

## ADSORPTION OF CO<sub>2</sub> IN A CONFINED FLUIDIZED BED OF A PELLETIZED 13X ZEOLITE: FLUIDIZATION VELOCITY AND PROCESS PERFORMANCE

Rossella Girimonte, Brunello Formisani\*, Flaviano Testa

<sup>1</sup> *Dipartimento di Ingegneria per l'Ambiente e il Territorio e Ingegneria Chimica,*

*Università della Calabria;*

*I 87030 Arcavacata di Rende (Cosenza), Italy*

\*Email: [brunello.formisani@unical.it](mailto:brunello.formisani@unical.it)

**Abstract** – Previous research has shown that when a bed of particles is fluidized in a confined environment like that provided by the voids of a fixed bed of coarser spheres, bubble flow is totally suppressed in favour of an increased ability of the bed to expand homogeneously. A "confined fluidized bed" (sometimes also termed "packed-fluidized bed") seems therefore likely to improve the efficiency of gas-solid processes for which the by-pass effect associated to bubbling represents a major drawback. To check these potentialities, the paper presents the results of an investigation on CO<sub>2</sub> adsorption by a fluidized bed of pellets of 13X zeolite.

The performances of a confined fluidized bed and that of a conventional system are compared in terms of moles of CO<sub>2</sub> adsorbed per unit mass of sorbent, breakthrough time and fraction of bed utilized at the breakpoint. The results obtained demonstrate that confinement of the bed allows exploiting fluidization technology in adsorption operations whose thermal control also results easier.

### INTRODUCTION

Among the several strategies proposed for containing CO<sub>2</sub> emissions, such as reducing energy consumption, increasing the efficiency of energy conversion, switching to the use of renewable energy sources, the techniques of carbon capture and storage (CCS) offer a valid tool in the short to medium term (Bhown, A.S., Freeman, B.C. 2011).

In the field of CCS the development of an innovative, efficient and cost-effective CO<sub>2</sub> capture technique based on adsorption on solid sorbents, can be a promising alternative whose success may depend not only on the availability of highly specific materials tailored at the molecular scale (Younas et al. 2016) but also on the improvement of the gas-solid contact efficiency (Raganati et al. 2014; R. Girimonte et al. 2016).

Various materials, such as zeolites, metal organic frameworks (MOFs), activated carbon and amine-modified silica show high capacity of adsorption of CO<sub>2</sub>. Exploiting advantages of fluidization technology such as high mass transfer rates and low pressure drop without suffering too low adsorption efficiencies requires the adsorption process to be run in the regime of particulate fluidization, i.e. in the absence of bubbly flow.

Adsorption can be carried out in systems often referred to as "packed fluidized beds" or "confined fluidized beds" (Girimonte and Vivacqua, 2013), i.e. beds of particles fluidized in the voids of a packing of coarser solids, usually spheres. This technique has been raising an increasing interest as its fluid-solid contact mode is particularly suitable for operations in which maximization of the conversion of a gaseous reactant is crucial. Such a goal can be reached thanks to the ability of these fluidized systems to prevent the formation of bubbles, a route through which part of the gas flow rate by-passes the contact with the solid phase, whether it is another reactant or a catalyst. Some zeolites commercially available as spheres of relative large size obtained by pelletizing the original powder are sorbents suitable for being used in a confined system like that employed in this investigation.

This paper illustrates how the adsorption performance of a commercial Zeolite 13X improves when the operation is conducted in a confined fluidized bed. Effectiveness of CO<sub>2</sub> capture has been assessed in terms of moles of CO<sub>2</sub> adsorbed per unit mass of adsorbent solid, breakthrough time and fraction of bed utilized at the breakpoint and a comparison is made with the results obtainable in a packed-bed and in a conventional fluidized bed.

## EXPERIMENTAL

The experimental investigation was carried out in the laboratory-scale fluidized bed apparatus sketched in Fig. 1, made of a Plexiglas column with an internal diameter of 50 mm and 700 mm high, equipped with a porous gas distributor at its bottom. The fine particle bed was fluidized by air, whose flow rates were regulated by two mass flow controllers covering the range 0÷6000 NI/h. The CO<sub>2</sub> concentration in the gas feed stream was adjusted by adding it from a cylinder to the air supplied by a compressor. A system for humidity abatement, made of a column filled with zeolites and activated carbon, was located before the CO<sub>2</sub> mixing point. The total pressure drop across the solid bed was measured by a U-tube water manometer.

The contact modes investigated ranged from the fixed to the bubbling regime in conventional fluidization and include the regime of homogeneous expansion in confined fluidization. During the CO<sub>2</sub> adsorption process the increase of bed temperature was monitored by a thermocouple vertically immersed in it. As concerns this effect, the amount of energy involved in physical adsorption of CO<sub>2</sub> is about 10 kcal/mol. The CO<sub>2</sub> concentration in the gas stream entering or leaving the adsorption unit was measured by a gas analyzer (Madur GA-21 plus) and acquired on a PC.

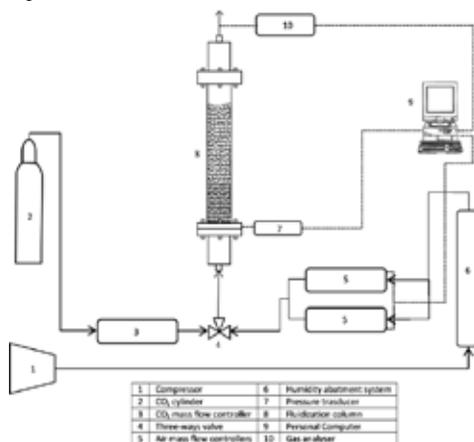


Fig. 1. Experimental apparatus.

A commercial zeolite, 13X-APG MOLSIV™ provided by UOP LLC, was used as adsorbent material. In it the ratio Si/Al is 1,7 and that Na/Al is 1, as obtained by EDAX analysis. A sample 800-900 μm was prepared by sieving and its particle size distribution was characterized by a laser diffractometer (Mastersizer 2000 by Malvern Instruments). The characteristic Sauter diameter of the sample,  $d_f$ , was 786 μm.

Sample morphology was characterized by SEM analysis using a FEI Inspect F50 instrument and particles of 13X zeolite, as obtained by granulation of its powder with a binder, showed a quasi-spherical shape with a size ranging from 400 to 2000 μm. Particle density was 1440 kg/m<sup>3</sup>.

The specific surface of the solid was determined according to the BET method, using N<sub>2</sub> adsorption at 77 K performed with a Micromeritics ASAP 2020 analyzer. Pore size distribution and volume were evaluated using a DFT equilibrium model. Sample was degassed at 350°C until a pressure of 30 mm Hg was reached. The sample have a BET surface area of 650 m<sup>2</sup>/g, pore volume of 0.24 cm<sup>3</sup>/g and pore size of 4.7 Å. The nature and the amount of the species adsorbed were determined by TG analysis carried out on a Netzsch STA 409 instrument. The weight loss of the sample is centered at about 200 °C, due to water desorption. Analogously, desorption of CO<sub>2</sub> from 13X zeolite samples previously used for adsorption occurs at 70°C and is signaled by a similar weight loss.

The zeolite sample was subjected to characterization of its regime of fluidization both when employing the conventional and the confined bed technique. These tests were performed at ambient temperature and pressure using dehumidified air as the fluidizing gas. The pressure drop and bed expansion curves were obtained by measuring the values of pressure and bed height both at increasing and decreasing superficial gas velocity and the results obtained were essentially the same (Girimonte and Vivacqua, 2011). The values of the minimum fluidization velocity and voidage were determined from the two diagrams of Figure 2; as

regards the conventional fluidized bed,  $u_{mf}$  was 19.22 cm/s with a value of  $\varepsilon_{mf}$  of 0.38, while for the confined system its value was 12.10 cm/s with  $\varepsilon_{mf}$  equal to 0.195.

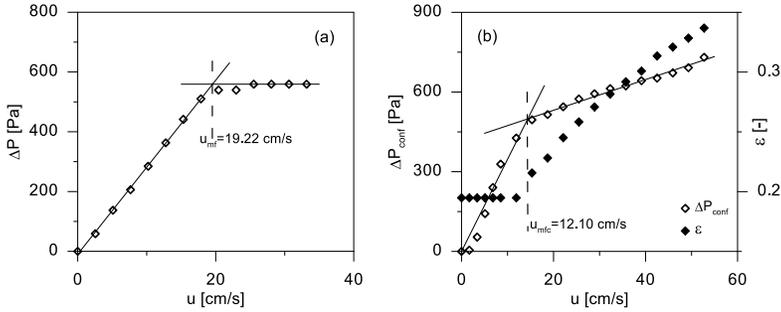


Fig. 2. Minimum fluidization velocities in the conventional and the confined bed.

In comparison with the conventional system, the confined bed undergoes suspension at a lower superficial gas velocity but the corresponding value of the interstitial velocity is higher because bed voidage is much lower, nearly half the value measured in the conventional fluidized bed (e.g. 0.195 instead of 0.380). Moreover, when the solid is fluidized according to the conventional technique, it immediately enters the bubbling regime past the incipient fluidization threshold. As regards the confined fluidized bed, instead, suspension coincides with the beginning of its homogeneous expansion, a regime that has been modeled by a modified form of the Richardson-Zaki's equation (Girimonte and Vivacqua, 2013). That confirms the ability of this gas-solid contact mode to enhance the fluidization quality. It has been shown, to this regard, that the amplitude of the interval of the regime of homogeneous expansion can be controlled by regulating the ratio between the height of the bed subjected to fluidization and that of the packed bed in which it is confined, a circumstance that qualifies confined fluidization as a noticeably attractive processing technique.

The conditions for all adsorption experiments were ambient temperature and pressure and inlet  $\text{CO}_2$  composition of 10%. Prior of each test, the sorbent solid has been heated up to 300 °C to remove any trace of moisture and of  $\text{CO}_2$  adsorbed. In a typical experiment based on conventional fluidization, the sorbent is loaded onto the column, then it is fluidized and defluidized in order to obtain a repeatable bed height. The adsorption process is preceded by a conditioning period of about 10 min, during which air is let flow through the particle bed in order to stabilize the regime for the gas-solid exchange at one of the values of superficial gas velocity indicated in Tab. 1.

Table1: Values of fluidization velocity for the absorption tests.

$u$ [cm/s]	$t_{c,conv}$ [s]	$\varepsilon$ [-]	$t_{c,conf}$ [s]
17.7	0.13	0.224	0.19
21.4	0.11	0.241	0.16
24.7	0.09	0.254	0.14
28.8	0.08	0.269	0.12
31.7	0.07	0.279	0.11
35.2	0.06	0.291	0.10
38.6	0.05	0.301	0.09

Such velocity values were selected to allow a comparison of adsorption data from experiments performed on either fluidized bed system (conventional or confined), where the same solid mass is crossed by a gas stream having the same flow rate and  $\text{CO}_2$  concentration. At the lowest velocity (17.7 cm/s) the conventional bed finds itself in the fixed state, whereas at the higher  $u$  it is crossed by bubbles; the packed-fluidized bed, instead, is always in the regime of fluidization and homogeneous expansion in the voids of the packing, with its voidage at the values reported in Tab.1.

The fluidization regime adopted for the process influences the contact time  $t_c$ , which is defined as the ratio between the free volume in the bed and the volumetric flow rate of the inlet gas. In the case of confined fluidization, homogeneous expansion of the solid occurs so that with the increase of bed voidage also the contact time between gas and sorbent increases.

In a typical experiment of confined fluidization, the coarse spheres (glass beads with  $d_p=1.1$  cm and  $\varepsilon_p=0.44$ ) are first poured onto the column to form a packing with a height of 44 cm; subsequently, 70 g of the finer solid are loaded and after a complete fluidization–defluidization cycle their height is recorded (6.6 cm). Then, air is fed to the column for about 10 min, to stabilize the regime at one of the selected values of superficial gas velocity reported in Tab. 1. In each adsorption test a gas mixture of air and carbonic anhydride with a fixed volume percentage of  $\text{CO}_2$  is fed to the column.  $\text{CO}_2$  concentration in the effluent gas is continuously monitored at the exit of the column until the gas composition reaches 95% of the inlet value, namely until sorbent saturation is practically reached.  $\text{CO}_2$  concentration is plotted in function of time (breakthrough curve) since the instant at which the gas mixture begins to flow from the fluidized bed to the analyzer. These measurements, carried out both in the conventional and in the confined fluidization apparatus, allow investigating the effect of fluidization velocity on adsorption efficiency.

- i. the breakthrough time  $t_b$ , or breakpoint. It is the time it takes for  $\text{CO}_2$  to reach 5% of the inlet concentration at the outlet of the adsorption column. In a continuous process it also represents the time at which the gas feed must be switched to a stand-by column while regenerating the saturated sorbent of the first one.
- ii. the fraction of bed  $W$  utilized at the breakpoint, namely the ratio between the amount of  $\text{CO}_2$  adsorbed up to the breakpoint and that adsorbed at saturation. This parameter is strictly related to the performance of the adsorber: given the contact time, a higher  $W$  means that a lower amount of sorbent is required. On the other hand, given the mass of solid in the column, a higher  $W$  means that sorbent saturation occurs after a longer time.
- iii. the mass of  $\text{CO}_2$  adsorbed per unit mass of adsorbent,  $m_{\text{CO}_2}$  (reported in this paper as  $\text{gCO}_2/\text{kg}_{13\text{X}}$ ), calculated by integration of the breakthrough curves;
- iv. the maximum temperature,  $T_{\text{max}}$ , reached during the adsorption test (as measured by the thermocouple immersed in the bed).

As  $\text{CO}_2$  adsorption is an exothermic process, any increase of temperature is unfavorable for the adsorption capacity of the solid bed. That is the reason for monitoring the bed temperature during the operation, so as to become aware of the variation of the adsorption capacity.

## RESULTS

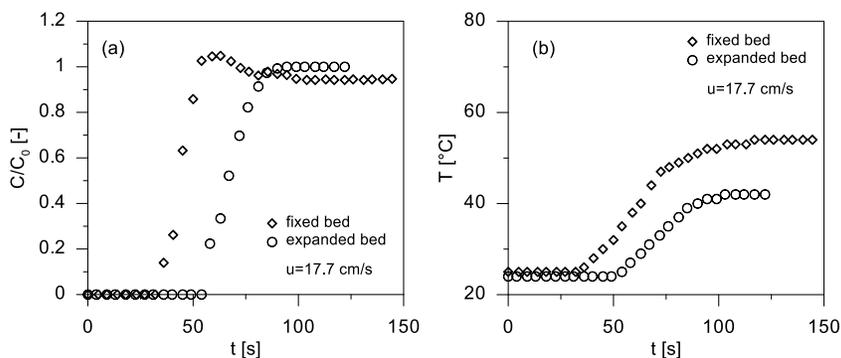


Fig. 3. Comparison of the breakthrough curves and temperature trends for two different regimes: fixed bed (conventional fluidization) and homogeneously expanded bed (confined fluidization).

Zeolite 13X, 800-900  $\mu\text{m}$ , 10%  $\text{CO}_2$  in air,  $u=17.7$  cm/s.

Figures 3a and 4a compare typical breakthrough curves, i.e. the trend of  $C/C_0$  vs time, obtained by experiments of conventional and confined fluidization. The experiments employed the same sorbent (zeolite 13X, 800-900  $\mu\text{m}$ ) and an inlet concentration of  $\text{CO}_2$  of 10% and were run at the same superficial gas velocity ( $u=17.7$  cm/s for Fig.3a and  $u=28.8$  for Fig.4a). At the velocity value chosen for the first experiments the conventional bed is still in its fixed state, while at the second value it is in bubbling regime; the confined bed finds itself over its incipient fluidization threshold, so that its state is that of a homogeneously expanded particle system. The related trends of the bed temperature are also reported in Figs 3b and 4b.

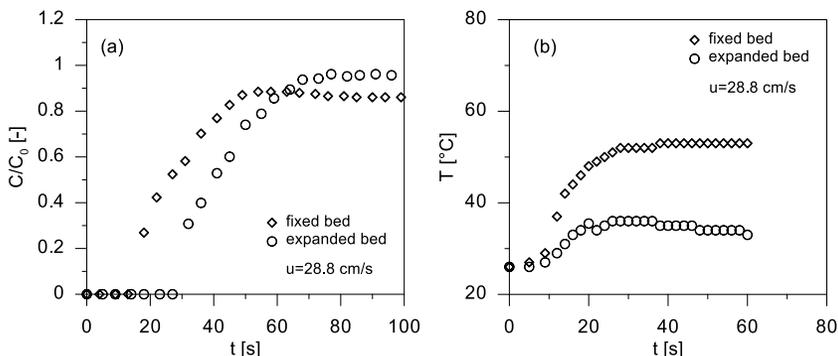


Fig. 4. Comparison of the breakthrough curves and temperature trends for two different regimes: fixed bed (conventional fluidization) and homogeneously expanded bed (confined fluidization).

Zeolite 13X, 800-900  $\mu\text{m}$ , 10%  $\text{CO}_2$  in air,  $u=28.8$  cm/s.

The analysis of the two pairs of curves suggests that the confined fluidization of the sorbent greatly enhances the breakthrough time and causes an increase of bed temperature smaller than that occurring in the conventional fixed bed. Table 2 reports all the parameters measured at the various operating velocities selected for the adsorption experiments of this work.

Table 2: Experimental results for the absorption tests in the different regimes.

$u$ [cm/s]	Conventional fluidization				Confined fluidization			
	$M_{\text{CO}_2}$ [g/kg <sub>13X</sub> ]	$t_b$ [s]	W% [g/g %]	$T_{\text{max}}$ [°C]	$M_{\text{CO}_2}$ [g/kg <sub>13X</sub> ]	$t_b$ [s]	W% [g/g %]	$T_{\text{max}}$ [°C]
17.7	70	39	54.5	54	80.5	57	81.0	42
21.4	72.5	28	56.0	50	74.5	39	77.5	35
24.7	66.0	24	51.5	52	69.0	29	62.0	37
28.8	58.5	17	33.0	53	76.0	26	56.5	34
31.7	61.5	17	44.0	52	78.0	23	59.5	33
35.2	59.0	16	41.5	53	83.5	23	58.0	33
38.6	63.0	14	42.0	53	84.0	22	61.5	35

In order to identify the effect of the operating velocity on the performance of the confined fluidized bed, figures 5 and 6 compare all the parameters of the adsorption tests conducted on the confined fluidized system at varying superficial gas velocity. Fig. 5a shows that in a confined fluidized bed the mass of  $\text{CO}_2$  adsorbed per unit mass of adsorbent,  $m_{\text{CO}_2}$ , calculated by integration of the breakthrough curves varies with velocity and is always higher. Fig. 5b illustrates the variation of the breakthrough time with operating velocity: it can be observed that in the confined bed  $t_b$  is always higher by about 40% than that typical of the conventional fluidized system.

Similarly, as shown by Fig. 6a, the fraction of bed W utilized at the breakpoint in the confined fluidized, i.e. the ratio between the amount of CO<sub>2</sub> adsorbed up to the breakpoint and that adsorbed at saturation, is always about 40% higher than that measured in the conventional bed. Finally, figure 6b shows how the maximum temperature reached during the adsorption process in the confined bed, nearly equal to 35°C, is always lower than that measured in conventional fluidization, around 53°C. The analysis of temperature trends indicates that the increase of gas velocity allows a better temperature control during the adsorption process: the decrease of T<sub>max</sub> at higher gas velocity is possibly due to a more effective mechanism of thermal exchange between the solid phase, whose temperature increases with the heat released by the process of adsorption, and the effluent gas. As these thermal effects are detrimental to the adsorption efficiency, gas velocity can be regulated in order to achieve a condition of good thermal control of the confined fluidized bed.

This effect is evidenced by the curves of Fig 5a and 6a, which exhibit a minimum at varying gas velocity: it can be inferred that a gas velocity of 28.8 cm/s is the optimum value for the adsorption process, as the fraction of bed W utilized at the breakpoint in the confined fluidized becomes nearly constant.

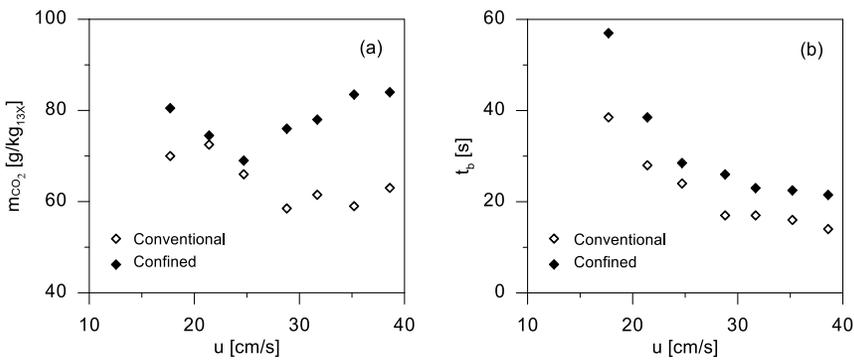


Fig. 5. Comparison of the mass of CO<sub>2</sub> adsorbed per unit mass of adsorbent (a) and breakthrough time (b) versus fluidization velocity for conventional fluidization and confined fluidization.  
Zeolite 13X, 800-900  $\mu$ m, 10% CO<sub>2</sub> in air.

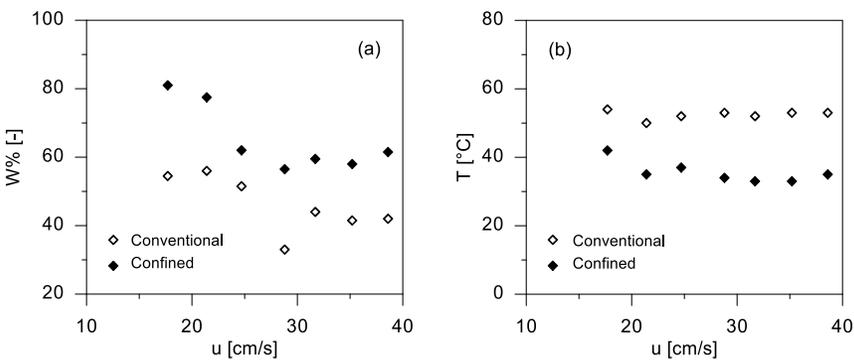


Fig. 6. Comparison of the fraction of bed utilized at the breakpoint in the confined fluidized (a) and the maximum temperature (b) versus fluidization velocity for conventional fluidization and confined fluidization.  
Zeolite 13X, 800-900  $\mu$ m, 10% CO<sub>2</sub> in air.

## CONCLUSIONS

In the present work the efficiency of the capture of CO<sub>2</sub> by a confined fluidized bed of pellets of 13X zeolite has been investigated. Adsorption tests have been performed both in a conventional and a confined fluidized apparatus and the effect of the superficial gas velocity has been analyzed.

The experimental results show that confined fluidization positively affects the efficiency of the adsorption process as it determines a remarkable increase of the breakthrough time as well as of the fraction of bed utilized up to the breakpoint and of the adsorbed mass of CO<sub>2</sub>.

The tests performed in the confined fluidized bed at a fixed CO<sub>2</sub> inlet concentration and at varying fluidization velocity show the dependence of the breakthrough time on the gas-solid contact time, which is inversely proportional to the fluidization velocity. In the confined fluidized bed, the increase of temperature associated to the exothermic nature of the process is small and can be controlled by regulating the superficial gas velocity, a favorable circumstance for the optimization of the performance of an apparatus based on this novel contact mode.

## NOTATION

A	column section, cm <sup>2</sup>	W	fraction of bed utilized at breakpoint, %
C	CO <sub>2</sub> concentration in the effluent gas, % vol	t	time, s
C <sub>0</sub>	CO <sub>2</sub> concentration in the inlet gas, % vol	t <sub>b</sub>	breakthrough time, s
d <sub>p</sub>	diameter of the packed solid, cm	t <sub>c</sub>	contact time, s ( $= \frac{AH_F - m_F / \rho_F}{Q}$ )
d <sub>F</sub>	Sauter's diameter of sorbent, μm		in the conventional bed;
H <sub>F</sub>	sorbent bed height, cm		$= \frac{A\varepsilon_p H_F - m_F / \rho_F}{Q}$ in the confined
m <sub>CO2</sub>	mass of CO <sub>2</sub> adsorbed per unit mass of sorbent, g <sub>CO2</sub> /kg <sub>13X</sub> ,		fluidized bed)
m <sub>F</sub>	mass of sorbent bed, g	T	temperature in the middle of the confined fluidized bed, °C
Q	volumetric gas flow rate, cm <sup>3</sup> /s	T <sub>max</sub>	maximum temperature in the middle of the confined fluidized bed, °C
u	superficial gas velocity, cm/s		
u <sub>mf</sub>	minimum fluidization velocity of the conventional bed, cm/s		
u <sub>mfc</sub>	minimum fluidization velocity of the confined bed, cm/s		
Greek symbols			
ΔP	pressure drop in the conventional system, Pa	ε <sub>mf</sub>	voidage at incipient fluidization in the conventional bed, -
ΔP <sub>conf</sub>	pressure drop in the confined system, Pa	ε <sub>p</sub>	voidage of the packed bed, -
ε	voidage in the packed-fluidized bed, -	ρ <sub>F</sub>	particle density of sorbent, g/cm <sup>3</sup>

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