



## CO<sub>2</sub> adsorption on a fine activated carbon in a sound assisted fluidized bed: Thermodynamics and kinetics



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### HIGHLIGHTS

- CO<sub>2</sub> adsorption on activated carbon was performed by sound assisted fluidization.
- Langmuir and Freundlich equations were used to model the CO<sub>2</sub> adsorption isotherms.
- Freundlich model was more suitable to describe CO<sub>2</sub> adsorption than Langmuir.
- CO<sub>2</sub> adsorption on the activated carbon is spontaneous, exothermic and physical.
- A pseudo-first order kinetic model was used to fit the experimental data.

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### ABSTRACT

Combustion of fossil fuels is one of the major sources of CO<sub>2</sub>, it is therefore necessary to develop technologies that will allow to utilize fossil fuels while reducing CO<sub>2</sub> emissions to the atmosphere. Removal of CO<sub>2</sub> from flue gases has become an effective way to mitigate CO<sub>2</sub> emissions and adsorption is considered to be one of the methods. In particular, adsorption on fine and ultra-fine sorbents in a sound assisted fluidized bed has been proved to be a promising alternative, being able to maximize CO<sub>2</sub> adsorption capacity and kinetics. However, before the design of an adsorption equipment, investigation of equilibrium and kinetics plays a decisive role.

In this work, the previous research was furthered into the investigation of the mechanism (isotherm), nature/strength (thermodynamics) and rate (kinetics) of CO<sub>2</sub> adsorption on a commercial activated carbon in a sound assisted fluidized bed. Langmuir and Freundlich equations were used to model the CO<sub>2</sub> adsorption isotherm in the low pressure region (i.e. typical of a combustion flue gas). The results revealed that Freundlich equation was more accurate for predicting the adsorbed amount than the Langmuir one, which indicates a heterogeneous surface binding. Then, adsorption behavior was elucidated by energy function such as standard Gibbs free energy, enthalpy and entropy, suggesting the spontaneity and feasibility of adsorption of CO<sub>2</sub> by activated carbon, and its exothermic and physical nature. The isosteric heat of adsorption was also evaluated; its decrease with surface loading further indicated the heterogeneity of adsorption sites and also variation in adsorbate–adsorbent interactions. Finally, this study also presented a kinetic analysis of CO<sub>2</sub> adsorption, from which CO<sub>2</sub> binding on activated carbon was deduced to follow pseudo-first order kinetic.

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## 1. Introduction

The CO<sub>2</sub> capture and storage (CCS) technologies from flue gases were considered to be cost-effective means for capture, utilization and sequestration of carbon dioxide (CO<sub>2</sub>) from large stationary sources, thus lessening the global warming issue [1]. Among the different CCS approaches, one potential scenario under which

CO<sub>2</sub> capture could be promptly deployed is represented by the post-combustion capture techniques, wherein the CO<sub>2</sub> is selectively removed from a power plant flue gas stream and sequestered through storage in underground geological formations [2]. Post-combustion flue gas is released at a temperature in the range of 40–160 °C, depending on the design and process operation of the power generation system, and at a total pressure of approximately 1 atm, wherein CO<sub>2</sub> is present at a relatively low partial pressure of 0.05–0.15 atm [3]. Thus, the adsorption capacity for CO<sub>2</sub> in the low-pressure region is critically important. With regard to the

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temperature, the cooling of the flue gas stream, even though possible, represents additional cost and cooling water consumption, and therefore, there is a desire to treat the flue gas stream without cooling.

In this framework, different CO<sub>2</sub> capture technologies, including absorption, adsorption, cryogenics, membranes, can be employed [1]. Among them, the absorption technology has been recognized as the most mature process so far, with amine-based or ammonia-based absorption processes receiving the greatest attention [4]. However, this technology presents a series of drawbacks for post-combustion applications, such as high energy requirement associated with sorbent regeneration (as much as 40% of the energy output of the power plant is required to release the CO<sub>2</sub> from the solutions), amine losses due to evaporation, corrosion problems and thermal and chemical degradation of the amines in the presence of oxygen [5].

As an alternative, adsorption is one of the most promising technologies for post combustion capture of CO<sub>2</sub> from flue gases, avoiding the weaknesses of aqueous amine systems and offering potential energy savings with lower capital and operating costs [6–8]. However, the success of this approach depends on the design of highly specific CO<sub>2</sub> adsorbent materials [9–11]. An ideal adsorbent should exhibit a high CO<sub>2</sub> adsorption capacity, fast adsorption/desorption kinetics, high CO<sub>2</sub> 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 [9–11]. In this framework, fine particles have the greatest potential since they can be easily tailored and/or functionalized on the surface with different ligands to induce significant changes in their physical and chemical properties (i.e. surface area, pore structure and the properties of surface chemistry) [9]. For instance, their adsorption capacity can be enhanced by introducing functional groups with a great chemical affinity towards CO<sub>2</sub> molecules (i.e. basic functionalities or some other polarizing groups) inside the porous structure. Typical examples are metal organic frameworks (MOFs) [12], supported ionic liquids (SILPs) [13], magnetite loaded carbon particles [14,15], etc. Besides, also common and commercially available adsorbent materials (such as activated carbons and zeolites) are generally in the form of fine powders. According to the literature, the activated carbons are among the most appropriate sorbents for CO<sub>2</sub> separation/capture [7,16]. Indeed, they are quite inexpensive since they can be produced from a wide variety of sources (coal, industrial byproducts, biomass sources, etc.), thus making them cheaper to produce on an industrial scale than other sorbents, they have generally a hydrophobic character and exhibit high surface area, high CO<sub>2</sub> adsorption capacity and thermal stability [7,16]. Physical adsorption on activated carbons has been widely used for the applications of separation and purification of gases and adsorption based gas storage systems [7,16–18].

However, as much as fulfilling an adsorbent material may be, each adsorbent strengths/weaknesses must be considered in the framework of a practical adsorption process for effective CO<sub>2</sub> separation [9]. Common adsorption operations are generally performed in fixed-bed reactors. However, this technology does not appear suitable to match the requirements related to the adsorbent materials, i.e. to fully exploit all the potential of an ad hoc manufactured fine adsorbent material. Indeed, for these fine materials to be used in fixed bed operations, a previous pelletization step is needed to overcome the prohibitively high pressure drops related to fine particles beds. However, the shaping process could negatively affect the adsorption process: i) the pelletization could lead to additional intraparticle diffusion resistance, thus reducing the global adsorption kinetics; ii) after the shaping processes, the specific surface area could dramatically decrease, and some pores

could be blocked, thus leading to a decline in adsorption capacity [19]. Therefore, serious benefits over fixed-bed adsorption methods are likely expected if a reliable and proper processing technology is developed to directly use these free-flowing fine powders.

All these considerations are also applicable to the testing phase. Indeed, the capture capacity of these fine materials (i.e. group C powders of Geldart's classification [20]) strongly depends on the technology adopted to perform the adsorption tests, i.e. the contact mode between the solid and gaseous phases. Common techniques, such as thermogravimetric analysis or fixed bed reactors, end up underestimating it, since these fine powders are organized in structures (aggregates), which can be difficult for the gaseous phase to permeate [19]. This means that the adopted technology is unavoidably a main limitation also when aiming to determine the effective and intrinsic adsorption performances of a fine solid sorbent. Therefore, the use of a proper test rig is necessary in order to maximize the gas–solid contact efficiency, thus minimizing as much as possible the limitations to the intrinsic adsorption capacity of the sorbents.

In this context, Raganati et al. [21,22] demonstrated the viability of sound assisted fluidization technology in processing, handling and testing sorbents in the form of free-flowing fine powders. The same Authors [23–26] also showed that sound assisted fluidized beds may be more feasible for commercial temperature swing adsorption (TSA) processes. In brief, the peculiar fluid-dynamic conditions present inside a sound assisted fluidized bed make it possible to remarkably enhance the CO<sub>2</sub> adsorption on fine sorbents [19] due to the enhancement of the fluidization quality and gas–solid contact [22,27,28]. In particular, the application of the sound greatly enhances the break-up and re-aggregation mechanism of fluidizing aggregates, thus constantly renewing and maximizing the surface exposed to the fluid, i.e. making the surface of the fine sorbent particles more readily available for the adsorption process [22,27,28]. As a consequence of this enhancement of the gas–solid contact efficiency, the application of the acoustic field also positively affects the adsorption efficiency in terms of remarkably higher breakthrough time, adsorption capacity, fraction of bed utilized until breakthrough and adsorption rate [19,21–25], with respect to both fixed bed (with pelletized materials) and ordinary fluidized bed operations [19]. Raganati et al. [19] also presented and discussed the main scale-up issues related to the proposed sound assisted fluidized bed adsorber/desorber unit. The first one arises from sound intensity attenuation across the bed height. In particular, for such fine materials and for low frequency sound waves (around 100 Hz), it can be estimated that the SPL is reduced by 10 dB for each 10 cm of bed [19]. Therefore, it would not be possible to use a bed higher than 40–50 cm. Accordingly, the only way to scale-up the process is represented by increasing the reactor diameter [19]. However, this diameter increase would lead to another cause of sound intensity attenuation, namely the divergence of the acoustic wave [19]. A feasible technique to avoid spherical spreading loss is to use an array of loudspeakers, which may produce a plane wave if conveniently placed on the cross-sectional area of the column [19]. Besides, the use of an array of loudspeakers would also provide a greater reliability for continuous operation, since replacement of one of the loudspeakers can be easily carried out without the interruption of the sound assisted process.

However, before the design of an adsorption equipment, the investigation of both equilibrium and kinetics is necessary. Thermodynamic data only provide information about the final state of a system (i.e. the equilibrium adsorption capacity), whereas kinetics deals with how the system changes in time, with particular attention to the rates of these changes. Among the properties expected in a good adsorbent, fast adsorption kinetics is one of the most important, since the efficiency of an adsorbent in

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