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VOC Adsorption in Circulating Gas Fluidized Bed

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Abstract. The purpose of the work is to show that CFB adsorption process is technically feasible to obtain an interesting pollution abatement, and to set the bases of a process design. Experimental results are presented, obtained with toluene being adsorbed from an air stream on polymeric adsorbent in a batch operation circulating fluidized bed. This results in a breakthrough behavior at the top of the riser, analogous to a fixed-bed experiment. The existence of breakthrough curves that are astonishingly sharp in spite of the strong mixing of the solid phase implies that efficient toluene abatement can be achieved. The breakthrough curves can be used to predict the behavior of the process in a continuous mode where the adsorbent would be partially regenerated, and which would lead to an less than total toluene abatement. The shape of the breakthrough curves clearly depends on the operating parameters, in particular the gas flow rate and the solids circulation rate. The EMMS model was adapted and implemented to describe the flow pattern of gas and solid. The model predicts the relative volume fractions of these phases, the volume fractions inside each, the superficial velocities of gas and solid in each phase, and the average cluster size. From this description, an estimation of the apparent gas/solid mass transfer coefficients may be done, and their dependence on operating conditions investigated.

Keywords: adsorption, circulating fluidized bed, volatile organic compounds

1. Introduction

Volatile Organic Compounds (VOC) are the most common air pollutants emitted from chemical, petrochemical and allied industries. Adsorption is one of the most effective methods of controlling VOC emission. Adsorption processes are usually carried out in fixed beds, the main reasons being that a 1arge number of theoretical plates is often required, and that adsorbents are subject to strong attrition. Under certain circumstances, these factors are not prohibitive, and fluidized bed may be an interesting alternative. The expected advantages are continuous processing, the ability to treat large flows under moderate pressure drop, the possibility to handle dusty gases or slurries, good fluid side mass and heat transfer between fluid and particles. Among

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fluidized bed processes, only "slow" fluidization has actually been considered and industrially carried out, meaning basically a fluid gently bubbling through successive layers of adsorbent held on perforated plates, for example. The present paper investigates a quite different regime; that of "fast" fluidization in an empty column, involving carry-over of the adsorbent particles. The purpose of the work is to show that it is technically feasible to obtain an interesting pollution abatement, and to set the bases of a process design. The starting point is the experience of LSGC-Nancy for VOC adsorption on an adsorbent which is relatively robust to attrition, and the experience of IPE-Beijing in circulating fluidized beds.

2. CFB Adsorption Experiments

A batch operation CFB adsorption experimental unit has been constructed and used for the experimental study. That is, the adsorption process will start with fresh or regenerated adsorbent until all adsorbent in the CFB system becomes saturated. Figure 1 is the schematic diagram of the experimental setup.

The CFB unit is basically composed of a riser, a downer and a two-stage gas-solid separator. The CFB riser, act as an adsorber, is a 2.88 m high tube with the inner diameter of 29 mm. Compressed air is used as the fluidizing gas and an activated carbon bed is installed after the air compressor to eliminate the possible oil vapor. Two rotameters are used to control the gas flow rate of primary fluidizing air and VOC evaporation air. The evaporation air flows through the VOC evaporator

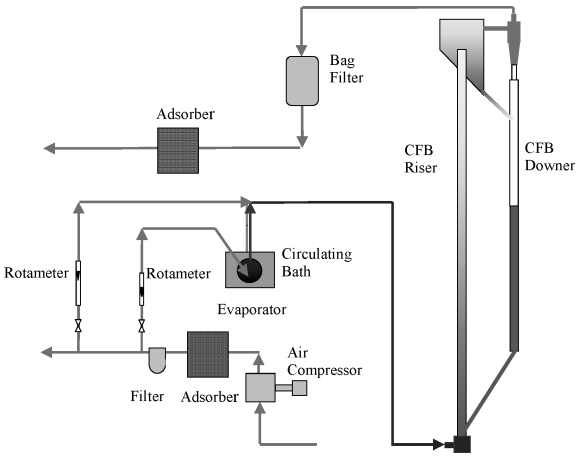

Figure 1. Schematic diagram of experimental setup.

first, which is immersed inside a circulating bath to maintain a stable temperature. The evaporation air is then directed to a mixer via a heated line to mix with the primary air. The desired VOC concentration is obtained by adjusting the air flow rate to the evaporator or the temperature of circulating bath.

The fluidizing air with stable VOC concentration is then directed into the CFB riser through the air distributor. It flows through the bed with the entrained solid adsorbents while adsorption is taking place. The gas and adsorbent particles are separated by a two-stage gas-solid separator at the top of the riser. The gas is then vented out via a bag filter to remove the dust and another activated carbon bed to remove the residual VOC substance. The overflowing adsorbent is continuously recycled at the bottom of the riser without being regenerated.

A polymeric adsorbent, Ambersorb 600 is used for the study. The adsorbents are in the form of small spherical beads with high attrition resistance and uniform particle diameter, which are desirable for fluidized bed application. The adsorption isotherm of toluene/adsorbent system could be described by Dubinin-Astakhov equation:

$$q = q_m \exp\left[-\left(\frac{RT}{E}\ln\left(\frac{C_{\text{sat}}}{C}\right)\right)^m\right] \qquad (1)$$

At 25°C, the maximum adsorption capacity q_m is 1.81×10^5 mg/kg and the saturation concentration of toluene C_{sat} is 1.538×10^5 mg/Nm^3; The other parameters in Eq. (1) are: $E = 21.51$ KJ/mol; $m = 1.17$. For a batch operation adsorption process, the adsorbate concentration distribution along the bed height is no longer stable, but changing with operation time. This results in a breakthrough behavior at the top of the riser analogous to a fixed-bed experiment. The compositions are measured at several points along the riser including the exit by a PGM-7600 VOC analyzer, which uses photoionization detector to measure the VOC concentrations.

3. Breakthrough Curves

Assuming the gas phase concentration at the exit of CFB system is in equilibrium with the adsorbent (this is the case when the CFB riser is long enough) and neglecting the influence of adsorption on the gas flow rate, solid density and temperature (as the adsorbate concentration is very low), the outlet VOC concentration C_{out} could be obtained from the mass balance and

adsorption isotherm of Toluene/Ambersorb 600 system:

$$\frac{dC_{\text{out}}}{dt} = U_g F(C_{\text{in}} - C_{\text{out}}) \Bigg/ \left[\frac{q_m m G R T}{C_{\text{out}} E} \left(\frac{RT}{E} \ln \frac{C_{\text{sat}}}{C_{\text{out}}} \right)^{m-1} e^{-(\frac{RT}{E} \ln \frac{C_{\text{sat}}}{C_{\text{out}}})^m} + \varepsilon_b F H \right] \quad (2)$$

The experiments are run in a "batch mode", The existence of breakthrough curves that are astonishingly sharp in spite of the strong mixing of the solid phase implies that efficient toluene abatement can be achieved. The shape of the breakthrough curves clearly depends on the operating parameters, in particular the gas flow rate and the solids circulation rate. With the dimensionless parameters, the VOC concentrations at exit of CFB riser with different gas flow rate, solid circulating rate and inlet VOC concentrations could be described by the same curve. The dimensionless form of gas and solid phase concentration is defined as: $Y = C/C_{\text{in}}$; $Y^*_{\text{in}} = C^*_{\text{in}}/C_{\text{in}}$, C^*_{in} is the gas phase concentration in equilibrium with initial solid phase concentration q_{in}; dimensionless solid phase concentration $X = q/q^*$. q^* is the solid phase concentration in equilibrium with C_{in} at corresponding temperature; Dimensionless time $\theta = t/t^*$, t^* is the stoichiometric breakthrough time and defined as: $t^* = G(q^* - q_{\text{in}})/Q_g C_{\text{in}}$.

Figure 2 shows the calculated dimensionless breakthrough curves. Experimental measurement results from six adsorption experiments with different gas flow rate, solid circulation rate and inlet VOC concentrations have also been plotted. The calculated results shows that the solid phase concentration q shows liner increase with time first ($\theta < 0.7$) and then slow down to it's saturation capacity. The predicted gas phase concentration agreed well with experimental values, while slight smaller values are predicted for the earlier period of operation. The gas and solid phase concentration reaches $0.52C_{\text{in}}$ and $0.93q^*$ respectively when stoichiometric time is reached. The breakthrough curves can be used to predict the behavior of the process in a continuous mode where the adsorbent would be partially regenerated and which would lead to an less than total toluene abatement.

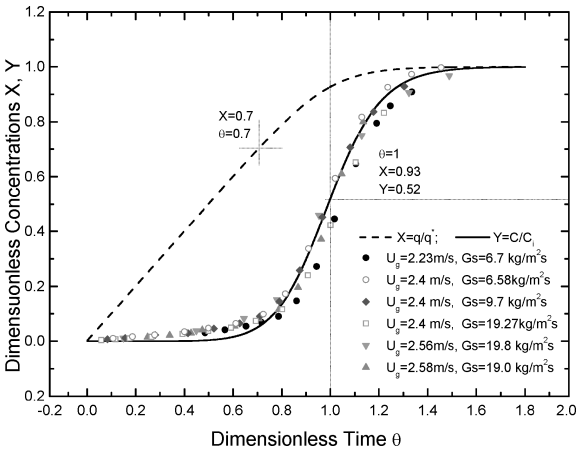

Figure 2. Dimensionless breakthrough curves.

4. Hydrodynamic Model

The EMMS (Energy-Minimization Multi-Scale) model (Li and Kwauk, 1994) was adapted to describe the gas-solid flow in CFB riser. The EMMS model divides the heterogeneous gas-solid system in CFB into two homogeneous gas-solid "pseudo-phases": a dilute phase consisting of gas and discrete individual particles, and a dense phase made of clusters of particles, which behave like large highly porous particles. The constitutive equations are based on force balances and an assumption relating cluster size to energy. The state variables introduced here are the overall voidage ε, the volume fraction f of the cluster pseudo-phase (thus $1-f$ of the dilute pseudo-phase), the volume fractions of gas ε_d in the dilute pseudo-phase and ε_c in the cluster pseudo-phase, the 4 superficial gas and solid velocities in each pseudo-phase U_{gd}, U_{gc}, U_{pd}, U_{pc} and the cluster size d_{cl}. The operating variables considered are the inlet flow-rates of gas and of solid, expressed here as the superficial velocities U_g and U_p respectively, based on the total column cross-section. The one-dimensional hydrodynamic model is formed by combining the EMMS model with a classical model (Kunii and Levenspiel, 1969) for axial voidage distribution.

$$\varepsilon = \varepsilon^* - (\varepsilon^* - \varepsilon_a) e^{-\alpha Z} \quad (3)$$

The "state variables" of the bed defined above can then be computed and represented as functions of each other. One may refer to the related references (Li et al., 1999; Song, 2003) for the details of this model.

5. Gas/Solid Mass Transfer in CFB Riser

Halder and Basu (1998) examined the mass transfer between gas and solid in CFB riser. It is found that the

mass transfer coefficient for the freely moving coarse particle in a fast bed of fine solids is lower than that obtained using superficial gas velocities. The slip velocity between gas and solid particle have a strong influence on the mass transfer rate and the correlation proposed for Sherwood number estimation is.

$$Sh = 2\varepsilon + 0.69\left(\frac{U_s d_p \rho_g}{\mu_g \varepsilon}\right)^{1/2} Sc^{1/3} \tag{4}$$

The mass transfer model between gas and solid particle in CFB riser is constructed according to the compartmentalization of two phases of Li's EMMS model. The mass transfer coefficient in dilute and cluster phase k_{gd}, k_{gc} are determined by the slip velocities between gas and solid particles in the respect phases U_{sd}, U_{sc} that could be obtained from EMMS model. Halder and Basu's equation is used to estimate this coefficient.

$$Sh_d = \frac{k_d d_p}{D_g} = 2\varepsilon_d + 0.69\left(\frac{U_{sd} d_p \rho_g}{\mu_g \varepsilon_d}\right)^{1/2} Sc^{1/3};$$
$$Sh_c = \frac{k_c d_p}{D_g} = 2\varepsilon_c + 0.69\left(\frac{U_{sc} d_p \rho_g}{\mu_g \varepsilon_c}\right)^{1/2} Sc^{1/3} \tag{5}$$

So the cross sectional averaged mess transfer coefficient between gas and solid k could be expressed as:

$$k = \frac{k_d(1-f)(1-\varepsilon_d) + k_c f(1-\varepsilon_c)}{1-\varepsilon} \tag{6}$$

It is obvious that this value is much smaller than that calculated with homogeneous gas/solid distribution assumption. This shows the formation of clusters is the main reason for the lower mass transfer coefficient between gas and solid particles in CFB. If $f = 0$, or clusters disappears and all the particles are discretely distributed in the fluid, the mass transfer coefficient for the bed k will equal that in dilute phase k_d. If $f \neq 0$, k will be smaller than k_d as the mass transfer coefficient in the cluster phase k_c is small. This explains why the mass transfer coefficient obtained with superficial gas velocity for the fluidized bed is less than that for single particle.

6. Adsorption in CFB Riser

In a stable continuous adsorption system, the solid-phase concentration is constant and the gas phase concentration is a function of bed height only. In the CFB riser the axial gas dispersion is relatively small. If we consider the gas is plug flow in the riser, the mass balance for adsorbate in a differential element height of CFB riser gives:

$$U_g \frac{dY}{dz} + \frac{6(1-\varepsilon)}{d_p} k\,(Y - Y^*) = 0 \tag{7}$$

Substitute Kunii and Levenspiel's entrainment model for axial voidage distribution (3) into (7). The integration of (7) from $z = 0$ to $z = z$ gives:

$$\frac{Y - Y^*}{1 - Y^*} = \mathrm{EXP}\left\{ -\frac{6k}{d_p U_g} \times \left[(1-\varepsilon^*)z + \frac{1}{a}(\varepsilon^* - \varepsilon_a)(1 - e^{-az})\right]\right\} \tag{8}$$

The left hand side of Eq. (8) is the dimensionless residual concentration at bed height z. For a CFB riser, the bed voidage is determined by superficial gas velocity and solid circulating rate, and its value is between 0.8–0.98. So the dimensionless residual concentration distribution in CFB riser will be determined by the mass transfer coefficient K, superficial gas velocity U_g and solid circulating rate G_s.

Figure 3 shows the calculated and experimental results of residual concentration distribution with different superficial gas velocities. As the change of U_g is relatively small in the experiments, the influence of U_g on the dimensionless residual concentration distribution is not obvious. The model predicted values for higher superficial velocities are also presented in Fig. 3.

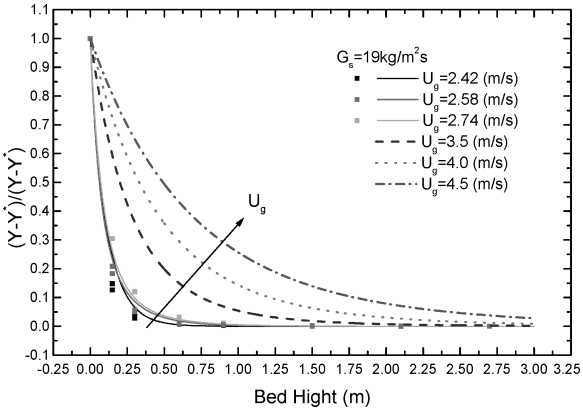

Figure 3. Residual concentration distribution along CFB riser with different gas velocities.

The results show that the superficial gas velocity has a strong influence on the adsorption process in CFB riser. The increase of U_g will increase the gas/solid mass transfer coefficient in the bed, this will result faster reduction of adsorbate concentration along the riser. On the other hand, the increase of U_g will also increase the mass flow rate of adsorbate and the voidage in the CFB riser, this will result in slow reduction of adsorbate concentration along the bed height. It is obvious that the latter influence is dominating and higher superficial gas velocities will result in slower concentration reduction along the bed height.

7. Conclusions

The batch operation experimental results show that, efficient VOC abatement can be achieved with CFB adsorption process. The breakthrough curves can be used to predict the behavior of the process in a continuous mode where the adsorbent would be partially regenerated, and which would lead to an less than total toluene abatement. The shape of the breakthrough curves clearly depends on the operating parameters, in particular the gas flow rate and the solids circulation rate.

A mass transfer model between gas and solid particle in CFB riser is constructed according to the compartmentalization of two "pseudo-phases" of EMMS model. The cross sectional averaged mass transfer coefficient between gas and solid is obtained and it is lower than that for homogeneous gas solid system. The VOC adsorption process in CFB riser is investigated with a one-dimensional model. The calculated and experimental results show that superficial gas velocity has a strong influence on the adsorption process in CFB riser. Higher superficial gas velocity results slower concentration reduction along the CFB riser.

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Nomenclature

C	Gas phase VOC concentration (mg/Nm^3)
C_p^*	Gas phase concentration in equilibrium with solid phase concentration (mg/Nm^3)
d	Diameter (m)
E_0	The characteristic energy of adsorbate (J/mol)
f	Cluster phase volumetric fraction
F	Cross sectional area of CFB riser (m^2)
G	Adsorbent inventory in the system (kg)
G_s	Solid circulation rate (kg/m^{2}s)
G_s^*	Saturation caring capacity of the gas (kg/m^{2}s)
H	Height of CFB riser (m)
k	Mass transfer coefficient between gas and solid (m/s)
q	Solid phase adsorbate concentration (mg/kg)
q^*	Solid phase concentration in equilibrium with inlet gas phase concentration (mg/kg)
R	Gas constant (J/mol K)
t	Time (s)
t^*	Stoichiometric breakthrough time ($t^* = Gq^*$/QgCi) (s)
T	Temperature (°C)
U	Superficial velocity (m/s)
X	Dimensionless solid phase concentration ($X = q/q^*$)
Y	Dimensionless gas phase concentration ($Y = C/C_{\text{in}}$)
Y^*	Dimensionless gas phase concentration in equilibrium with solid phase concentration, (C_p^*/C$_{\text{in}}$)
Z	Characteristic length (m)

Subscript

c	Cluster phase
d	Dilute phase
g	Gas
in	Inlet
m	Maximum
out	Outlet
p	Solid particle
s	Slip
sat	Saturation

Greek symbols

ε	Cross sectional averaged voidage in CFB riser
ε^*	Characteristic voidage
ρ	Density (kg/m^3)
θ	Dimensionless time ($\theta = t/t^*$)

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