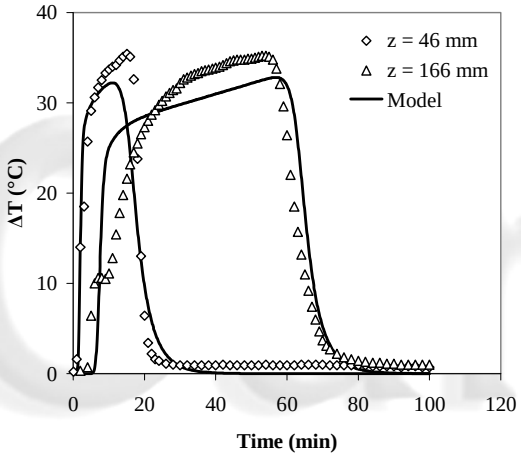

Fig. 3 Modeling temperature profiles along the adsorber

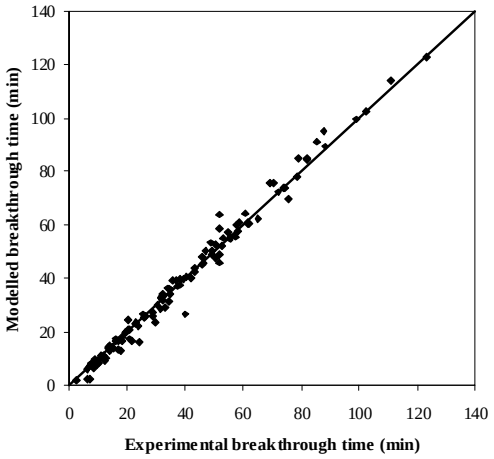

Fig. 4 Results of the simulation – Breakthrough times

As stated above, the simulation was fitted to experimental results by adjusting the rate of adsorption. This rate of adsorption was in the range 32.4-1125 s^{-1}, but no clear relationship with one operating conditions (type of adsorbate/adsorbent, superficial velocity, gas concentration) could be established.

Furthermore, the coefficient for the axial dispersion of mass was between 0 and 0.0021 $m^2.s^{-1}$ and its analog for the dispersion of heat, between 0 and 0.86 $W.m^{-1}.K^{-1}$.

The efficiency of the model was mainly limited by the isotherm model used. In fact, if this model wasn't chosen properly, i.e. it did not describe the adsorption behaviors over the entire range of temperature, then the simulation was shown to deviate significantly from the measured breakthrough curves. Special care is demanded on the selection of the isotherm model.

Conclusions

Coupled heat and mass transfers were modeled for a variety of VOCs and activated carbons. After the adjustment of the adsorption rate, the model was shown to fit accurately the experimental breakthrough curves and temperature profiles. However, the study put forward the influence of the model used to describe the equilibriums.

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