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The balancing of VOC concentration fluctuations by adsorption/desorption process on activated carbon

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Abstract Volatile organic compounds (VOCs) are mostly toxic and carcinogenic substances. The technologies for cleaning of exhaust gases containing the constant concentrations of VOCs are commercially available. However, if concentration fluctuations occur in the range of several orders of magnitude, it can cause problems for a subsequent gas cleaning e.g. by thermal or catalytic oxidation. The balancing of VOC concentrations in flue gases can be a great simplification of a subsequent reduction of VOC emissions from sources with time-variable concentrations. Paint shops belong to the important sources of VOCs and are an example of periodic processes with time-variable concentrations of VOCs. One of the main aims was to experimentally determine the conditions, such as the minimal mean residence time, to balance out the fluctuations of inlet VOC concentrations at the laboratory model. After that, the verification of obtained results was applied for a real exhaust gas from a paint shop.

Keywords Volatile organic compounds · Concentration fluctuations · Balancing · Activated carbon · Adsorption

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Nomenclature

c^{o}_{iso}	Concentration fluctuation of isooctane at the column inlet (ppm)
$\bar{c}_{iso}$	Measured average concentration of isooctane at the column outlet per a cycle (ppm)
$\bar{c}^{o}_{iso}$	Calculated average concentration of isooctane at the column inlet per a cycle (ppm)
$\bar{c}_{VOC}$	Average VOC concentration measured at the column outlet (ppm)
Δp	Pressure drop in the column (Pa)
Q_v	Volume flow ($m^3\ h^{-1}$)
τ_{iso}	Part of cycle when isooctane-air mixture flows through the column (min)
τ_{cycle}	Duration of one cycle (min)
$\bar{t}$	Mean residence time (s)
v_0	Superficial velocity ($cm\ s^{-1}$)

1 Introduction

Volatile organic compounds (VOCs) are organic compounds with vapor pressure at 20 °C equal or higher than 0.13 kPa. They can be released from solvents, fuels, paints and coatings, detergents and cosmetics, etc. They are mostly toxic and carcinogenic substances harmful to human health and some of them are destroying a stratospheric ozone layer and causing the greenhouse effect.

Methods used to control emissions of VOCs are based on the separation of VOCs by suitable separation methods (absorption, adsorption) or based on the principle of chemical conversion of VOCs to harmless substances (catalytic and thermal oxidation). The new methods for VOCs abatement include gas turbines (Portanen 2004), photocatalytic destruction in the presence of a catalyst based on TiO_2 (Zou et al. 2006), simultaneous adsorption and catalytic destruction (Kucherov et al. 2007), a combination of plasma technology and heterogeneous catalysis (Van Durme et al. 2008), etc.

The described processes are suitable for VOC abatement in flue gases with constant concentrations of VOCs. However, if concentration fluctuations occur in a range of several orders of magnitude, it can cause problems for a subsequent gas cleaning e.g. by thermal or catalytic oxidation. The need for balancing the concentration of organic vapors in flue gases also appears for the facilities of VOCs destruction, such as a thermal destruction of VOCs. The requirement for a complete oxidation of organic vapors is to keep the thermal destruction in a relatively narrow temperature range for which the facility is designed. When the temperature drops below the lowest value of temperature range, this can lead to an incomplete oxidation. When the temperature rises above the highest value of temperature range, this can cause damages on the facility. Therefore, the facility is protected from accidental shutdowns, in this case, however, the flue gas goes into the atmosphere without treatment. Paint shops are also an example of periodic processes with time-variable concentrations of VOCs and belong to an important source of VOCs. A great simplification of subsequent destruction of VOC emissions from any sources with time-variable concentrations can be done by balancing the concentration fluctuations of VOCs.

An issue of balancing the concentration fluctuations on a commercial level has not been solved yet. In our recent research (Cervenka and Obalová 2010; Cervenka et al. 2011; Potyková et al. 2011), it was found out that the layer of a suitable sorbent saturated by adsorbate is capable, in certain conditions, to effectively reduce the periodical changes of concentrations in the gas entering to the layer (Fig. 1).

For physical adsorption and desorption, the same equilibrium is valid but the rates are different. Adsorption is rapid, desorption is slow. For a slow desorption, time delay of flue gas in a sorbent layer is important. At longer residence time, higher amount of component is desorbed into the flue gas. The concentration of component in the flue gas at the outlet of sorbent layer increases during a period of low concentrations. The part of sorption capacity of the layer is available. A free sorption capacity is used for the adsorption of the component when its concentration at the inlet to the layer is high. Therefore, the balancing of periodically changing inlet concentrations can be achieved if the residence time at the sorbent layer is long enough. After an initial adsorbent saturation, the adsorbent bed is operated in a quasi-steady state which can be indicated by the fact that an average adsorbate concentration at the inlet per the time-period duration (one cycle) is equal to an average concentration measured at the outlet of the sorbent layer.

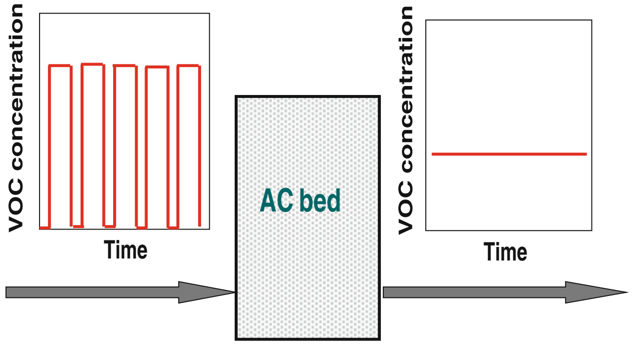

Fig. 1 Schematic diagram of balancing the concentration fluctuations by the flow through AC bed

Reversible adsorption and a sufficient mean residence time belong to necessary conditions for the balancing process described above. A mean residence time had to be experimentally determined at a laboratory model. The effectiveness of balancing process is also dependent on a sorption capacity of adsorbent for particular adsorbate. A higher adsorption capacity improves the effectiveness of adsorbent bed for handling the fluctuating inlet concentrations (Potyková et al. 2011). The literature describes a number of adsorption materials with different sorption capacities for different VOCs. As a material suitable for the adsorption of VOCs appears an activated carbon prepared from anthracite which has an advantage of high porosity (Lillo-Ródenas et al. 2002). The new progressive adsorption materials include water foams (Gautam and Mohanty 2004) and materials based on silica fibers (Chu et al. 2002). According to literature sources and market research, active carbons (AC) were chosen as suitable adsorbents for VOC adsorption in our experiments.

The aim of the presented work was to find the minimal mean residence time when the AC bed is able to damp concentration fluctuations of VOCs in air entering the bed. The results obtained from laboratory model were used for a design of AC bed capable to balance the concentration fluctuations of a real VOC mixture in flue gas from the industrial paint shop.

2 Experimental methods

2.1 Activated carbon

Non-modified granulated AC (MA C6 D40 CZ, Resorbent), prepared from black coal by high-temperature steam activation, was used as the adsorbent in laboratory and industrial experiments without any pre-treatment. The surface area and porous structure of AC were evaluated by adsorption/desorption of nitrogen at −198 °C using ASAP

Table 1 Properties of activated carbon used in this study

Raw material	Black coal
Particle porosity	0.65
Average particle diameter (mm)	4
Micropore volume (cm^3 g^{-1})	0.44
Pore diameter (Å)	2–10
BET surface area (m^2 g^{-1})	1,124
Bed density (kg m^{-3})	649

2010 instrument (Micromeritics, USA) and determined by modified 3-parameters BET method (Schneider 1995) and Horvath-Kawazoe methods, respectively. Prior to the measurement, the samples were dried in a drying box at 105 °C for 1 h, then evacuated in the ASAP instrument. The physical properties of AC are summarized in Table 1.

2.2 Laboratory experiments

Isooctane was selected as the model VOC for laboratory experiment because it was found out among the most abundant components of exhaust gas in the selected real paint shop. To prepare the mixture of isooctane-air, liquid isooctane (manufacturer Penta) with a purity of 99.5 % was used.

A laboratory experimental apparatus for the simulation of VOC concentration fluctuation and their balancing consisted of three sections: (1) dosing and mixing of air polluted by isooctane, (2) an adsorption column with the adsorbent, (3) an analytical part. Layout of laboratory model is depicted in Fig. 2. To simulate concentration fluctuations, there were two pumps (APS400, Tetra) which were connected to the network via a 24 h digital timer. Timers were set so that the air was pumped through either a washer with isooctane or clean air with the same volume flow was supplied. The third pump (LA 80B, Medo) was permanently connected to the network and provided a continuous flow of clean air. The regulation of air flows was performed by needle valves and volume flows of air were measured by rotameters.

The glass adsorption column (i.d. 20 cm) was filled with 3,100 g of activated carbon and the bed height was 20 cm.

2.3 VOC analysis

For the analysis of total organic carbon (TOC) in both laboratory and industrial experiments, a flame-ionization detector Multi-Fid 100 (Hartmann and Braun) was applied. Nitrogen was used as a carrier gas and a certified calibration gas (196 ppm C_3H_8/N_2) was used for adjusting the analyzer. The concentration of isooctane was expressed in

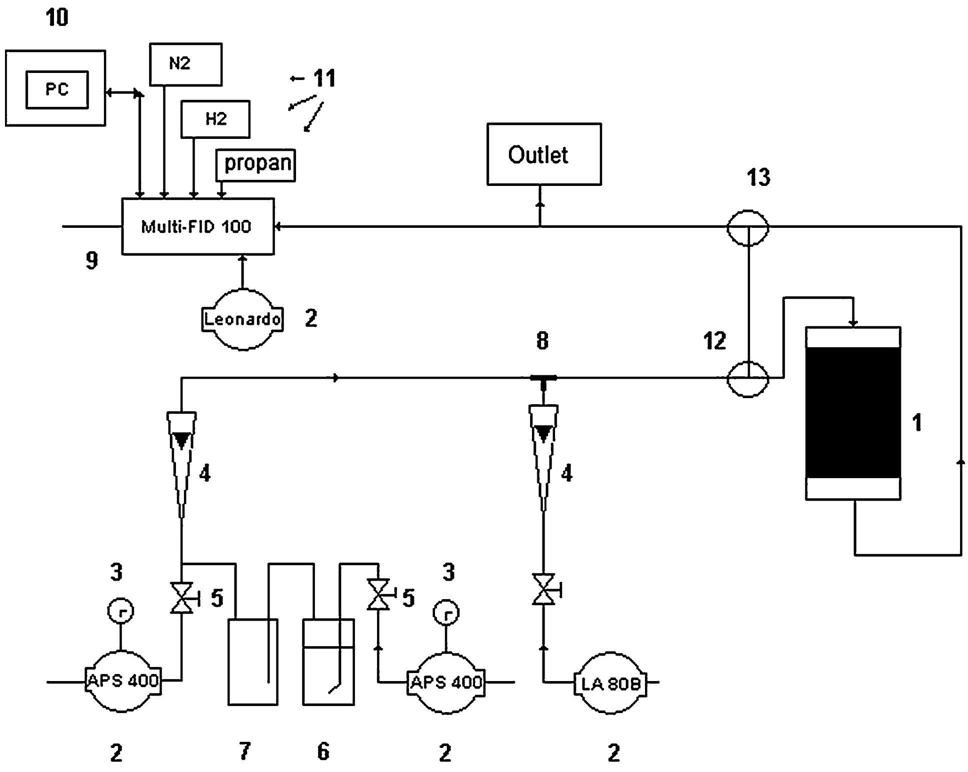

Fig. 2 Laboratory model for balancing the VOC concentration fluctuations. *1* Column with activated carbon, *2* Air pump, compressor, *3* Clock switch, *4* Flow meter, *5* Needle valve, *6* Washer with isooctane, *7* Demister, *8* T-valve, *9* TOC analyzer, *10* PC, *11* Calibration gases, *12*, *13* Three-way valve

ppm of propane C_3H_8. A compressor (Leonardo, Atlas Copco) was applied for the compressed air, before entering the analyzer, the air was filtered.

2.4 Industrial experiments

An industrial verification to balance VOC emissions in waste gases was performed on a painting line for railway axles. An application of paints in paint lines belongs to the periodic processes due to non-continuous painting. Therefore, the concentration of VOCs in the sucked-off waste gases varies significantly. An example of time dependence of VOC concentrations is depicted in Fig. 3. The graph shows sudden sharp rises of VOC concentrations corresponding to time when the painting was performed. Maxima of these fluctuations are in the range from 130 to 250 ppm TOC, their average duration was from one to 2 h. In the period between the concentration fluctuations, the concentration of VOC was in the range from 10 to 50 ppm TOC. Concentrations of particular VOCs were also measured. The naphtha fraction and xylene were the most principal VOC fractions.

On the basis of a material balance of used paints and organic solvents during 6 months, an average daily TOC concentration of 200 ppm (C_3H_8) was determined. Concentrations of particular VOCs were also calculated. The results were in agreement with the operational measurements and isooctane as a representative of naphtha fraction at the concentration 200 ppm (C_3H_8) was chosen for laboratory experiments which were basics for the scale up.

A pilot plant adsorber for balancing of VOC concentrations in the waste gas from the paint shop is showed in Fig. 4. The adsorber was filled with 51 kg of activated carbon, the bed length was 60 cm and the bed cross area was 0.199 m^2. Maximal volume flow was 60 m^3 h^{-1} corresponding to the residence time of 7 s and the minimal volume flow was 10 m^3 h^{-1} corresponding to the residence time of 44 s.

Fig. 4 Pilot plant adsorber for balancing of VOC concentrations in exhaust gas from the paint shop

3 Results and discussion

3.1 Laboratory experiments

The aim of laboratory experiments for balancing the concentration fluctuations of isooctane was to estimate the

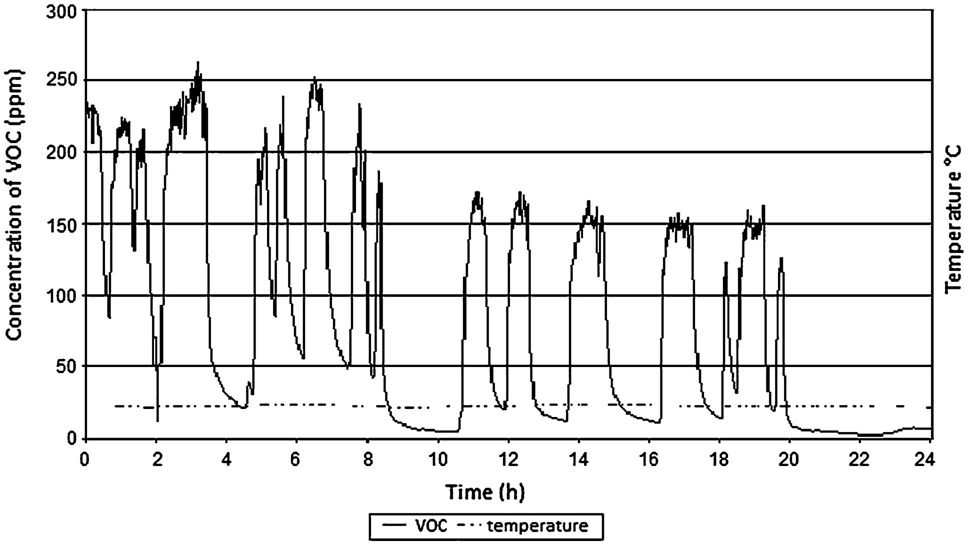

Fig. 3 Time dependence of the VOC concentrations (average minute values) and temperature in the off-gas from paint shop

mean residence time applicable for balancing a real mixture of VOCs from paint lines.

All experiments were done so that 24 h cycles were repeated. During one cycle, the isooctane-air mixture flowed through AC bed for the certain time period while the pure air flowed for the rest time of cycle. At the beginning, the layer of activated carbon was saturated. After that, the mode of cyclic concentration fluctuations of isooctane at the inlet of the adsorption column was set using the switch clock and the apparatus with set parameters was allowed to stabilize. The stabilization time was at least 48 h (two cycles). Concentration fluctuations were about 3,000–3,100 ppm TOC and their distributions were three and six fluctuations per 24 h cycle. The concentration of isooctane in the air at the column inlet apart from the evaporation was assumed to be zero. The mean residence time of the gas in column was 15–17 s which was accounted to the gas flow of 1.5–1.7 cm s^{-1} (STP).

For each experiment, the average concentration of isooctane in the air at the column inlet per a cycle $\bar{c}^{o}_{iso}$ calculated by Eq. 1 and the average concentration of isooctane at the column outlet during a cycle (from the measured TOC concentrations) $\bar{c}_{iso}$ were determined.

$$\bar{c}^{o}_{iso} = c^{o}_{iso} \cdot \frac{\tau_{iso}}{\tau_{cycle}} \qquad (1)$$

where c^{o}_{iso} is concentration fluctuation of isooctane at the column inlet, τ_{iso} is the part of cycle when isooctane-air mixture flows through the column and τ_{cycle} is the duration of one cycle.

The concentration at the column outlet was considered to be balanced if the fluctuations of outlet TOC concentrations were lower than 10 % of the average concentration of isooctane at the column outlet during a cycle.

It was assumed that for a certain value of isooctane average concentration $\bar{c}^{o}_{iso}$, a minimum value of residence time, at which balancing is achieved, could be determined. The recently published results imply that the minimum residence time necessary for balancing the fluctuating VOC vapors increases as the average VOC concentration per a cycle in the flowing gas $\bar{c}^{o}_{iso}$ increases (Cervenka et al. 2011; Potyková et al. 2011).

Time profiles of isooctane concentrations at the column inlet and outlet for the cycle 3 × 30 min (3,100 ppm C_3H_8)/23.5 h (air) at mean residence time of 15 and 17 s are depicted in Figs. 5 and 6. The local maxima and minima of concentrations of isooctane at the column outlet were in the range of 10 % from the measured average concentrations of isooctane. The concentration fluctuations were also balanced when the cycle 6 × 15 min (3,000 ppm C_3H_8) was applied keeping the average VOC concentration $\bar{c}^{o}_{iso}$ at the same level (Fig. 7). This is in agreement with our results published recently (Cervenka et al. 2011).

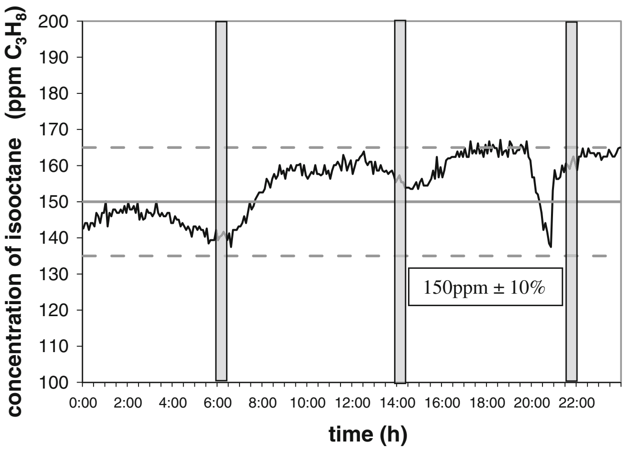

Fig. 5 Time dependence of isooctane concentrations at the inlet (*grey*) and outlet (*black*) of adsorption column at the residence time 17 s

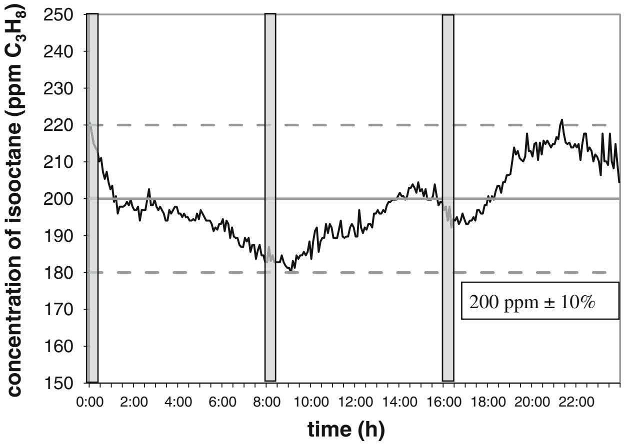

Fig. 6 Time dependence of isooctane concentrations at the inlet (*grey*) and outlet (*black*) of adsorption column at the residence time 15 s

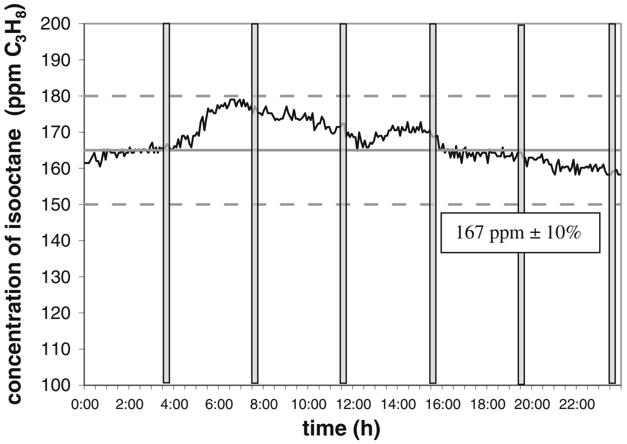

Fig. 7 Time dependence of isooctane concentrations at the inlet (*grey*) and outlet (*black*) of adsorption column at the residence time 15 s

The estimation of minimum residence time of 15–17 s was used as the basis for a design of pilot-plant adsorber for balancing the concentration fluctuations of a real mixture of VOCs.

Conditions: concentration fluctuations of isooctane at the inlet: 3,100 ppm TOC, cycle: 3 × 30 min (isooctane in air)/22.5 h (air), $\bar{c}_{\text{iso}} = 150 \pm 10\,\text{ppm}$ TOC, superficial velocity 1.5 cm s^{-1}.

Conditions: concentration fluctuations of isooctane at the inlet: 3,100 ppm TOC, cycle: 3 × 30 min (isooctane in air)/22.5 h (air), $\bar{c}_{\text{iso}} = 200 \pm 10\,\text{ppm}$ TOC, superficial velocity 1.3 cm s^{-1}.

Conditions: concentration fluctuations of isooctane at the inlet: 3,000 ppm TOC, cycle: 6 × 15 min (isooctane in air)/22.5 h (air), $\bar{c}_{\text{iso}} = 167 \pm 10\,\text{ppm}$ TOC, superficial velocity 1.3 cm s^{-1}.

3.2 Industrial experiments

The aim of industrial experiments was to find the minimal mean residence time sufficient for balancing the VOC concentration fluctuations in a real off-gas from the paint shop. Minimal mean residence time of 15–17 s estimated from the laboratory experiments was taken as the orientation value for the design of an industrial pilot adsorption column. During the experiments, the volume flow through the adsorber was decreased and TOC concentrations at the column outlet were continuously monitored. Results are summarized in Table 2. The VOC concentrations at the column outlet were considered to be balanced if the column worked in a quasi-steady state and maximal concentrations corresponding to abrupt changes of VOC concentrations at the inlet did not appear at the outlet of column. Quasi-steady state is reached when the average VOC concentrations measured at the column outlet were equal to the average VOC concentrations at the column inlet during the cycle (24 h). Deviations of concentrations ± 20 % were tolerated compared to the average VOC concentrations. We can see that the average concentration of 173 ppm TOC was balanced at residence time of 30 s, while residence time of 40 s was necessary to balance the average concentration of 198 ppm. During the experiment No. 5, the inlet and outlet VOC concentrations were measured simultaneously by two TOC analyzers (Fig. 8).

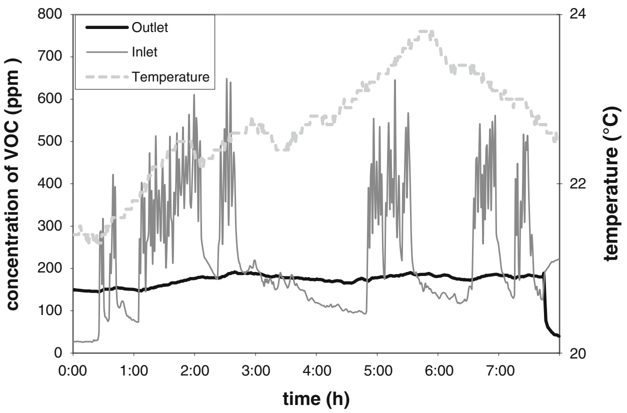

Fig. 8 Time dependence of the VOC concentrations at the inlet and outlet of the pilot adsorption column. Measurement no. 5 (Table 2)

Pilot adsorption column for the balancing of VOC concentration fluctuations in the real off-gas from the paint shop was working for 4 months. No change in efficiency was observed. After this period, the porous structure of AC and bed density were analyzed. 36 % decrease in specific surface area as well as 43 % decrease of micropore volume was observed. Bed density (depended on moisture content and granularity of AC particles) stayed unchanged and no AC powder particles were observed leading to the conclusion that no comminuting occurred during the operation or pilot adsorption column.

4 Conclusions

The presented experiments confirmed the possibility of balancing the concentration fluctuations of isooctane and a real mixture of VOCs in the gas flowing through the layer of activated carbon. The minimal mean residence time required for balancing a real VOC mixture was about twice higher than for balancing the isooctane concentration

Table 2 Results of balancing the concentration fluctuations of a real VOC mixture

No.	Q_v (m^3 h^{-1})	v_0 (cm s^{-1})	$\bar{t}$ (s)	Δp (Pa)	$\bar{c}_{VOC}$ (ppm)	Result
1	43.2	6.0	10	28	185	Non-balanced
2	30.6	4.3	14	20	362	Non-balanced
3	14.4	2.0	30	4	366	Non-balanced
4	10.0	1.5	40	3	198	Balanced
5	14.4	2.0	30	4	173	Balanced

fluctuations conducted in the laboratory. The reason can be different composition of a real mixture from industry paint shop.

Generally, the outlet VOC concentration from an adsorbent bed is the function of concentrations, equilibrium adsorption amounts, and adsorption and desorption rates of individual components as well as operating conditions such as flow rate, bed length, total pressure, and temperature. Furthermore it also depends on the properties of the adsorbent used. Therefore, the results in this manuscript are valid only for the given operation, namely the balancing of the exhaust gas from the chosen paint shop and determined minimal mean residence time cannot be generalized for any other adsorption system at all.

However, the paper showed how the needed residence time can be determined by a relatively simple device situated directly in operation. This device constructed using a column with the sorbent, a flow meter, a flow control valve and a gas pump is attached to the waste gas pipe system and part of the waste gas is drawn off through the column. The minimal mean residence time for given real waste gas composition is then determined by changing the volume flow through adsorbent bed and its value can be used directly to the scale-up.

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