Journal of Environmental Chemical Engineering 6 (2018) 4573–4587

Contents lists available at ScienceDirect

Journal of Environmental Chemical Engineering

journal homepage: www.elsevier.com/locate/jece

Evaluation of two fibrous clay minerals (sepiolite and palygorskite) for CO_2 Capture

J.A. Cecilia[a], E. Vilarrasa-García[b], C.L. Cavalcante Jr.[b], D.C.S. Azevedo[b], F. Franco[a], E. Rodríguez-Castellón[a,*]

[a] *Universidad de Málaga, Departamento de Química Inorgánica, Cristalografía y Mineralogía, Facultad de Ciencias, 29071 Málaga, Spain*
[b] *Universidade Federal do Ceará, Departamento de Engenharia Química, GPSA-Grupo de Pesquisa em Separaçoes por Adsorçao, Campus do Pici, 60455-760 Fortaleza, Brazil*

ARTICLE INFO

Keywords:
Sepiolite
Palygorskite
CO_2 adsorption
Microwave treatment

ABSTRACT

Two fibrous clay minerals (sepiolite and palygorskite) have been employed as adsorbents to assess their adsorption capacity of pure CO_2 in a volumetric setup. The raw sepiolite reached a CO_2 uptake of 1.48 mmol g^{-1} due to the presence of nanocavities acting as a molecular sieve. Both sepiolite and palygorskite were modified by microwave-assisted acid treatment, which led to an increase in specific surface area and pore volume due to Mg^{2+} leaching, particularly in the case of sepiolite. However, the partial digestion of these fibrous structures does not improve CO_2 adsorption uptake due to the progressive increase of the size of nanocavities. In a next step, both fibrous clay minerals were functionalized with amine species by different procedures (grafting with (3-Aminopropyl) triethoxysilane (APTES), impregnation with polyethyleneimine (PEI) and double functionalization by grafting with APTES and then impregnation with PEI. In all cases, it can be observed that the incorporation of amine species favors the chemical interaction between the amines species and the CO_2 molecules, although it also produces obstruction of the nanochannels so the adsorption takes place mainly on the outer surface of the fibers. Finally, the incorporation of amine species by double functionalization led to the highest CO_2 adsorbed concentration of 2.07 mmol g^{-1} at 760 mm Hg and 65 °C due to a larger proportion of available amines sites as well as the use of higher adsorption temperature, which favored the diffusion of CO_2 molecules within the adsorbent.

1. Introduction

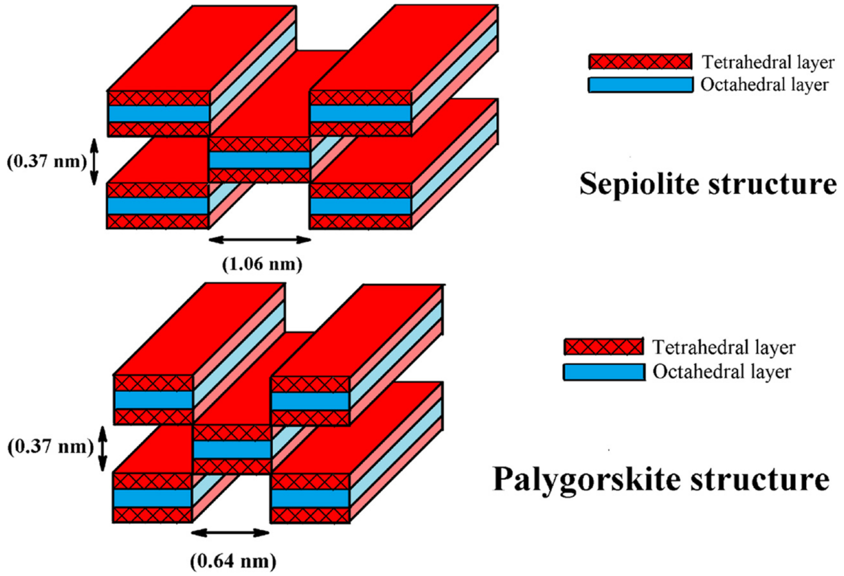
In recent years, the consequences of global warming by the greenhouse effect have become more evident. The Intergovernmental Panel on Climate Change (IPCC) has predicted that the average temperature of the Earth will have increased 4 °C in the year 2100 as a consequence of the emission of anthropogenic CO_2, which is mainly attributed to the combustion of the fossil fuels [1]. This inflicts harsh consequences on the planet. Among others, the acidification of the oceans seriously affects marine organisms by the reducing the concentration of carbonate ions, which causes the dissolution of shells of macro invertebrates and coral-reef [2]. Global warming also gives rise to more unstable rain regimes, torrential in many cases, followed by long periods of drought. This causes a great impact on agriculture and ranching and serious problems with availability of potable water, leading to the consumption from aquifers with poor quality, which has become a significant source of diseases. In addition, the higher frequency of extreme weather events can also have an important impact on the migrations, particularly when less developed countries are affected [3].

Taking into account the consequences of global warming, stringent environmental regulations have been put forward to limit the emissions of anthropogenic CO_2. The proposed strategy relies on the premise that reducing the current energy demand by increasing energy efficiency and productivity and promoting the transition to a low-carbon sustainable economy is the best way to avoid CO_2 emissions and boost economic growth. Even though more sustainable processes with net zero-carbon balance are under development, such as fuel cells or batteries, CO_2 release is still unavoidable due to steam reforming (hydrogen production) or combustion (power generation) of carbon, natural gas, or biomass [4]. Considering these premises, CO_2 capture and storage (CCS) is the most realistic strategy to minimize CO_2 emissions at short- and mid terms, especially from stationary sources. Previous research has reported that the most costly step in the CCS process is attributed to CO_2 capture, which account for 50–90% of the total cost

---

[*] Corresponding author.
E-mail address: castellon@uma.es (E. Rodríguez-Castellón).

https://doi.org/10.1016/j.jece.2018.07.001
Received 28 April 2018; Received in revised form 19 June 2018; Accepted 1 July 2018



Scheme 1. Elemental structures of sepiolite and palygorskite.

[4–6]. Therefore, a great deal of effort is focused on the development of efficient technologies for CO_2 capture. In the last decades, several technologies have been proposed for this goal. Among them, membrane selective permeation, cryogenic distillation, absorption in liquid amines and adsorption onto porous materials have been proposed [4,7], although each of these technologies has some intrinsic limitations. Membrane selective permeation has been used in gas separation with interesting results for highly concentrated CO_2 streams, but the efficiency of this process decreases for low CO_2 concentrations. Cryogenic distillation is also an effective technology to separate components by compression, cooling and expansion steps; however, it requires high energy consumption, so it tends not to be feasible on a small scale. The most mature technology used in CO_2 capture is absorption in liquid amines or chilled ammonia. The process itself is relatively inexpensive in comparison to other technologies and it displays high yields of CO_2 capture [8]. On the other hand, it has a number of drawbacks related to the volatility of the amines, which causes the equipment corrosion and the progressive loss of capture efficiency. In addition, amine regeneration requires high temperature, which increases the cost of the process [9].

The use of solid adsorbents has shown to be an alternative in CO_2 capture. Several solids with basic properties, such as CaO [10,11], MgO [12,13] or mixed oxides coming from hydrotalcites [14,15] have been highly used due to their low-cost, high availability and high capacity to capture CO_2. However, the interaction between these oxides and CO_2 molecules is very strong so that high temperatures are required to regenerate them and subsequently there is a high energy penalty involved. Other solids act as sieves to retain CO_2. With this respect, the literature brings an increasing number of reports of metal organic frameworks (MOFs), formed by organic-inorganic structures with high specific surface area and high microporosity, which may provide high capacity and selectivity to adsorb CO_2 [16,17]. Recently, new hybrid materials such as graphene-organic frameworks (GOFs) [18] or gyroid mesoporous materials [19] have shown high potential to retain CO_2.

The design and synthesis of porous silica has evolved a lot over the last 25 years since Mobil scientific discovered a family with regular array of uniform mesopores, denoted as M41S [20]. Thus, porous silica with different textural parameters, such as SBA-15 [21–25], MCM-41 [26,27], MCM-48 [28], HMS [29,30], KIT-6 [31] or mesocellular silica foams [23,25,32,33] have been investigated for CO_2 adsorption processes. The possibility of tailoring pore size, as in the case of zeolites [34–36] or activated carbons [37,38], renders these materials suitable properties as sieves to retain CO_2.

As mentioned previously, the most expensive step of the CCS process is the CO_2 capture. Most of the solids reported in the literature have a high potential in adsorption processes; however their large-scale synthesis would prohibitively raise the cost of CCS. In order to cheapen the costs, low-cost adsorbents with high availability and reduced energy demand for their regeneration have been developed for CO_2 capture. With this respect, natural zeolites have been pointed out as alternative adsorbents in the purification and separation of gases [39]. Clay minerals are another abundant component on the terrestrial surface with a wide range of applications in the field of adsorption and catalysis [40]. Several authors have investigated clay minerals as CO_2 adsorbents by using, for example, kaolinite [41], montmorillonite [42,43] or sepiolite [45,46] as starting materials.

The aim of this work is to evaluate CO_2 adsorption capacity of fibrous clay minerals sepiolite and palygorskite. Both minerals are relatively abundant on the surface of the Earth, which can potentially reduce the cost of the CCS process. Both fibrous clay minerals contain ribbons with 2:1 type layer structure, where each ribbon is linked to the next inverted SiO_4 tetrahedral sheet by Si-O bonds. Thus, tetrahedral apices point in opposite direction in adjacent ribbons. The width of the apical oxygen atom strip consists of a tetrahedral ring in palygorskites and 1.5 ring in sepiolites. The ideal chemical composition of sepiolite is $Si_{12}O_{30}Mg_8(OH)_4(H_2O)_8$ where the trioctahedral positions are occupied by Mg^{2+} and small proportions of Al^{3+} and Fe^{3+}. However, the ideal chemical composition of palygorskite is $Si_8O_{20}(Al_2Mg_2)(OH)_2(OH)_4(H_2O)_4$, which has a dioctahedral character, where the octahedral positions are occupied by Mg^{2+} and Al^{3+} generating voids in the octahedral sheets [47,48].

These inversions of the tetrahedral position lead to the formation of channels with dimensions of 0.37 nm × 1.06 nm in the case of sepiolite and 0.37 nm × 0.64 nm for palygorskite, where the charge deficiency is counterbalanced by the presence of protons and small number of exchangeable cations and zeolitic water [47,49] (Scheme 1). The formation of these microcavities may be an interesting feature of these materials for the adsorption of small gas molecules such as CO_2. On the other hand, the physicochemical properties of these materials have been modified by microwave-assisted acid treatment to increase their surface specific area and pore volume according to the methodology proposed by Franco et al. in previous research [50]. The microwave activation is an interesting method to modify the magnesian clay minerals since it requires shorter activation times than traditional acid