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# $CO_2$ Capture by Adsorption on Fine Activated Carbon in a Sound Assisted Fluidized Bed

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Among all the carbon capture and storage strategies, post-combustion capture can provide a near-term solution for stationary fossil fuel-fired power plants, eliminating the need for extensive modifications to existing combustion processes and facilities. In this respect, adsorption using solid sorbents has the potential, in terms of energy saving, to complement or replace the current absorption technology. Therefore, the design of highly selective $CO_2$ adsorbents materials is needed. In this framework, great interest is focused on nanomaterials, whose chemico-physical properties can be tuned at the molecular level. As regards the handling of such materials, sound-assisted fluidization is one of the best technological options to improve the gas–solid contact by promoting a smooth fluidization regime. The present work is focused on the assessment of sound-assisted fluidization in the $CO_2$ capture on fine activated carbon. Tests have been performed in a laboratory scale experimental set-up at ambient temperature and pressure, pointing out the effect of sound intensity and frequency. The experimental results show that the acoustic field positively affects the fluidization quality and adsorption efficiency of the powder in terms of remarkably longer breakthrough time, adsorption capacity, fraction of bed utilized until breakthrough and adsorption rate. In particular, sound intensities higher or equal to 125 dB 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 (50–120 Hz) providing the best performance.

## 1. Introduction

The scientific community agrees that anthropogenic $CO_2$ emission, mainly generating by fossil-fuel power plants, is among the main contributors to global warming (Song, 2006). Although the transition of the existing infrastructure from carbon-based sources to cleaner alternatives would be ideal in this regard, such a change requires considerable modifications to the current energy framework, and many of the proposed technologies are not yet sufficiently developed to facilitate large-scale industrial implementation. Thus, carbon capture and sequestration (CCS) technologies that efficiently capture $CO_2$ from existing emission sources will play a vital role until more significant modifications to the energy infrastructure can be realized. Post-combustion $CO_2$ capture processes have the greatest near-term potential for reducing greenhouse gas emissions because existing units can be easily retrofitted, thus providing a quicker solution to mitigate $CO_2$ environmental impacts (Ramli et al., 2014). Among all the post-combustion technologies, adsorption processes on solid sorbents are attractive due to their low energy requirements, operating flexibility and general low maintenance costs (Wahby et al., 2010). However, for adsorption to become one of the leading capture technologies, the design of highly selective $CO_2$ adsorbent materials is re-quested. An ideal adsorbent for capturing $CO_2$ from post-combustion flue gas should exhibit a high $CO_2$ adsorption capacity, fast adsorption/ desorption kinetics, high $CO_2$ selectivity, mild conditions for regeneration, stability during extensive adsorption–desorption cycling, tolerance to the presence of moisture and other impurities in the feed and adequate mechanical strength of adsorbent particles (D'Alessandro et al., 2012).In this framework, great interest is focused on ultra-fine

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materials because their chemico-physical properties can be tuned at the molecular level (Raganati et al., 2014c). In particular, they can be easily tailored and/or functionalized on the surface with different ligands, thus inducing significant changes in their physical and chemical properties (Alfe et al., 2015). Moreover, it is worth noting that also common adsorbent materials, such as activated carbon (Raganati et al., 2014a) and zeolites (Raganati et al., 2014b) are generally commercially available in the form of fine powders.
In this respect, gas fluidization is generally considered to be one of the best available techniques to handle and process large quantities of powders (Raganati et al., 2011a). Moreover, as regards the adsorption process, fluidized beds can also give several advantages over fixed beds: higher heat and mass transfer rate between gas and particles (Valverde et al., 2013). Nevertheless, on the basis of their primary particle size and material density, fine powders fall under the Geldart group C (<30 μm) classification (Raganati et al., 2011b), which means that fluidization is expected to be particularly difficult (i.e. characterized by plug formation, channeling and agglomeration) because of cohesive forces (such as van der Waals, electrostatic and moisture induced surface tension forces) existing between particles and becoming more significant as the particle size decreases (Ammendola and Chirone, 2010). In this framework sound-assisted fluidization has been indicated as one of the best technological option to smoothly fluidize fine and ultra-fine powders (Raganati et al., 2015).
In this work the $CO_2$ capture on a fine activated carbon in a sound assisted fluidized bed has been investigated. Firstly, 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 140 dB) and frequencies (20 to 300 Hz). Then, adsorption tests have been performed at ambient temperature 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. Then, the effects of sound frequency and SPL have been investigated.

## 2. Materials and methods

### 2.1 Experimental apparatus

$CO_2$ adsorption experiments have been carried out in a laboratory scale sound assisted fluidized bed apparatus (Raganati et al. 2014a). The fluidized bed consists of a Plexiglas column of 40mm ID and 1000 mm 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 mass flow controllers (Bronkhorst), and subsequently mixed before entering the bed; a uniform distribution of gas flow has been ensured by a 300 mm high wind-box filled by Pyrex rings. The bed pressure has been measured by a pressure transducer installed at 5 mm above the gas distributor. The acoustic field is introduced inside the column through a sound wave guide located at the top of it. The sound-generation system is made of a digital signal generator to obtain an electric sinusoidal wave of specified frequency whose signal is amplified by means of a power audio amplifier rated up to 40 W. The signal is then sent to a 8 W woofer loudspeaker connected to the be through a sound wave guide. The $CO_2$ concentration in the inlet and outlet gas streams has been measured by an ABB infrared gas analyzer (AO2020).

### 2.2 Material

An activated carbon DARCO FGD (Norit) has been used as adsorbent material. Its particle size distribution has been characterized by using a laser granulometer (Master-sizer 2000 Malvern Instruments), after dispersing the powders in water under mechanical agitation of the suspension and with or without the application of ultrasound (US). Superficial area measurements have been carried out according to the BET method using $N_2$ at 77K with a QUANTACHROM 1-C analyzer.

### 2.3 Preliminary fluid-dynamic characterization

The activated carbon has been previously characterized to assess its fluidization quality both in ordinary and sound assisted conditions (for 125, 130, 135 and 140 dB, and for 20, 50, 80, 120 and 300 Hz). All the tests have been performed at ambient temperature and pressure using $N_2$ as fluidizing gas in order to prevent any agglomeration of fine particles enhanced by air moisture. For all the tests 110 g of activated carbon has been loaded in the fluidization column in order to obtain a bed height of about 15 cm. For each test, pressure drop and bed expansion curves have been obtained, by measuring the pressure drops and bed height when the superficial gas velocity was decreased (DOWN) and increased (UP), even though no significant hysteresis phenomena were observed between fluidization and de-fluidization tests. Then, the minimum fluidization velocity, $u_{mf}$, has been calculated from the pressure drop curves by means of a graphic procedure (the plot of pressure drop vs superficial gas velocity can be fitted by two lines: one line fits the data for flow through a packed bed, whereas, the second line is a fit of the data for a fully fluidized bed, which is a horizontal line; $u_{mf}$

is evaluated as the superficial gas velocity corresponding to the intersection of these two lines is the minimum fluidization velocity). Finally, the bed expansion data have been elaborated in order to estimate the size of the fluidizing aggregates (the method is explained in the work of Raganati et al. 2011b).

### 2.4 Adsorption tests

All 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 140 °C, in order to remove any trace of moisture. In a typical experiment, the sorbent (110 g) was loaded in the column in order to obtain a bed height of 15cm. Then, in a pre-conditioning step of about 10min, $N_2$ was 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 was followed by the adsorption step in which a $CO_2/N_2$ gas mixture at a fixed $CO_2$ concentration was fed through the column. The $CO_2$ concentration in the column effluent gas is continuously monitored as a function of time (breakthrough curve) until the gas composition approaches 99 % of the inlet 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 to flow 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 90 s).

## 3. Results and discussion

### 3.1 Materials characterization

The granulometric analysis shows that the powder is in the form of relatively large aggregates and the application of ultrasound (US), namely the application of an external force brings about the break-up of large aggregates into smaller ones, down to about 40 nm. The corresponding Sauter diameter is 0.39 and 2 μm with and without ultrasound treatment, respectively. Accordingly, the activated carbon belongs to Group C of Geldart classification. The activated carbon is characterized by a broad pore size distribution (i.e. pore size ranging from the mesoporous (2 nm < d < 50 nm) to the microporous (d < 2 nm)) and by a relatively large surface area (1,060 $m^2/g$).

### 3.2 Preliminary fluid-dynamic characterization

In Figure 1a the dimensionless pressure drops and bed expansion curves obtained in ordinary and sound assisted (140 dB – 80 Hz) conditions are reported. In particular, the dimensionless pressure drops values have been obtained dividing the actual pressure drop ($\Delta P$) by that equal to the weight of particles per unit area ($\Delta P_0$), the last being 88 mm $H_2O$. Similarly, the dimensionless bed expansion values have been evaluated dividing the actual bed height (H) by the initial value ($H_0$), the last being 15 cm. The fluidization quality in these conditions (i.e. without the application of any acoustic field) was particularly poor (channeling), as clearly confirmed by the fact that asymptotic value reached by the pressure drops is less than 1. In contrast, pressure drops and expansion curves obtained with the assistance of sound were far more regular, both qualitatively and quantitatively: the pressure drops always reach the asymptotic value of 1 and the bed expansion ratio was always larger than that obtained under ordinary fluidization conditions. Therefore, the application of the sound is required to achieve a proper fluidization regime, which is closely related to an efficient break-up of the large aggregates (as a result of cohesive forces) into smaller particles prone to be fluidized (Raganati et al. 2011a). In particular, an in-depth study has been carried out in order to evaluate the most effective acoustic conditions, namely whether it is possible or not to find optimal values of SPL and frequency. Figure 2b reports the effect of SPL (at fixed frequency, 80 Hz) and frequency (at fixed SPL, 140 dB) on the minimum fluidization velocity ($u_{mf}$). Firstly, all the sound assisted tests are characterized by lower $u_{mf}$ with respect to the test performed in ordinary conditions, thus confirming the ability of the sound in enhancing the fluidization quality. As regards the role played by the SPL, $u_{mf}$ is sharply decreased passing from 120 to 125 dB and then it holds steady even when SPL is further increased. Sound intensities higher than or equal to 125 dB are enough to obtain a good fluidization quality. In other words, 125 dB is a kind of threshold value for this activated carbon. Indeed, all the tests performed at higher SPL (125, 135 and 140 dB) are characterized by the same $u_{mf}$ (i.e. quite similar pressure drops and expansion curves), which means that any additional increase of sound intensity does not succeed in further decrease of $u_{mf}$. The results of the test performed at 120 dB provided remarkably higher $u_{mf}$, which confirms that the break-up mechanism is less efficient because less energy is introduced inside the bed. As regards the sound frequency, the results show that it has a not monotone effect on the fluidization quality. Actually, it is possible to find an optimum range of frequency (50-120 Hz) giving the lower values of $u_{mf}$ (i.e. best fluidization performance). Either too low or too high frequencies, which fall out of this

range (20, 300 Hz), correspond to worse fluidization qualities. This behaviour is due to the fact that the frequency directly affect the relative motion between larger and smaller aggregates, which, in turn, promotes the essential break-up and reaggregation mechanism: for frequencies higher than 120 Hz the acoustic field generally cannot properly propagate inside the bed, whereas, for frequencies lower than 50 Hz the relative motion between smaller and larger sub-aggregates is practically absent.

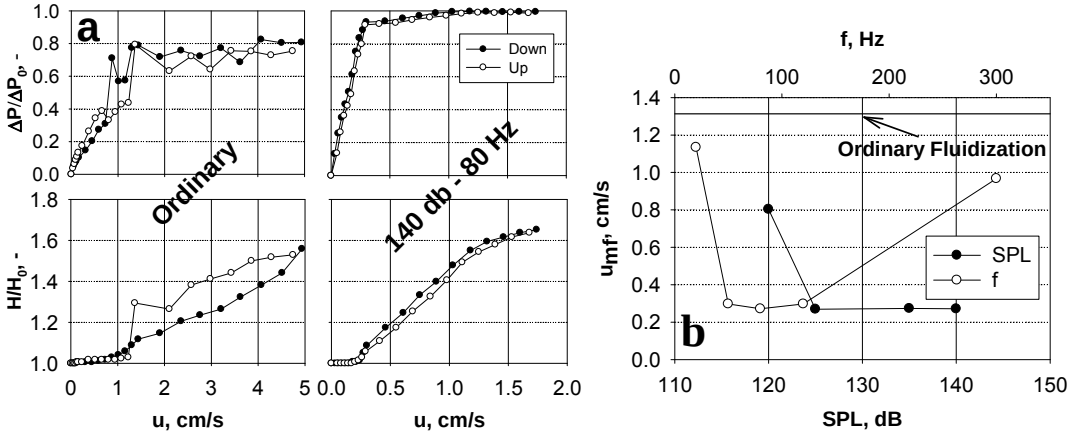


*Figure 1: a) Dimensionless pressure drop and bed expansion as functions of superficial gas velocity; b) Minimum fluidization velocity as a function of SPL (f = 80 Hz) and of frequency (SPL = 140 dB)*

### 3.3 Adsorption tests

Figure 2 reports the typical 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 (140 dB–80 Hz). In particular, a $CO_2$ inlet concentration of 10 %vol. and a fluidization velocity of 1.5 cm/s have been used in this case. These 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 reach the 5 % of the inlet concentration at the adsorption column outlet; 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.

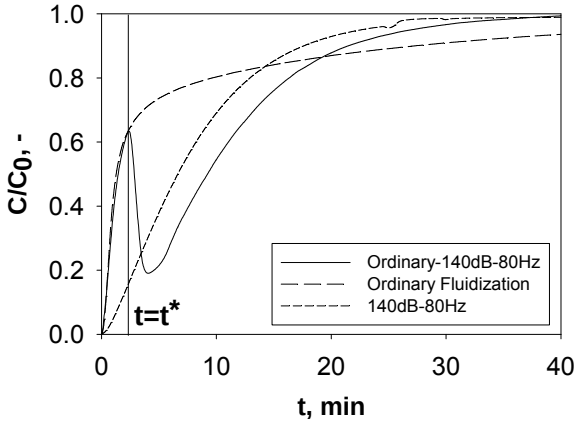


*Figure 2: Breakthrough curves obtained in ordinary and sound assisted conditions and breakthrough curve obtained switching on the sound at t = t*. u = 1.5 cm/s; $C_0$ = 10 %vol*

The analysis of the curves suggests that the application of the sound greatly enhances the breakthrough time, which in sound assisted tests (63 s) is more than five times the value obtained in ordinary conditions (12 s). The application of the sound affects also the global adsorption capacity. Indeed, $n_{ads}$ moves from 0.31 mol/kg, in ordinary conditions, to 0.37 mol/kg, in sound assisted conditions. 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. 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 (60 min for the sound assisted test against 120 min for the test performed in ordinary conditions), 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 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 (Raganati et al. 2011a), thus constantly renewing the surface exposed to the fluid. In other words, the peculiar fluid-dynamic conditions in the fluidization column under sound assisted conditions (i.e. the continuous aggregates break-up and re-aggregation mechanism) increase the surface of the activated carbon available for the adsorption process, thus also significantly increasing the amount of $CO_2$ adsorbed until complete saturation of the bed. 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 above-mentioned change of slope typical of ordinary adsorption tests, the sound has been switched on (Figure 3). 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. 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.

*Effect of SPL and frequency*

The effect of SPL and frequency on $CO_2$ adsorption efficiency has been evaluated by carrying out tests at fixed frequency (80 Hz) and different sound intensity (from 120 up to 140 dB) and at fixed SPL (140 dB) and varying the sound frequency (from 20 to 300 Hz). The comparison among all the tests performed in terms of moles of $CO_2$ adsorbed, $t_b$ and W are reported in Figure3. The data obtained in ordinary conditions have also been reported for comparison.

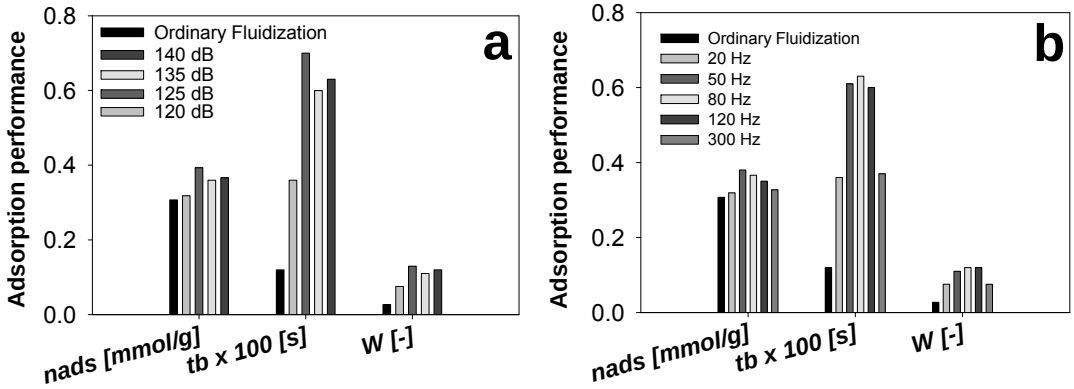


*Figure 3: Effect of (a) SPL at fixed frequency (80Hz) and (b) frequency at fixed SPL (140dB) on $CO_2$ adsorption in terms of $n_{ads}$, $t_b$ and W. u = 1.5cm/s; $C_0$ = 10%vol*

The SPL effect on $CO_2$ adsorption process reflects what was observed in the fluidization tests. Indeed, the adsorption process undergoes a significant enhancement only when SPLs higher or equal to 125 dB are applied, which is perfectly consistent with the obtained activated carbon fluid-dynamic behaviour. Indeed, 125 dB 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.
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 300 Hz are remarkably worse.
These results are an additional proof of the tight link existing between the adsorption efficiency and the fluid-dynamics of the system.

## 4. Conclusions

In the present work the efficiency of $CO_2$ capture by sound assisted fluidized beds of high surface particles of fine activated carbon has been investigated. Adsorption tests have been performed both in ordinary and sound assisted conditions; in particular, the effect of sound parameters (SPL and frequency), $CO_2$ inlet concentration and superficial gas velocity has been studied.
The experimental results show that the acoustic field positively affects the fluidization quality and adsorption efficiency of the powder in terms of remarkably higher breakthrough time, increased 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, actually, it is possible to find an optimum range of frequency (50-120 Hz) providing the best performances.

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