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DEVELOP OF NANOMATERIALS FOR CO_2 GEO-STORAGE IN SHALLOW RESERVOIRS

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Abstract

The Intergovernmental Panel on Climate Change-IPCC and International Energy Agency-IEA propose the carbon capture and storage process (CCS) as an effective method to control the anthropogenic CO_2 emissions from industry, which could be reduce by approximately 22% at 2035. The CCS implementation needs reduce technical-economical costs related to two main stages: 1) CO_2 separation from flue gas, and 2) CO_2 injection in deep geological deposits, more than 300 m, where CO_2 is in supercritical conditions; in this case the volume occupation is the main reason for CO2 storage. This study proposes, for the first time, an enhanced CCS process (e-CCS), in which the stage of CO_2 separation is eliminated, and the flue gas is injected directly in shallow reservoirs located at less than 300 m deep, where the adsorptive phenomena control CO_2 storage. Carbon nanomaterials were used as modifying agents of the reservoir porous texture in order to improve both the CO_2 adsorption capacity and selectivity. For this purpose, sandstone was impregnated with nanofluids composed of carbon nanospheres dispersed in deionized water. CO_2 adsorption was evaluated at different pressures (atmospheric pressure and from 3×10^{-3} MPa to 3.0 MPa) and temperatures (0, 25 and 50°C) to mimic the reservoir conditions. As a main result, the best materials for industrial application allows increase the adsorption capacity at 0°C to an increment factor of 499 (from 0.00125 to 0.6265 mmol g^{-1}) with only 20 % of nanomaterials at atmospheric pressue, and by more than 800 (from 0.00125 to 1.1 mmol g^{-1}) at 3.0 MPa. The increment factor of adsorption capacity under shallow reservoir conditions (50°C and 3.0 MPa) was more than 670 (from 0.00125 to 0.9 mmol g^{-1}).

Keywords: Carbon Capture and Storage process (CCS); adsorption; nanomaterials; carbon dioxide (co_2) and shallow reservoirs

Resumen

El Panel Interguvernamental de Cambio Climático-IPCC y la Agencia Internacional de Energía-IEA promueven el proceso de captura y almacenamiento de carbono (CCS por sus siglas en inglés, Carbon capture and storage process) como un método efectivo para controlar las emisiones antropogénicas de CO_2 *provenientes de la industria; por medio de este proceso se podrían reducir las emisiones de* CO_2 *hasta un 22% a 2035. Pero su implementación a nivel industrial se ha visto afectada por los costos tecnico-económicos relacionados con dos etapas principales: 1) Separación del* CO_2 *desde el gas de combustión y 2) Inyección de* CO_2 *en depósitos geológicos con profundidades mayores a 300 m, en las cuales el* CO_2 *esta a condiciones supercríticas y el llenado del volumen de la roca es la principal razón de almacenamiento. Este trabajo propone, por primera vez en la literatura, un proceso CCS mejorado, e-CCS, en el cual la etapa de separación de* CO_2 *es eliminada y el gas de combustión es inyectado directamente en el yacimiento somero, a profundidades menores de 300 m. A esta profundidad el proceso de adsorción selectivo controlaría la captura y almacenamiento de* CO_2*. Para esto es necesario modificar la superficie del yacimiento con el fin de mejorar la capacidad de adsorción y selectividad al* CO_2*. Para esto, nanomateriales de carbono han sido sintetizados, caracterizados y usados para modificar la superficie de la roca. Arenisca ha sido usada como medio geológico, la cual ha sido impregnada por medio de nanofluidos compuestos por nanoesferas dispersas en agua desionizada. Posteriormente el desempeño en el proceso de adsorción de* CO_2 *ha sido evaluado bajo diferentes condiciones de presión (ambiental y desde* 3×10^{-3} *MPa a 3.0 MPa) y temperatura (0, 25 y 50 °C), con el fin de caracterizar el proceso y llevarlo a las condiciones similares de un yacimiento. Como resultado principal, con solo 20% del mejor material que presenta condiciones de escalamiento industrial y a 0°C se obtiene un incremento en la capacidad adsorbida de 499 veces (De 0.00125 a 0.6265 mmol* g^{-1} *a presión atmosférica y de 800 veces a 3 MPa (De 0.00125 a 1.1 mmol* g^{-1}*). A condiciones de yacimiento, 50 °C y 3 MPa, el factor de incremento es de 670 (De 0.00125 to 0.9 mmol* g^{-1}*).*

Palabras clave*: Proceso de captura y almacenamiento de carbono (CCS); adsorción; nanomaterials; dióxido de carbono (*CO_2*) y yacimientos someros*

1. Introduction

The anthropogenic emissions of carbon dioxide-CO_2 from fossil fuel combustion and industrial processes contributed about 78 % of the total greenhouse gases emissions (US-EPA 2019; Edenhofer et al. 2014; Tan et al. 2016), and since pre-industrial times, CO_2 emissions have increased in 46 % (NASA 2019). An advantage of industrial processes are the fixed sources of emissions and can be controlled in-situ, but the current methods (absorption by solvents, adsorption, membranes, among others) are not enough (NASA 2019; Conti et al. 2016). For this reason, it is necessary to expand the portfolio of methods for significant reduction of CO_2 emissions in the coming years (Metz, Davidson, and De Coninck 2005). The Intergovernmental Panel on Climate Change (IPCC) promotes the Carbon Capture and Storage process (CCS), which allows the geological storage of CO_2 emitted by the industry for a long term (Tan et al. 2016; Metz, Davidson, and De Coninck 2005; Cook et al. 2014). The CCS process could decrease CO_2 emissions by approximately 22%

in 2035 (IEA 2011; Balat and Öz 2007). The CCS process has three main stages: 1) capture and separation of the CO_2 from flue gas, 2) transport of the CO_2 to the storage site, and 3) injection of CO_2 into the deep geological storage site, 300 to 4000 m, an average of 800 m^2 (Cook et al. 2014). In this case, the volume occupation in porous media is the main reason to capture and storage of CO_2. Figure 1-a presents a scheme of the CCS process.

However, its in-situ industrial implementation has been unsuccessful mainly due to technical-economical cost related to the first and third stages. In general, the cost of CO_2 capture is 70–80% of the total costs of carbon capture, transport, and storage system (Balat and Öz 2007; Gough 2008, 2016). This work proposes an alternative to modifying the first and third stage of the CCS process to minimize the technical-economic cost for the viability of the process. The Figure 1-b presents a new configuration of CCS process (e-CCS), in which the stage of CO_2 capture/separation is suppressed, and the flue gas is injected directly in shallow deposits, with depths lower than 300 m. In this case, CO_2 remains in a gaseous state, and the adsorption process controls the capture and storage. The density of CO_2 is very different at gaseous or supercritical conditions, which affect the stored amount of CO_2 in e-CCS process. For this, it is necessary a modifying agent of the porous media surface to improve the adsorption capacity and selectivity to CO_2. Also, the agent must conserve the naturally porous structure of the deposit avoiding operational problems.

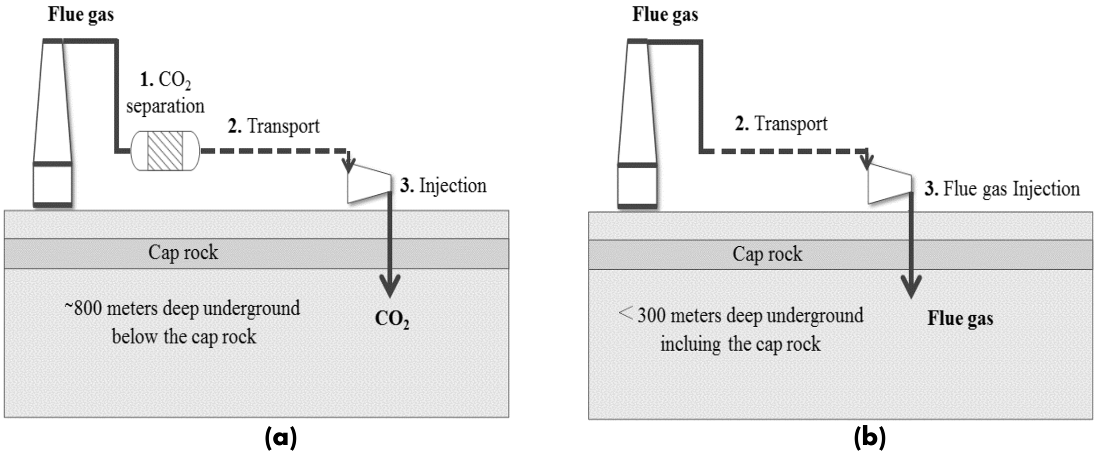


Figure 1. Configuration of carbon capture and storage process: (**a**) Conventional-CCS process; (**b**) Proposed e-CCS process

Nanostructured materials are a vast and active field of research in various areas, due to its characteristics can be adjusted according to their application, such as size, structure, molecular affinity, high surface area-volume ratio, high surface activity, dispersion capacity, optical and electronic properties, among others (Bailon-García 2018). At the reservoir level, different nanoparticles have been used to resolve several problems, mainly associated with recovery of oil and gas and modifying physicochemical properties of reservoirs (Franco et al. 2013). The nanoparticles have been used for the alteration of wettability of reservoirs, adsorption and catalysis of heavy crude compounds like asphaltenes, stabilization of fines in reservoirs, among others (Franco, Zabala, and Cortés 2017). The obtained results demonstrate its efficacy without obstructions to the porous media. In this way, nanospheres can be an option for the modification of the surface in shallow reservoirs for the e-CCS process. The nanoparticles have been evaluated for the conventional CCS process as a nanofluid used to improve CO_2 transport in saline aquifers [34]. Nevertheless, nanoparticles have been employed for modification of the rock for improving the storage capacity such as in the proposed e-CCS process.

Many carbon nanostructures are evaluated for CO_2 capture, within them are nanofibers, nanosheets and nanotubes (adsorption capacity between 0.26 to 4.15 mmol g^{-1} at atmospheric conditions) (Wang et al. 2014; Lithoxoos et al. 2010; Bikshapathi et al. 2011; Chowdhury and Balasubramanian 2016; Alonso et al. 2017); but it is not possible its application in reservoirs due to the structure and dimensions that could affect the naturally porous structure of reservoir. Whence, carbon nanospheres are the best option for e-CCS process. Chen et al. (Chen et al. 2016) reported hollow carbon nanospheres for CO_2 adsorption, where the capacity of adsorption is 3.65 mmol g^{-1} at atmospheric conditions (Chen et al. 2016), which is competitive compared with other carbon nanomaterials as fibers, nanosheets and nanotubes metal organic frameworks, zeolites, alkali metal carbonates, amoung others (Wang et al. 2014). For applications at high pressure, a high surface area is essential, but the CO_2 molecule has an acid character, whereby a high nitrogen content in adsorbent could enhance the adsorption capacity and selectivity. In literature (Wang et al. 2014; Bandosz et al. 2016) there are some methods to increase the nitrogen content like impregnation with amines, but this is an additional stage, increasing the cost of material. Also, the amines could obstruct the microporous structure of nanomaterial, decreasing the adsorption capacity. Therefore, it is desirable to incorporate the nitrogenous groups from the synthesis process of nanomaterial (Dong et al. 2008). Hence, the main objective of this manuscript is to experimentally study the possibility to enhance the CCS process by nanotechnology. For this, carbon nanospheres were synthesized and characterized. Then, sandstone as porous media was impregnated with the nanospheres using different mass ratios of nanoparticles. The adsorption process of CO_2 is evaluated at atmospheric and high-pressure conditions.

2. Materials and methods

Synthesis of nanomaterials. The synthesis process is adapted from Yong-Rong et al. [45], changing the lysine concentration, reaction time and the resorcinol/water molar ratio. A solution (S1) of resorcinol/formaldehyde in a 1:2 molar ratio, and deionized water is stirred at 25 °C for 1 hour. Parallel, a solution (S2) of L-lysine and deionized water is stirred at 60 °C for 1 hour. The molar ratio of resorcinol/L-lysine is 1:0.16. Subsequently, the solutions S1 and S2 are mixed at 60 °C for 1 hour to obtain the solution S3. After, the solution S3 is maintained at 25 °C for 20 hours to benefit the natural precipitation of the nanomaterial. Finally, the obtained polymer is dried at 120 °C for 12 hours and carbonized in N2 at 1 °C min-1 to 800 °C and 60 ml min-1 for 5 hours using a tubular furnace. The molar ratios of resorcinol/water were varied for decreasing the concentration of the reagents, which could allow the reduction of the particle size. The employed molar ratios of resorcinol/water were 1:2778 (without dilution), 1:5556 (dilution 1) and 1:11112 (dilution 2) for obtaining the CN.LYS1, CN.LYS2, and CN.LYS3 materials, respectively.

Impregnation of sandstone. Ottawa sandstone (SS) is impregnated with CN.LYS2 at mass fractions of 0.01, 0.1, 1, 5, 10 and 20 % using the impregnation method by immersion and soaking. Initially, a nanofluid composed of nanoparticles and deionized water is sonicated at 40

°C for 4 hours. Subsequently, the sandstone is introduced in the nanofluid at 60 °C at two different conditions: 1) 6 hours and 600 rpm, and 2) 24 hours without stirring. The last method simulates the reservoir conditions at which the porous medium could be impregnated. Finally, the impregnated material is dried at 110 °C for 12 hours. The same procedure is followed for impregnating the sandstone from a real reservoir (RS) at a mass fraction of 20 % of nanoparticles and 24 hours of soaking.

Characterization of materials. The size and structure of nanomaterials was evaluated by transmission electron microscopy-TEM. All materials are characterized by N_2 and CO_2 adsorption at -196 and 0 °C respectively, using a surface characterization analyzer-3-Flex (from Micromeritics-Particulate-Systems). The total adsorption volume ($V_{0.95}$) is the physisorbed volume of N_2 at P/P_0 = 0.95. Brunauer-Emmett-Teller-BET model obtains the surface area (S_{BET}). Micropore volume (V_{mic}), average pore size (L_0) and CO_2 adsorption energy (Eads-CO_2) by Dubinin-Radushkevich model. The mesopore volume (V_{meso}) is obtained by Gurvich and Barrett-Joyner-Halenda-BJH models. The chemical characterization is analyzed by ultimate analysis-CHON.

Adsorption of CO_2. The CN.LYS2, sandstone and impregnated sandstone (at mass fractions of 10 and 20 %) are evaluated by automatic adsorption equipment-HPVA II-200 (from Micromeritics-Particulate-Systems) at 0 °C, 25 °C and 50 °C and different pressures from $3x10^{-3}$ MPa to 3.0 MPa.

3. Results

The results are divided into two main sections: a) Characterization of materials (nanoparticles and sandstone), b) Study of the interaction between CO_2/nanoparticles/sandstone by adsorption isotherms at different operation conditions (T, P).

Characterization of material. The Figure 2-a is CN.LYS1, Figure 2-b is CN.LYS2 and Figure 2-c is CN.LYS3. CN.LYS2 present smaller particles (< 50 nm) after first dilution. These particles are more transparent than are those of the CN.LYS1 and CN.LYS3 materials, due to the more mesoporous texture of the CN.LYS2 material. It can be seen that a gel was formed around the spheres CN.LYS3. The L-lysine acts as a catalyst in the reaction, and therefore if its amount is limited for the third dilution process, it might be the reason for the formation of a gel coating the spheres instead of producing more nanospheres, which obstructs the porous structure of CN.LYS3. These results can be compared with Table 1.

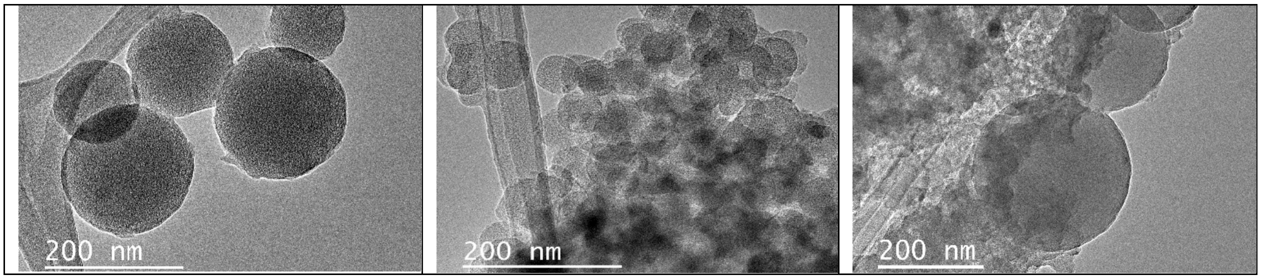


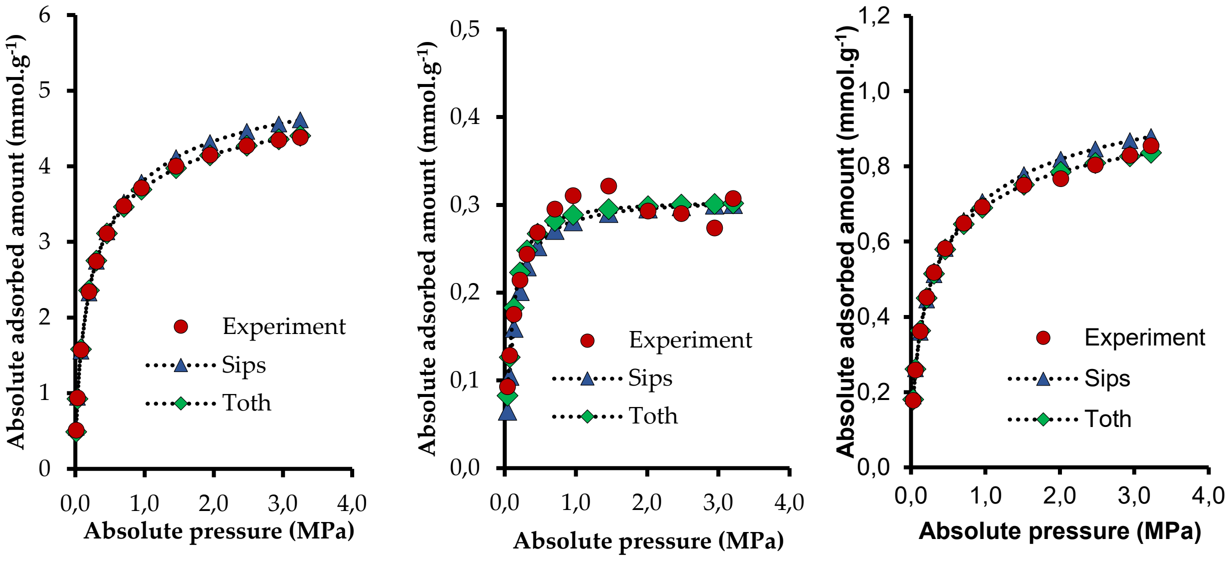
Figure 2. TEM images of carbon nanospheres synthesized with L-lysine. (**a**) Gel.LYS1, (**b**) CN.LYS1, (**c**) Gel.LYS2, (**d**) CN.LYS2, (**e**) Gel.LYS3 and (**f**) CN.LYS3

The CN.LYS1 structure is moderately mesoporous (28.6 %). After the first dilution the CN.LYS2 structure is a little more mesoporous (36.6 %) but after the third dilution CN.LYS3 has a predominantly microporous structure. The adsorption capacity obtained (3.48 mmol g^{-1}) is in the range reported in the literature but this synthesis process is most easy than other reported (Wang et al. 2014; Alonso et al. 2017; Cavenati, Grande, and Rodrigues 2004). The sandstone presents an S_{BET} of 0.438 m^2 g^{-1}, a $V_{0.95}$ of 0.0001 cm^3 g^{-1} and its CO_2 adsorption capacity is not detectable, less than 0.0013 mmol g^{-1} at 0 °C and atmospheric pressure. The sandstone impregnated with a mass fraction of 0.1 and 0.01 % does not have a significant increase in its surface properties. The nitrogen content is 2% after carbonization for all samples.

Table 1. Parameters obtained from adsorption isotherms (N_2 at -196°C and CO_2 at 0°C) for nanomaterials synthesized with melamine (CN.MEL) and L-lysine (CN.LYS)

	S_{BET} (m^2 g^{-1})	$V_{0.95}$ (cm^3 g^{-1})	V_{mic-N2} (cm^3 g^{-1})	$V_{mic-CO2}$ (cm^3 g^{-1})	V_{mes} (cm^3 g^{-1})	L_0 (nm)
CN.LYS1	385	0.22	0.16 (72.7 %)	0.18	0.06	0.84
CN.LYS2	612	0.36	0.23 (63.9 %)	0.25	0.13	0.56
CN.LYS3	320	0.13	0.12 (92.3 %)	-	0.01	0.62
SS-1	2	0.003	0.002	0.002	0.001	0.56
SS-5	20	0.016	0.01	0.012	0.006	0.53
SS-10	49	0.035	0.021	0.023	0.014	0.51
SS-20	99	0.067	0.042	0.044	0.025	0.52

Adsorption of CO_2. To observe the pressure effect on the adsorption capacity of CN.LYS2, the N_{ads} at atmospheric pressure and 0°C (3.48 mmol g^{-1}) was compared to N_{ads} at 3 MPa and 0°C (5.80 mmol g^{-1}). The increase of pressure produced an increase of N_{ads} of 66.6 %, indicating physisorption as the main adsorption mechanism. At 50°C, as expected, the adsorption capacity decreased by 20 % due to the exothermic character of adsorption. The obtained adsorption capacity is competitive compared to other results reported for nanomaterials under similar conditions. The effect of pressure on the impregnated sandstone was also observed by comparing N_{ads} at atmospheric pressure and 0°C (0.34 mmol g^{-1} for SS-10 and 0.63 mmol g^{-1} for SS-20) to N_{ads} at 3 MPa and 0°C (0.47 mmol g^{-1} for SS-10 and 1.04 mmol g^{-1} for SS-20). The corresponding increases were 38.2 % (SS-10) and 66.0 % (SS-20), respectively. The maximum N_{ads} under reservoir conditions was 0.85 mmol g^{-1} at a mass fraction of 20 % of CN.LYS2 (Figure 3).



(a) (b) (c)

Figure 3. Adsorption isotherms of CO_2 at 50 °C and high pressure (3×10^{-3} up to 3.0 MPa) for: (**a**) CN.LYS2, (**b**) Sandstone impregnated with a mass fraction of 10 % and (**c**) Sandstone impregnated with a mass fraction of 20 %

4. Conclusions

This is the first research proposing a possible new configuration of the CCS process in which the storage is performed in shallow reservoirs (less than 300 m), where the adsorption phenomena control capture and storage.

N-rich carbon nanospheres allowed increasing the adsorption capacity by 67 700 % with a mass fraction of only 20 % under realistic reservoir conditions (50°C and 3 MPa). This has been possible thanks to the higher surface area and to the favorable chemical composition, which promoted the capture and storage of CO_2. Therefore, this research opens an interesting line of research that would expand knowledge in the field of carbon nanospheres for application in the adsorption and geological storage of CO_2.

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