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CO_2 CAPTURE ON FINE ACTIVATED CARBON UNDER SOUND ASSISTED FLUIDIZATION CONDITIONS

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ABSTRACT
The present work is focused on the CO_2 capture by sound-assisted fluidization of fine activated carbon. The effect of CO_2 partial pressure, gas velocity, sound intensity and frequency has been investigated. Sound positively affects the adsorption efficiency in terms of remarkably higher breakthrough time, adsorption capacity, fraction of bed utilized until breakthrough and adsorption rate.

INTRODUCTION
Although there is not universal agreement on the cause, many climate scientists believe that growing level of CO_2 in the atmosphere is the main cause of global warming (1). It is then generally recognized that massive reduction in CO_2 emissions must be achieved in order to avoid permanent damage to the environment (2). Carbon Capture and Storage (CCS) embodies a group of technologies consisting in the separation of CO_2 from large industrial and energy-related sources, transport to a storage location and long-term isolation from the atmosphere (3). Among all the approaches for CCS, post-combustion capture provides a means for near-term CO_2 capture from new and existing stationary power plants. In this respect, adsorption has been recognized to be one of the most promising alternatives, having the potential, in terms of energy saving, to substitute the present absorption technology. However, for adsorption to become the leading capture technology, enhancement of solid sorbents efficiency represents one of the foremost challenges (4). Since the adsorption efficiency of a given material is the result of a complex combination of its chemical and physical properties the development of highly efficient adsorbents, whose properties can be tuned and controlled at a molecular level, is needed (5). In this respect, nanometric and micronic materials can be very easily tailored and functionalized on the surface by means of the introduction of functional groups with great affinity towards CO_2 molecules. Among gas-solid contact technologies, fluidization is one of the best available techniques to handle and process large quantities of powders. Nevertheless, fluidization of fine materials is particularly difficult due to cohesive forces existing between particles (6). The use of sound assisted fluidization has been indicated to improve fluidization quality of fine powders (7,8). In the present work CO_2 adsorption by sound assisted fluidized beds of fine activated carbon particles (mean size 0.49μm) has been investigated. Preliminarily to adsorption tests, the effectiveness of sound on the fluidization quality of the powder has been characterized by carrying out fluidization tests under ordinary and sound assisted conditions, with different sound intensities (125 to 140dB) and frequencies (20 to 300Hz). Adsorption tests have been performed at ambient temperature and pressure in a laboratory scale reactor in ordinary conditions and under the effect of the above-mentioned acoustic fields. In particular, effectiveness of CO_2 adsorption has been assessed in terms of the moles of CO_2 adsorbed per unit mass of adsorbent, the

breakthrough time and the fraction of bed utilized at breakpoint. The effects of sound frequency (f) and sound pressure level (SPL), the superficial gas velocity (1, 1.5, 2cm/s) and CO_2 concentration in the feed stream (5, 10 and 15%vol. in N_2) have been investigated too.

EXPERIMENTAL APPARATUS, MATERIALS AND PROCEDURE

CO_2 adsorption experiments have been carried out in a laboratory scale sound assisted fluidized bed apparatus, schematized in Fig. 1.

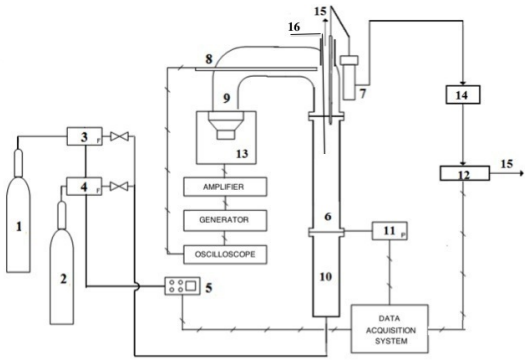

Fig. 1. Experimental apparatus: (1) N_2 cylinder; (2) CO_2 cylinder (3) N_2 flow meter; (4) CO_2 flow meter; (5) controller; (6) 40mm ID fluidization column; (7) filter; (8) microphone; (9) sound guide; (10) wind-box; (11) pressure transducer; (12) CO_2 analyzer; (13) loudspeaker; (14) pump; (15) stack; (16) thermocouple.

The fluidized bed consists of a Plexiglas column of 40mm ID and 1000mm high, equipped with a porous plate gas distributor located at the bottom of the column. N_2 and CO_2 flowrates have been set by means of accurate mass flow controllers (Bronkhorst, NL), and subsequently mixed before entering the bed; a uniform distribution of gas flow has been ensured by a 300mm high wind-box filled by Pyrex rings. The bed pressure has been measured by using a pressure transducer installed at 5mm above the gas distributor. The acoustic field is introduced inside the column through a sound wave guide located at the top of the freeboard. The sound-generation system is made of a digital signal generator to obtain an electric sine wave of specified frequency whose signal is amplified by means of a power audio amplifier rated up to 40W. The signal is then sent to a 8W woofer loudspeaker placed downstream the sound wave guide. The CO_2 concentration in the inlet and outlet gas streams has been measured by an ABB (CH) infrared gas analyzer (AO2020). An activated carbon DARCO FGD (Norit) has been used as adsorbent material. Its particles size distribution has been characterized by using a laser granulometer (Master-sizer 2000 Malvern Instruments, Worcestershire, UK). The relative Sauter mean diameter is 0.39 and 2μm with and without ultrasound application, respectively. Accordingly, the activated carbon belongs to Group C of Geldart classification. Superficial area measurements have been carried out according to the BET method using N_2 at 77K with a QUANTACHROM 1-C (USA) analyzer. The activated carbon is characterized by a broad pore size distribution, i.e. pore size ranging from the mesoporous ($2nm < d < 50nm$) to the microporous ($d < 2nm$), and by a relatively large surface area ($1060 m^2/g$). The activated carbon has been previously characterized to assess its fluidization quality both in ordinary and sound assisted conditions. All the tests have been performed at ambient temperature and pressure using N_2 as fluidizing gas. In particular, sound intensities higher or equal

to 125dB are enough to obtain a good fluidization quality. Whereas, sound frequency has a not monotone effect on the fluidization quality and adsorption efficiency, actually, it is possible to find an optimum range of frequency (50-120Hz) providing the best performances. Also adsorption tests have been carried out at ambient temperature and pressure. The sorbent material has been treated prior to each adsorption test by heating the powder up to 393K, in order to remove any trace of moisture. In a typical experiment, the sorbent (110g) is loaded in the column in order to obtain a bed height of 15cm. Then, in a pre-conditioning step of about 10min, N_2 is fluxed in the column in order to stabilize a fluidization regime at fixed operating conditions in terms of superficial gas velocity and sound parameters. This is followed by the adsorption step in which a CO_2/N_2 gas mixture at a fixed CO_2 concentration is fed through the column. The CO_2 composition in the column effluent gas is continuously monitored as a function of time (breakthrough curve) until the composition approaches the inlet gas composition value, i.e., until bed saturation is reached. CO_2 concentration profiles have been obtained as a function of time t, which has been counted from the time the gas mixture takes from the fluidized bed to the analyzer. This transit time has been previously measured for each gas flow rate by flowing the gas mixture through the empty bed (about 90s). Each adsorption test has been performed both in ordinary and sound assisted fluidization conditions. In particular, the effect of sound parameters (SPL and frequency), fluidization velocity and CO_2 partial pressure on adsorption efficiency has been investigated. Table 1 reports all the operating conditions selected for the adsorption experiments carried out in this work.

Table 1. Operating conditions of the adsorption tests.

Fluidization velocity, cm/s	0.1, 0.25, 0.5, 0.75, 1, 1.5, 2
CO_2 inlet concentration, %vol. in N_2	5, 10, 15
Sound Pressure Level, dB	120, 125, 135, 140
Frequency, Hz	20, 50, 80, 120, 300

RESULTS AND DISCUSSION

Fig. 2a reports the typical breakthrough curves (i.e. C/C_0 versus time t, C and C_0 being the CO_2 concentration in the effluent and feed stream, respectively) obtained in ordinary and sound assisted conditions (140dB-80Hz). In particular, a CO_2 inlet concentration of 10% and a fluidization velocity of 1.5cm/s have been used in this case. Each test has been performed three times and similar results have been obtained, thus confirming the repeatability of the tests. All the curves have been worked out to evaluate: i) the moles of CO_2 adsorbed per unit mass of adsorbent (n_{ads}) calculated by integrating the breakthrough curves; ii) the breakthrough time (t_b) or breakpoint, which is the time it takes for CO_2 to be detected at the adsorption column outlet (5% of the inlet concentration); iii) the fraction of bed utilized at breakpoint (W), namely the ratio between the CO_2 adsorbed until the breakpoint and that adsorbed until saturation. In order to highlight the most significant portion of the curve, namely the section before and soon after t_b, the same graph has also been reported in logarithmic scale (Fig. 2b). The analysis of the curves suggests that the application of the sound greatly enhances the breakthrough time, which, as reported in Table 2, in sound assisted tests (63s) is more than four times the value obtained in ordinary conditions

(12s). The application of the sound affects also the global adsorption capacity. Indeed, the total amount of CO_2 adsorbed until saturation, n_{ads}, moves from 0.31mol/kg, in ordinary conditions, to 0.37mol/kg, in sound assisted conditions (Table 2). The fraction of bed utilized at break point (W) is also greatly enhanced by sound, moving from values lower than 3%, in the tests performed in ordinary conditions, up to values higher than 10%, in the sound assisted tests.

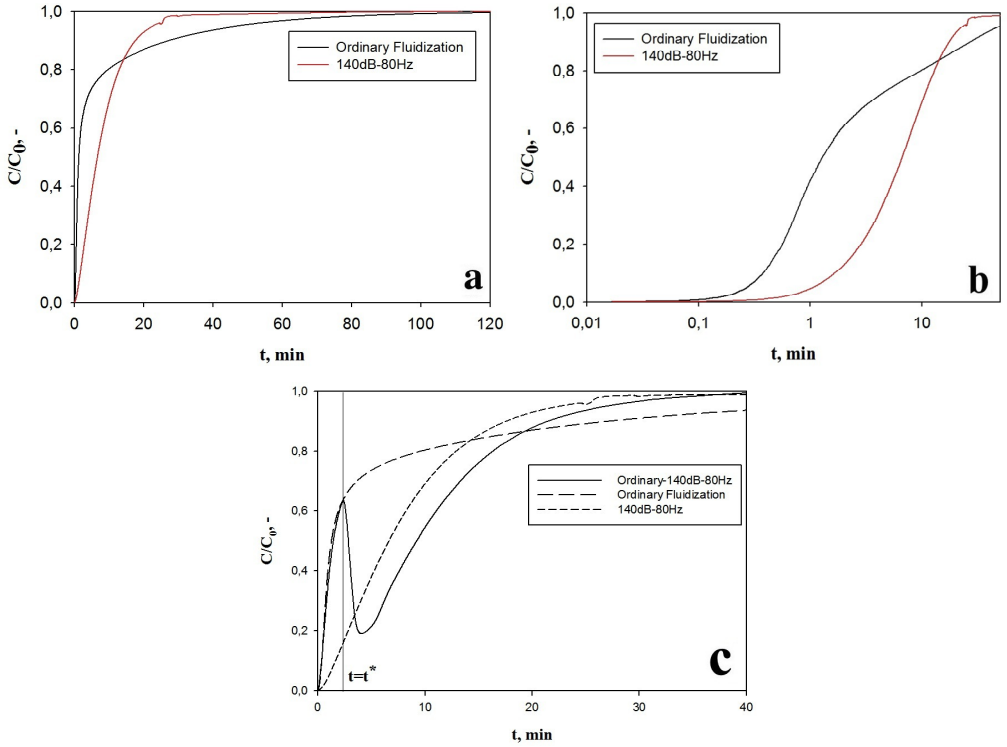

Fig. 2 Breakthrough curves obtained in ordinary and sound assisted conditions, in (a) linear and (b) logarithmic scale. u=1,5cm/s; C_0=10%vol. c) Breakthrough curve obtained switching on the sound at t=t*. u=1,5cm/s; C0=10%vol.

Finally, the application of the sound greatly improves the kinetics of the entire process. Indeed, the application of acoustic fields allows to speed up the adsorption process: under sound assisted conditions the time for CO_2 to approach the saturation value is remarkably decreased (60min for the sound assisted test against 120min for the test performed in ordinary conditions, Fig. 2a), being both the values of n_{ads} and average rate of CO_2 adsorption higher than those obtained in ordinary conditions. The beneficial effect shown by the sound is probably due to the enhancement of the fluidization quality (which brings better gas-solid contact and mass transfer coefficients) with respect to the tests performed in ordinary conditions, namely without the aid of any external force. In particular, the application of the sound greatly enhances the break-up mechanism and re-aggregation of fluidizing aggregates (7,8), thus constantly renewing the surface exposed to the fluid. In other words, the continuous aggregates break-up and re-aggregation mechanism makes the surface of the activated carbon more readily available for the adsorption process. In order to verify these considerations a further test has been carried out. This test has been started in ordinary condition, and only at a time t=t* the sound has been switched on (Fig. 2c). The analysis of the obtained breakthrough curve clearly shows that

for t<t* the CO_2 concentration profile is reasonably the same as that obtained in ordinary conditions (i.e. the bypassing gas makes the CO_2 concentration abruptly rise up). Then, at t=t* the CO_2 concentration suddenly drops down before rising up again, but following now the typical trend of the sound assisted tests. This behaviour confirms the ability of the sound to better exploit the adsorption capacity of the activated carbon.

Table 2. Results of the adsorption tests.

			CO_2 inlet concentration								
			5%			**10%**			**15%**		
			t_b **s**	n_{ads} **mol/kg**	W **%**	t_b **s**	n_{ads} **mol/kg**	W **%**	t_b **s**	n_{ads} **mol/kg**	W **%**
Superficial gas velocity cm/s	***2***	*Ordinary*	15	0.22	3.6	8	0.30	2.7	7	0.37	2.7
		125dB-80Hz	71	0.28	14	55	0.39	13	48	0.44	15
		140dB-80Hz	65	0.26	15	51	0.34	12	43	0.46	15
	1.5	*Ordinary*	19	0.23	3	12	0.31	2.7	10	0.38	2.8
		125dB-80Hz	114	0.28	15	65	0.39	14	67	0.49	14
		140dB-80Hz	80	0.27	11	63	0.37	15	58	0.44	14
	1	*Ordinary*	27	0.23	2.8	20	0.31	3	15	0.38	2.7
		125dB-80Hz	212	0.31	17	185	0.42	21	169	0.55	21
		140dB-80Hz	185	0.28	16	165	0.38	20	155	0.47	23

Effect of SPL and frequency

The effect of SPL on CO_2 adsorption efficiency has been evaluated by carrying out tests at fixed frequency (80Hz) and different sound intensity (from 120 up to 140dB). The comparison among all the tests performed in terms of breakthrough curves, moles of CO_2 adsorbed, t_b and W is reported in Fig. 3a. The data obtained in ordinary conditions have also been reported for comparison. The analysis of these results is rather clear: the SPL effect on CO_2 adsorption process reflects what observed in the fluidization tests. Indeed, the adsorption process undergoes a significant enhancement only when SPLs higher or equal to 125dB are applied, which is perfectly consistent with the obtained activated carbon fluid-dynamic behaviour. Indeed, 125dB is a sort of threshold intensity beyond which any further increase of SPL is ineffective, and sure enough all the tests performed at higher SPL are very similar in terms of breakthrough curves shape, moles of CO_2 adsorbed, t_b and W. Whereas, the behaviour observed at 120dB is intermediate. These results are an additional proof of the tight link existing between the adsorption efficiency and the fluid-dynamics of the system. Then, in order to point out the effect of sound frequency on CO_2 adsorption efficiency, tests have been performed at fixed SPL (140dB) and varying the sound frequency (from 20 to 300Hz). The comparison among all the tests performed in terms of breakthrough curves shape, moles of CO_2 adsorbed, t_b and W is reported in Fig. 3b. As well as for the SPL, also the results obtained in these tests are in perfect agreement with those obtained from the fluidization tests. Indeed, the best results in terms of CO_2 adsorption efficiency can be achieved when sound frequencies falling in the same optimum range (50-120Hz) are applied. Indeed, the tests performed at intermediate frequencies (50, 80 and 120Hz) are characterized by very similar behaviours (breakthrough curves, n_{ads}, t_b and W). Whereas, the adsorption tests carried out at 20 and 300Hz are remarkably worse.

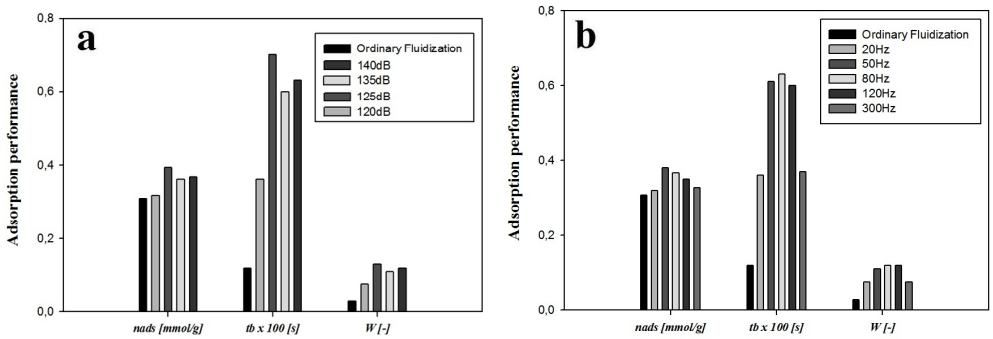

Fig. 3 Effect of SPL (a) and frequency (b) on CO_2 adsorption efficiency.

Effect of CO_2 partial pressure and fluidization velocity

The effect of the CO_2 partial pressure on the adsorption process has been highlighted by performing tests at three different CO_2 inlet concentrations (5, 10 and 15%vol. in N_2) for each investigated superficial gas velocity (1, 1.5 and 2cm/s) and both in ordinary and sound assisted conditions (125/140dB-80Hz). The overall results are reported in Table 2. As expected, the CO_2 capture capacity of the adsorbent (n_{ads}), at a fixed superficial gas velocity and fluidization conditions (with or without the sound), is increased with CO_2 partial pressure. This trend is absolutely consistent from a thermodynamic point of view, since the CO_2 partial pressure represents the driving force of the adsorption process. Moreover, as clearly reported in Table 2, an increase of the CO_2 inlet concentration results in a decrease of the breakthrough time (t_b), in spite of the increased adsorption capacity. This behaviour is probably due to the adsorption process becoming faster at higher CO_2 inlet concentration; indeed, the higher the CO_2 inlet concentration, the more the CO_2 molecules entering the bed per unit time, the quicker the bed saturation, all the other operating conditions being the same. The experimental results have been elaborated and fitted by the Langmuir equation:

$$n_{ads} = n^{s}_{CO_2} \frac{bP_{CO_2}}{1 + bP_{CO_2}} \qquad (1)$$

where n_{ads} are the moles of CO_2 adsorbed per unit mass of activated carbon, $n^{s}_{CO_2}$ the moles adsorbed until saturation, b an affinity coefficient between the adsorbent and adsorbed phases and P_{CO2} the CO_2 partial pressure in the gaseous phase. Fig. 4a reports the adsorption isotherms obtained for the tests performed at 2cm/s both in ordinary and sound assisted conditions (y_{CO2} being the CO_2 inlet molar fraction). Analysis of the curves highlights the beneficial effect played by the application of the acoustic field on adsorption performances. Under sound assisted fluidization the adsorption isotherms move to more favorable adsorption conditions. The results of the same tests have been elaborated in order to point out the effect of the fluidization velocity on the adsorption process. In particular, the dependence of breakthrough time on the contact time (t_c), defined as the ratio between the mass of adsorbent and the CO_2 volumetric flow, has been highlighted. The curves obtained for a CO_2 inlet concentration of 10%vol. in N_2 are shown in Fig. 4b. As a matter of fact, the fluidization velocity is expected to affect the breakthrough time because the mere increase of the fluidization velocity results in decrease of the contact time. However, the

dependence of the breakthrough time on the contact time, i.e. the fluidization velocity, is linear, as one could expect, only for the tests performed in ordinary conditions. Whereas, the breakthrough time is found to exponentially increase with the contact time, namely decreasing the fluidization velocity from 2 to 1cm/s, for the sound assisted tests. This evidence is likely due to the role played by fluidization velocity in sound assisted tests. Indeed, in ordinary conditions the system is quite insensible to changes of fluidization velocity, being the fluidization quality always very poor. Therefore, the observed linear increase of the breakthrough time with the decrease of the fluidization velocity is only due the CO_2 taking more time to flow through the bed.

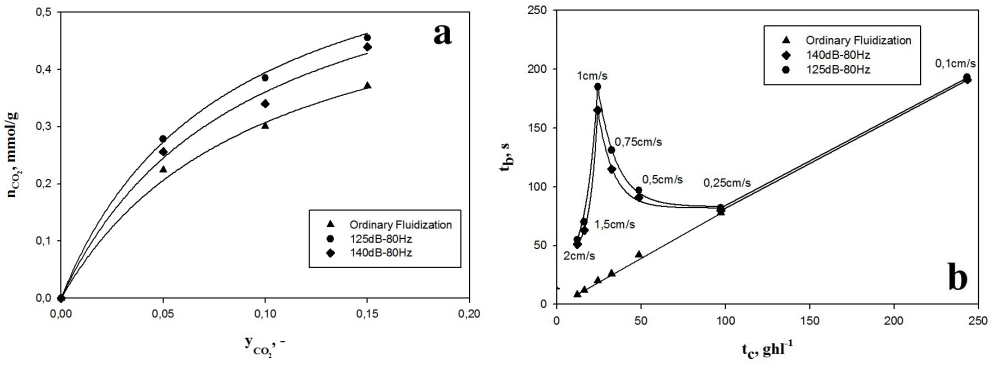

Fig. 4. a) Activated carbon adsorption isotherms in ordinary and sound assisted test, u=2cm/s; b) Breakthrough times as functions of contact time for ordinary and sound assisted tests, C_0=10%vol. in N_2

On the other side, in sound assisted fluidization tests, changes of the fluidization velocity greatly affect the fluid dynamics of the system. In particular, the decrease of the fluidization velocity results in a more homogeneous fluidization regime, which is characterized by a lower by-pass of gas through the bed with respect to the tests performed at higher fluidization velocity. All the results presented in Table 2 have been performed at velocities higher than the minimum fluidization velocities (about 0.3cm/s in sound assisted conditions and 1.3cm/s in ordinary conditions). Then, further tests have been performed at lower superficial gas velocities lower than 1cm/s and at 10%vol. of CO_2 in the inlet stream, in order to fully investigate the effect of the fluidization velocity on the breakthrough time. The analysis of Fig. 4b suggests, as reasonably expected, that in ordinary conditions the breakthrough time keeps linearly increasing even for fluidization velocities lower than 1cm/s. However, the most remarkable observation is that the trend obtained for the sound assisted tests is not monotone. In particular, after the above-mentioned exponential increase, two more sections can be identified, corresponding to different windows of fluidization quality. In particular, a further increase of the contact time (passing from from 1cm/s down to 0.25cm/s) results in an exponential decrease of the breakthrough time; whereas, a linear increase of the breakthrough time is obtained by finally decreasing the fluidization velocity down to 0.1cm/s. It is worth noting that in this last section the breakthrough times obtained in the sound assisted tests are basically the same obtained in the tests performed in ordinary conditions. The first exponential decreasing trend of the breakthrough time is due to the worsening of the fluidization quality as a result of the further decrease of the fluidization velocity. Indeed, for superficial gas velocities lower than 1cm/s the bed is not entirely fluidized. On the other hand, the last section of the curve, namely the linear

increase of t_b, is due to the fact that the bed is not actually fluidized in the tests performed at the lowest velocities (0.25 and 0.1cm/s), being the minimum fluidization velocity 0.3cm/s. In other words, the bed behaviour is qualitatively very similar to that of the tests performed in ordinary conditions. That is the reason why the breakthrough times trend is quantitatively and qualitatively the same as the tests performed without the assistance of any acoustic field.

CONCLUSIONS

In the present work the efficiency of CO_2 capture by sound assisted fluidization of high surface particles of fine activated carbon has been investigated. The experimental results show that sound positively affects the fluidization quality and adsorption efficiency of the powder in terms of remarkably higher breakthrough time, adsorption capacity, fraction of bed utilized until breakthrough and adsorption rate. In particular, sound intensities higher or equal to 125dB are enough to obtain a good fluidization quality. Whereas, sound frequency has a not monotone effect on the fluidization quality and adsorption efficiency; 50-120Hz is the optimal range. As regards the influence of CO_2 partial pressure, the CO_2 capture capacity of the activated carbon increases with increasing the CO_2 inlet concentration. Finally, the dependence of the breakthrough time on the contact time is linear for the tests performed in ordinary conditions whereas it is not monotone for the sound assisted tests.

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REFERENCES

1. J. D. Figueroa, T. Fout, S. Plasynski, H. McIlvried, R.D. Srivastava. Advances in CO_2 capture technology—The U.S. Department of Energy’s Carbon Sequestration Program. Int. J. Greenh. Gas Con., 2: 9–20, 2008.
2. A. Yamasaki. An Overview of CO_2 Mitigation Options for Global Warming-Emphasizing CO_2 Sequestration Options. J. Chem. Eng. Jpn., 36: 361–375, 2003.
3. H. Yang, Z. Xu, M. Fan, R. Gupta, R.B. Slimane, A.E. Bland, I. Wright. Progress in carbon dioxide separation and capture: a review. J. Environ. Sci. 20: 14-27, 2008.
4. D.M. D’Alessandro, B. Smit, J. R. Long. Carbon dioxide capture: prospects for new materials. Angew. Chem. Int. Ed., 49: 6058-82, 2010.
5. S. Choi, J. H. Drese, C. W. Jones. Adsorbent materials for carbon dioxide capture from large anthropogenic point sources. ChemSusChem, 2: 796-854, 2009.
6. X. Wang, R.F. Rahman, M.J. Rhodes. Nanoparticle fluidization and Geldart’s classification. Chem. Eng. Sci., 62: 3455–3461, 2007.
7. P. Ammendola, R. Chirone, F. Raganati. Effect of mixture composition, nanoparticle density and sound intensity on mixing quality of nanopowders. Chem. Eng. Process. 50: 885-891, 2011.
8. P. Ammendola, R. Chirone, F. Raganati. Fluidization of binary mixtures of nanoparticles under the effect of acoustic fields Adv. Powder Technol. 22: 174-183, 2011.