20th International Congress of Chemical and Process Engineering CHISA 2012
25 – 29 August 2012, Prague, Czech Republic

Off-gas-treatment by application of selective adsorbents

Y. Dong, T. Täffner, J. F. Fernández, B. Niemeyer a*

Helmut-Schmidt-University / University of the Federal Armed Forces Hamburg,
Faculty of Mechanical Engineering - Holstenhofweg 85, 22043 Hamburg, Germany

Abstract

The breakthrough behavior of a fixed bed adsorber in pilot scale was investigated in this study. The adsorber has been constructed to remove odour compounds and simulate practical conditions, especially those found in the catering industry and small restaurants. In order to facilitate an optimal employment of this adsorption system for odour control, the breakthrough behavior of two adsorbents, HSU 100-100 and HSU 100-300, were determined under different flow rates and input concentrations for isopropanol and xylene. Results showed the effect of changing the flow rate and/or the input concentration for each adsorbent-adsorptive system on breakthrough time and loaded amount of adsorptive. Besides, the adsorbent HSU 100-300 turned out to be a promising candidate for odour control applications due to longer breakthrough times and efficient thermal regeneration. Finally, the Yoon-Nelson Model was applied for breakthrough curve comparison and loading estimation.

Keywords: Breakthrough curves; fixed bed adsorber; odour control; Yoon-Nelson model; thermal desorption; VOC

1. Introduction

The problems caused by air pollution become more and more compelling with the drastic increase of anthropogenic activities. Emissions from industrial processes, catering industry or small restaurants and live-stock agriculture come nowadays into severe conflict with the growing of residential zones. Even though smelling components appear in low concentration level (ppb), such components are easily...
recognized by human olfactory sensation and could case annoying feelings. Therefore, odour control measurements are indispensable [1-3].

**Nomenclature**

| Symbol | Definition                                      |
|--------|------------------------------------------------|
| C      | Exit gas concentration (mg/m³)                |
| C₀     | Input gas concentration (mg/m³)               |
| C/C₀   | Relative concentration (-)                    |
| k'     | Rate constant (h⁻¹)                           |
| logP_{ow} | Octanol-water partition coefficient (-)       |
| N_{ADS} | Amount adsorbed according to Yoon-Nelson model (mg) |
| t      | Time (h or min)                               |
| t_{½}  | 50% input concentration breakthrough time (h) |
| V      | Volumetric gas flow (m³/h)                    |
Several technologies are widely used for odour control purposes. Among these, fixed bed adsorption is one of the most powerful and promising methods since it can achieve high efficiencies even at low concentration levels [4]. In order to seek opportunities for improving the performance of fixed bed adsorption systems, two major fields are subject to study. One is the suitable application of new functionalized adsorbents for specific requirements [5-9]. The second one is the optimization of technical operations. Both measures result in higher efficiency due to improved selectivities, and higher separation capacities for the relevant compounds. These effects can be investigated mainly through the breakthrough behavior which describes the dynamics of the mass transfer zone and reflects the performance of a fixed bed. Up to date, most of the studies in this field are focused on modeling and simulation with experimental verifications in lab-scale [10, 11].

Some parameters may exert undesired influence on the breakthrough behavior when lab-scale equipment is used. To overcome this drawback, a pilot scale experimental setup was constructed for this study. Two functionalized adsorbents were selected (HSU 100-100 and HSU 100-300), while isopropanol (hydrophilic, logP<sub>ow</sub> = 0.05) and xylene (hydrophobic, logP<sub>ow</sub> = 3.12-3.20) were chosen as adsorptive. For each adsorptive-adsorbent system, experiments were carried out under different flow rates and input concentrations. In this case, the relatively high flow rates (70-150 m<sup>3</sup>/h) and low-level input concentrations (< 100 ppm) were notably different from other experiments already published. The breakthrough time and loading capacity were used for evaluating the performance of the fixed bed adsorber.

In addition, the Yoon-Nelson model was used. It is a theoretical model applying the principle of gas adsorption kinetics. The idea behind is that the rate of adsorption is proportional to the rate of molecular collisions with unoccupied adsorption sites. It is used for modeling the entire breakthrough curve with two parameters (k’ and t<sub>1/2</sub>) calculated from the experimental data. The parameter k’ is the rate constant which reflects the slope of the breakthrough curve, while t<sub>1/2</sub> is the time when the exit concentration is 50% of the input concentration.

The amount adsorbed in a fixed bed can be calculated as follows, and the model is readily to apply by fitting the experimental results and does not demand detailed information about the adsorbent-adsorptive system [12-14].

\[ N_{ADS} = C_0 \times V \times t_{1/2} \] (1)
2. Experimental

2.1. Materials

Isopropanol and xylene, both with p.A. grade from Merck KGaA (Darmstadt, Germany), were employed as received. Adsorbent HSU 100-100 is an unfunctionalized silica gel, while adsorbent HSU 100-300 is a mixture of three functionalized adsorbents (silica gel HSU 100-50, zeolite HSU 300-50 and silica gel HSU 100-100.1) in a proportion of 2:2:1. All adsorbents are mesoporous materials with specific surfaces ranging from 250 to 500 m²/g.

2.2. Pilot scale system

A pilot scale system was designed, set-up and commissioned for this work (Fig.1). The whole system can be divided into three parts: 1) the adsorptive generation, 2) the fixed bed adsorber and 3) the concentration measuring system.

![Fig. 1. Flow diagram of the experimental setup.](image-url)
The gas containing the adsorptive was generated by evaporation of pure adsorptive liquid placed in a glass basin. Ambient air, which was sucked in by the cooker hood, carried the evaporated adsorptive and passed through the adsorber. In order to vary the input concentration in a defined way, two basins containing the liquid adsorptive were used simultaneously.

The fixed bed has a cross section of 40 x 29.5 cm² and a height of 13.5 cm. The ambient air containing the adsorptive flowed downstream to avoid the axial movement of solids. A certain power input on the Fan 100 axial centrifugal fan (ACword, Trinec, Czech Republic) was set to create a corresponding flow rate of the input air. The two heaters (one for heating the gas and one for the catalyst bed) were shut down when adsorption is taking place. Therefore, the catalyst bed does not function at room temperature.

Thermal desorption was applied after every breakthrough determination. When running the desorption process, the two heaters were switched on and the two temperature controls were set to be 300°C. Air flows in a closed loop and the circulating hot air transfers the heat to the fixed bed where the adsorptive is desorbed. The adsorptive carried by the hot air passes through the catalyst bed where it is oxidized into water and carbon dioxide. After cycles of 20 minutes of duration, humid air was purged through. The whole process was repeated four more times after which the adsorbent could be considered as regenerated.

Concentrations of isopropanol and xylene were determined by using a 2110 μP FID-equipment (AMLUK GmbH, Oberaudorf, Germany) and the values were saved automatically in a 5 seconds interval.

3. Results and Discussion

3.1. Adsorptive generation

Figure 2 shows the variation of the input concentration for isopropanol during a one-day measurement. The observed deviations of the mean value are due to the ambient temperature (and/or ambient pressure) changes during day and night, and they are in good agreement with the expected behavior of real emissions.

![Fig. 2. Determination of the input concentration: One day measurement with one basin containing isopropanol.](image_url)
3.2. Effect of input concentration and flow rate

The breakthrough curves obtained from the experiments (Fig. 3) provide information about the adsorption dynamics as well as the utilization of the fixed bed. The breakthrough time and the shape of the curve are analyzed by comparison of two different flow rates and two different concentrations for the isopropanol – HSU 100-100 system.

In both cases, increasing the flow rate at constant input concentration or increasing the input concentration at constant flow rate, a faster breakthrough and lower adsorbed amount (calculated as the area above the breakthrough curves) are observed.

According to the solute movement theory and mass transfer kinetics, a higher flow rate results in speeding up the displacement of the mass transfer zone as well as the external diffusion. However, it reduces the loading capacity due to the shorter residence time while the dispersion effect is favoured.

The influence of the input concentration is more complex. A higher input concentration increases the equilibrium loading considering the adsorption isotherm. Besides, it promotes the mass transfer due to the higher concentration gradient. However, the effects on the speed and shape of the mass transfer zone are relevant to the type of adsorption isotherm.

For a favorable adsorption isotherm, as usually the case for low-level concentrations, the displacement of the mass transfer zone increases with increasing input concentration. Therefore, faster breakthrough is expected. In addition, the dispersion effect is strengthened with increasing input concentration. This can broaden the mass transfer zone, but a higher loading capacity and faster mass transfer may buffer the dispersion effect to some extent.
3.3. Effect of the adsorbent used

By changing the adsorbent from HSU 100-100 to HSU 100-300 a better performance was obtained: a significant longer breakthrough time and a higher adsorbed amount were achieved (Fig. 4). The effects of adsorbent functionalization and the selected mixture of different types of inorganic adsorbents are responsible for the results obtained. Due to the significantly better performance of HSU 100-300 with both adsorptives, it could be employed for efficient odour control.

Fig. 4. Improvement of the breakthrough behavior for isopropanol (top) and xylene (bottom) by changing the adsorbent.
3.4. Desorption experiments

Figure 5 shows desorption profiles for both adsorptives on HSU 100-300. By purging the humid air, peak values were observed. The measured concentrations decreased with time and at the end the outcome concentration drops nearly to zero. It shows that the thermal desorption method applied in this work is efficient for adsorbent regeneration. Additionally, it demonstrates the potential of the adsorbent HSU 100-300 for industrial application because it can provide long adsorption cycles followed by short desorption cycles.

Fig. 5. Desorption profiles for isopropanol and xylene on HSU 100-300.
3.5. Application of the Yoon-Nelson model

Figure 6 shows the fitting according to the Yoon-Nelson model for two sets of experimental data derived from the adsorbent HSU 100-300. In this case, it is important to mention that the simplicity of the model avoids the details concerning the use of a mixture of adsorbents, each one exhibiting different properties and adsorption behavior.

The parameters $k'$ and $t_{1/2}$, as well as the amount of two odorous model substances adsorbed, are summarized in Table 2 for the breakthrough curves presented in Figure 6.

Table 1. Characteristics of the adsorbents used in this study.

| Adsorptive   | Rate constant, $k'$ (h$^{-1}$) | 50% input concentration breakthrough time, $t_{1/2}$ (h) | Amount adsorbed, $N_{ADS}$ (g) |
|--------------|-------------------------------|--------------------------------------------------------|-------------------------------|
| Isopropanol  | 0.267                         | 22.8                                                   | 344.7                         |
| Xylene       | 0.756                         | 4.4                                                    | 41.8                          |

4. Conclusions

Both adsorbents demonstrated stronger affinity and higher loading capacity for isopropanol than for xylene. Furthermore, the adsorbent HSU 100-300 showed longer breakthrough times as well as higher capacities for both adsorptives than the adsorbent HSU 100-100. Additionally, the Yoon-Nelson model turned out to be in agreement with the experimental data. Aspects related to the measurement of odorant compounds in a reliable way as well as an optimized regeneration procedure should be considered.
Finally, the influence of the bed height and the air humidity levels should be considered for better design and scale-up.

References

[1] Thiesen PH, Mahlke IT, Niemeyer B. Characterization of adsorbents for odour reduction. Progr Colloid Polym Sci 2002;121:23–27.
[2] Cartellieri A, Thiesen PH, Niemeyer B. Development of a basic procedure to design sorption processes. Waste Manage 2005;25:985–993.
[3] Robers A, Figura M, Thiesen PH, Niemeyer B. Desorption of odor-active compounds by microwaves, ultrasound, and water. AIChE J 2005;51:502–510.
[4] Rosenfeld H, Peper S, Täffner T, Köthe M, Fonka MA, Temme H, Niemeyer B. Effektive Stofftrennung in Gas- und Flüssigphase durch selektive Adsorption. Chem Ing Tech 2011;83:1229–1236.
[5] Braass O, Thiesen PH, Behrens V, Niemeyer B. Adsorptionskinetik von geruchsaktiven Substanzen an funktionalisierten Silicagelen und Aktivkohle. Chem Ing Tech 2002;74:1331–1334.
[6] Täffner T, Birkenseer M, Liu Y, Bischoff M, Niemeyer B. Selektive Adsorbentien zur Optimierung der Abluftbehandlung in Lebensmittelverarbeitenden Betrieben. Chem Ing Tech 2010;82:2171–2178.
[7] Täffner T, Niemeyer B, Puls A, Dreisbach F. Evaluation of adsorbents for removal of isopropanol from humid air. Open Chem Eng J 2012;6:1–7.
[8] Sternik D, Staszcuk P, Majdan M, Gladysz-Plaska A, Dabrowska E, Bigda K. Studies of physico-chemical properties of mixed adsorbent in the zeolithe/SiO2 system. J Therm Anal Calorim 2006;86:69–75.
[9] Sidorchuk VV. Changes in the pore structure of silica in chemical modification with organic compounds. Russ J Appl Chem 2006;79:66–70.
[10] Bidner Ms, Vampa VC. A general model for convection-dispersion-dynamic adsorption in porous media with stagnant volume. J Pet Sci Eng 1989; 3:267–281.
[11] Park I, Knaebel KS. Adsorption breakthrough behaviour: Unusual effects and possible causes. AIChE J 1992;38:660–670.
[12] Yoon YH, Nelson JH. Application of gas adsorption kinetics. I. A theoretical model for respirator cartridge service life. Am Ind Hyg Assoc J 1984;45:509–516.
[13] Yoon YH, Nelson JH. Application of gas adsorption kinetics. II. A theoretical model for respirator cartridge service life and its practical applications. Am Ind Hyg Assoc J 1984;45:517–524.
[14] Yoon YH, Nelson JH. Breakthrough time and adsorption capacity of respirator cartridges. Am Ind Hyg Assoc J 1992;53:303–316.