CO_2 ADSORPTION ON FINE POWDERS IN A SOUND-ASSISTED FLUIDIZED BED

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Abstract
This work is focused on the CO_2 capture by sound assisted fluidized beds of fine activated carbon particles with high specific surface particles ($1060 m^2/g$). The powder fluidization quality has been preliminarily characterized by performing ordinary and sound assisted fluidization tests. Then, CO_2 adsorption tests have been performed pointing out the effect of the sound application (125-140dB, 80Hz), the CO_2 partial pressure (5, 10, 15%vol. in N_2) and the fluidization velocity (1, 1.5, 2cm/s).

Introduction
Several studies of the past three decades indicated the growing level of CO_2 in the atmosphere as the main cause of global warming. It is then generally recognized that massive reduction in CO_2 emissions must be achieved in order to avoid permanent damage to the environment [1]. Carbon capture and storage (CCS) is a group of technologies that may reduce emissions into the atmosphere from large fixed industrial sources [2]. It has been estimated that the CO_2 capture stage represents two thirds of the total CCS cost. Therefore, the development of an efficient and cost-effective CO_2 capture technique is considered to be one of the highest priorities in the field of CCS. Adsorption using solid sorbents is a promising alternative to the most popular chemical absorption since it appears to offer potential energy savings together with lower capital and operating costs [3]. Since the adsorption efficiency of a given material is the result of a complex combination of chemical and physical properties the necessity exists to realize new highly specific materials whose properties can be tuned at a molecular level. In this respect, nanomaterials are very versatile and simple to adjust according to the desired application, indeed, solely owing to their special size and shape, they are particularly suitable to be easily tailored and/or functionalized on the surface with different ligands to induce significant changes in their physical and chemical properties [3]. Then, in order to use such materials without being previously pelletized, the development of a proper processing technology is needed. Sound assisted fluidization has been indicated as a valid technological option to smoothly fluidize fine powders. This work is an assessment of the possibility to utilize

sound-assisted fluidized beds to promote CO_2 capture, by means of physical adsorption on fine porous solid particles of activated carbon. Firstly, the material has been fluid-dynamically characterized by performing ordinary and sound assisted fluidization tests. Then, CO_2 adsorption tests have been performed varying the CO_2 content in the gas stream, the gas velocity and the sound intensity and frequency.

Experimental

Fluidization and CO_2 adsorption experiments have been carried out in a laboratory scale fluidization column, schematized in Fig. 1. N_2 and CO_2 flowrates have been set by means of accurate mass flow controllers (Bronkhorst), 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 fluidized bed consists of a Plexiglas column of 40mm ID and 500mm high, with a porous plate gas distributor located at the bottom of the column.

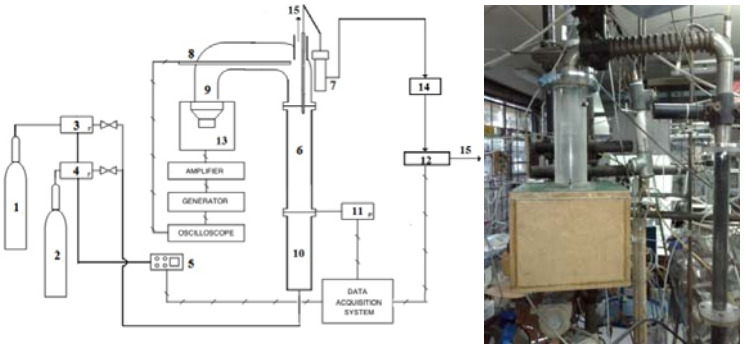

Figure 1. Experimental apparatus: (1) nitrogen cylinder; (2) CO_2 cylinder (3) N_2 flow meter; (4) CO_2 flow meter; (5) controller; (6) 40mm ID fluidization column; (7) filter; (8) microphone; (9) sound guide; (10) wind-box; (11) pressure transducer; (12) CO_2 analyzer; (13) loudspeaker; (14) pump; (15)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

The temperature of the bed has been monitored by means of a thermocouple placed inside the solids at the center of the bed. The bed pressure has been measured by means of a pressure transducer installed at 5mm above the gas distributor. The composition of the outlet gas stream has been measured by an infrared gas analyzer for CO_2 (ABB). The sound-generation system is made of a digital signal generator whose signal is amplified by means of a power audio amplifier. The signal is then sent to a loudspeaker. Fluidization tests have been performed feeding only N_2. All fluidization and adsorption tests have been carried out at ambient temperature and pressure. An activated carbon DARCO FGD (Norit) has been used as adsorption material. The powder has been characterized by a laser granulometer (Master-sizer 2000 Malvern Instruments) after the dispersion of the powders in water under mechanical agitation of the suspension and with or without the application of ultrasound (US). In particular, the activated carbon belongs to the Geldart group C

(mean size 0.39-2μm with and without US, respectively). It is also characterized by a large specific surface area (1060m^2/g), obtained according to the BET method using N_2 at 77K with a QUANTACHROM 1-C analyzer.
The adsorbent 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 (100g) 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. 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 at the same operating conditions. 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 saturation is reached.
Each adsorption test has been performed both in ordinary and sound assisted conditions. Table 1 reports 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	1, 1.5, 2
CO_2 inlet concentration, %vol.	5, 10, 15
SPL, dB	125, 140
Frequency, Hz	80

Results and discussion
Before the adsorption tests the activated carbon has been previously characterized, from a fluid-dynamic point of view, by performing ordinary and sound assisted fluidization tests. A beneficial effect of the sound application in terms of more regular pressure drops and bed expansion curves has been observed. Fig. 2a reports the breakthrough curves (i.e. C/C_0 versus time, C and C_0 being the CO_2 concentration in the effluent and feed stream, respectively) obtained in ordinary and sound assisted conditions for the experimental test performed at 1.5cm/s with a CO_2 concentration in the inlet stream of 10%vol. Analogous trends have been obtained for the other operating conditions. Indeed, as clearly shown in Fig. 9, no abrupt change of slope is present. These curves have been worked out to calculate: i) the moles of CO_2 adsorbed per unit mass of adsorbent, n_{ads}, 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. The application of the sound clearly affects the global adsorption capacity. Indeed,

the total amount of CO_2 adsorbed until saturation is strongly improved by the application of the sound (Table 2). Moreover, the application of the sound also results, for all the tests, in a great enhancement of W, which moves from values lower than 4%, in the tests performed in ordinary conditions, up to values higher than 20%, in the sound assisted tests.

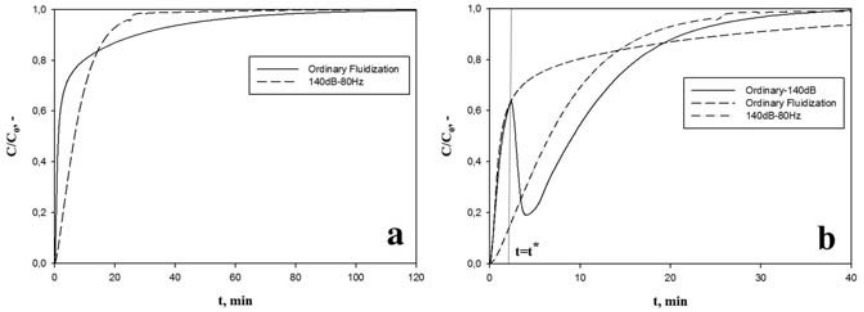

Figure 2. a) Activated carbon breakthrough curves in ordinary and sound assisted conditions. C_0=10%vol.; u=1.5cm/s; b) Breakthrough curve obtained switching on the sound at t=t*. u=1,5cm/s; C_0=10%vol.

The beneficial effect on the adsorption efficiency shown by the sound is probably due to the enhancement of the fluidization quality with respect to the tests performed in ordinary conditions, namely without the aid of any external force. In particular, as already shown in our previous works [4], the fluidization of cohesive powders is based on a break-up and re-aggregation mechanism, which is greatly enhanced by the application of suitable acoustic fields. In other words, the continuous aggregates break-up and re-aggregation mechanism makes the internal 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*, corresponding to the change of slope typical of ordinary adsorption tests, the sound has been switched on. The analysis of the obtained breakthrough curve (Fig. 2b) 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). 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. As regards the amount of CO_2 adsorbed, it is the same as that obtained in the sound assisted test. This behaviour confirms the ability of the sound to better exploit the adsorption capacity of the activated carbon. Indeed, as soon as the sound has been switched on, that specific surface, precluded to the fluid in ordinary conditions, suddenly becomes available causing CO_2 concentration to drop down because of the renewed activated carbon adsorption capacity.

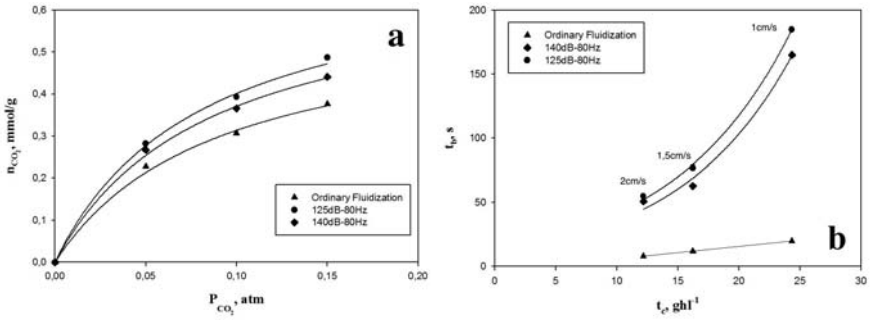

Figure 3. a) Activated carbon adsorption isotherms in ordinary and sound assisted fluidization. u=1.5cm/s; b) Activated carbon breakthrough time as function of contact time in ordinary and sound assisted conditions. C_0=10%vol.

As regards the influence of CO_2 partial pressure. The analysis of the results reported in Table 2, shows, as expected, that the CO_2 capture capacity of the adsorbent increases with CO_2 partial pressure; this trend is absolutely consistent from a thermodynamic point of view; in fact, the CO_2 partial pressure represents the driving force of the adsorption process, so its increase corresponds to higher adsorption capacity. Then, the experimental results have been elaborated and fitted by Langmuir equation in order to obtain the activated carbon adsorption isotherms. Fig. 3a reports the obtained adsorption isotherms in ordinary and sound assisted tests at 1.5cm/s. From the analysis of the curves the above-mentioned beneficial effect played by the application of the acoustic field can be inferred. It is indeed clear that with sound assisted fluidization the adsorption isotherms move to more favorable adsorption conditions. In order to point out the effect of the fluidization velocity on the adsorption process tests have been performed at three different gas velocities (above the minimum fluidization velocity) for each CO_2 inlet concentration and both in ordinary and sound assisted conditions). In particular, the dependence of breakthrough on the contact time (the ratio between the mass of adsorbent and the CO_2 volumetric flow) has been pointed out. The dependence of the breakthrough time on the contact time (which is inversely proportional to the fluidization velocity) is linear for the tests performed in ordinary conditions, due to the system insensibility to changes of fluidization velocity (i.e. there is no deeper interaction between adsorption and fluidization velocity than the obvious CO_2 front taking more time to flow across the bed at lower superficial gas velocity). 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 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. Finally, in all the tests the increase of temperature due to the exothermicity of the process is very small (2-3°K).

Table 2. Experimental results obtained for activated carbon.

2cm/s	**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*** **%**
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	14	48	0.44	15
140dB-80Hz	65	0.26	15	51	0.34	15	43	0.46	15
1.5cm/s	**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*** **%**
Ordinary	19	0.23	3	12	0.31	2.7	10	0.38	2.8
125dB-80Hz	114	0.28	15	65	0.39	13	67	0.49	14
140dB-80Hz	80	0.27	11	63	0.37	12	58	0.44	14
1cm/s	**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*** **%**
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

Acknowledgement
This work was financially supported by MiSE-CNR "Carbone pulito-CO_2 Capture" Project (Italy).

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10.4405/35proci2012.VI12