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Research paper

Production and characterization of activated carbon from barley straw by physical activation with carbon dioxide and steam

Javier Pallarés*, Ana González-Cencerrado, Inmaculada Arauzo

Universidad de Zaragoza- IUI mixto CIRCE, Campus Río Ebro, Mariano Esquillor Gómez, 15, 50018 Zaragoza, Spain

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ABSTRACT

In recent years, the growth of environmental protection policies has generated an increase in the global demand for activated carbon, the most widely used adsorbent in many industrial sectors, and with good prospects of implementation in others such as energy storage (electrodes in supercapacitors) and agriculture (fertilizer production). This demand is driving by the search for renewable, abundant and low-cost precursor materials, as an alternative to traditional fossil sources. This study investigates the production of activated carbon from barley straw using physical activation method with two different activating agents, carbon dioxide and steam. Experimental tests under different conditions at each stage of the process, carbonization and activation, have been conducted in order to maximize the BET surface area and microporosity of the final product. During the carbonization stage, temperature and heating rate have been found to be the most relevant factors, while activation temperature and hold time played this role during activation. Optimal conditions for the activation stage were obtained at 800 °C and a hold time of 1 h in the case of activation with carbon dioxide and at 700 °C and a hold time of 1 h in the case of activation with steam. The maximum BET surface area and micropore volume achieved by carbon dioxide activation were of 789 m^2/g and 0.3268 cm^3/g while for steam activation were 552 m^2/g and 0.2304 cm^3/g, which represent respectively an increase of more than 43% and 42% for the case of activation with carbon dioxide.

1. Introduction

Adsorption in solids is one of the best available techniques for the purification of water and the control of atmospheric and aquatic pollution, with activated carbon being the most widely used adsorbent in industry. In the last decade, global consumption of activated carbon has grown by an average annual increase of 5.5% and it is forecasted to continue to do so at an even higher rate in the coming years (8.1% in 2018 [1]).

The increase in the demand for activated carbon has been associated with its traditional uses in the treatment and purification of water and polluting gases, especially in the most industrialized regions of the world, where more restrictive environmental regulations have been imposed. In Asian countries, led by China and India, this demand growth has been even greater due to the rapid industrial development and high population growth, the implementation and improvement of drinking water treatment systems, the increase in ownership rates of motor vehicles, the intensification of agriculture and the increase of environmental regulations to manufacturing industries.

On the other hand, activated carbon demand has also increased as a result of new applications, amongst which stands out the interest aroused in the use of these adsorbents in mitigation of mercury emissions from coal thermal power plants. Another application of activated carbon attracting interest today is its use as an adsorbent in post-combustion systems for the reduction and capture of CO_2 emissions [2,3]. Moreover, the use of activated carbon electrodes in supercapacitors taking advantage of its microporous structure to reduce the electrode's electrical resistance and improve energy storage performance is growing, promoted by the great interest in developing a new generation of batteries that definitely boost the electric car [3,4]. Finally, there are numerous studies that demonstrate the positive effect that the activated carbon has on the fertility of agricultural soils, with the consequent increase in crop yields [5]. Its use as an amendment can achieve important benefits on the reduction of N_2O, NH_3 and nitrogen leachates [6,7].

Activated carbon is an adsorbent obtained from carbonaceous materials with a disorganized crystallographic structure, constituted by randomly distributed microcrystals. This microcrystalline structure is built from elementary structures such as graphene sheets and fullerene or quasi-graphitic fragments. However, this microcrystalline

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* Corresponding author.
E-mail address: jpallare@unizar.es (J. Pallarés).

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arrangement does not extend on a macroscopic scale resulting in a disordered and highly nanoporous structure. Consequently, these materials present a high specific surface area (500–1500 m^2/g), a wide variety of functional groups (carboxylates, carbonyls, hydroxyls, amines) and a pore size distribution ($< 1–100$ nm). All these characteristics give them an extraordinary capacity to adsorb a great diversity of molecules [8].

The characteristics of activated carbon as an adsorbent, both in capacity and in selectivity towards the species to be adsorbed, depend on the degree of disorganization of the microcrystalline structure, which is conditioned by both the nature of the precursor material and the process to which it has been subjected for transformation into activated carbon. This is because the resulting porosity can vary both in shape and in dimensions, with pores ranging from less than 1 nm to more than 1000 nm. The final application of a determined activated carbon will depend mainly on its porosity and on the chemical properties of its surface.

There are basically two processes for the production of activated carbons: physical activation and chemical activation. The most common activated carbon production process is physical activation. This process takes place in two stages. During the first stage, called carbonization, the precursor material is pyrolyzed, in an inert atmosphere at a medium-high temperature (300–800 °C). During this process, the breaking of the less stable bonds releases the volatile fraction of the precursor material, which is formed by permanent gases and tars, and a carbonaceous residue enriched in carbon aromatic rings is obtained, the so-called char, which has a rudimentary porous structure. This initial porosity has a low adsorption capacity, since part of the products released during the decomposition, mostly tars, re-polymerize and condense on the surface of the particle, filling or blocking the pores. That is why a subsequent activation stage is required, through which these tar deposits will be eliminated, thus enlarging the existing porosity and increasing the adsorption capacity.

During the second stage, char is activated at a higher temperature (700–1000 °C) in the presence of an activating agent. Throughout this process, the carbonaceous matrix of the fuel, exposed to a reducing atmosphere, undergoes several heterogeneous reforming reactions leading to a partial gasification of the char, developing a large porous structure and increasing its specific surface area. During the initial stage of the activation process, the following processes take place: elimination of the tar deposits, opening of rudimentary pores formed during pyrolysis and development of new pores. After a long activation period, pore-widening becomes the dominant effect while pore deepening and new pore formation are severely reduced. Consequently, more meso and macropores are evolved and BET surface area and pore volume decrease with increasing activation time [9].

Carbon dioxide and steam are the most widespread activating agents because the endothermic nature of their reactions facilitates process control. Generally, the use of carbon dioxide is preferred due to its lower reactivity at high temperature, which makes the activation process easier to control. In addition, from the initial stages of activation, carbon dioxide activation favors microporosity formation, whereas steam activation favors microporosity widening, and thus activated carbons prepared with steam exhibit a lower micropore volume at the expense of larger meso and macropore volumes [10]. In any case, the most determinant factors in the development of the microporous structure are the gasifying agent's partial pressure and the conditions of the activation process, and thus, both CO_2 and steam can be suitable gasifying agents depending on the choice of precursor material and process conditions [11–13].

Activated carbon can also be produced by a chemical activation process. In this case the precursor is impregnated with activating chemical agents such as KOH, H_3PO_4 or $ZnCl_2$. Subsequently, the precursor is subjected to a carbonization process at moderate temperatures (550 °C) and, finally, the resulting activated carbon is washed to remove activator traces which might remain in the material and to recover the chemical agent for successive generation cycles of activated carbon. However, at an industrial scale, physical activation is preferred because it allows for the optimization of the pyrolysis stage by enabling a greater control over microporosity development and eliminates the requirement for chemicals, reducing both the process' costs and associated pollution.

The production of activated carbon has traditionally been obtained from wood, coal, petroleum residues, lignite and polymers, all of which are very expensive and, with the exception of wood, non-renewable. Consequently, in the search for renewable and cost-competitive alternatives, scientific interest in the production of activated carbon from byproducts and biomass residues (so-called activated biochar) has grown in recent years [14–16]. The main advantage of activated carbon derived from alternative sources, compared to traditional activated carbon, lies in its high availability and low cost. In addition, tests performed with these alternative activated carbon materials in various applications (e.g. water purification, elimination of polluting gases, mercury removal or control-release fertilizers) have presented at least an equivalent behavior, than commercial activated carbon or other much more expensive alternatives, such as carbon nanotubes and graphene [3].

On the experimental field, since 2000, numerous studies have been conducted using a diverse range of precursor materials of residual biomass origin (corn, rapeseed, barley, almond shells, walnut, pistachio, peanut, acorn, rice, palm, olive pomace, cherry bones, date bones, bamboo, cotton stalks, miscanthus, sicyos, …), being currently a field of study in growing expansion. With regards to the physical activation process, most published studies focus on the preparation of activated carbons from residual biomass sources, optimizing the conditions of the activation process with carbon dioxide or steam and the subsequent physical and chemical characterization [11–13,17–26]. Other studies, in a much smaller number, have analyzed the influence of the carbonization process conditions in the subsequent activation stage [27–30]. Finally, for specific applications such as the adsorption of heavy metals, where it is important to increase the content of certain carboxyl, hydroxyl and amino functional groups that can be combined with the metals by ion exchange, complexation or electrostatic attraction, studies have focused on the maximization of these groups. In the case of adsorption of pollutants of organic origin, studies have aimed at increasing the hydrophobicity and polarity of activated biochar [3]. In general, all the studies have concluded that using as precursors material of biomass origin can either match or improve the properties of commercial activated carbon obtained from traditional sources.

Within this context, the specific objective of this study is to investigate the capacity of barley straw as a biomass precursor material for the production of activated carbon under different operating conditions and activating agents via the physical activation process. Barley, besides being one of the main products contributing to the world diet, and the crop with greater territorial base and distribution in Spain, presents adequate characteristics for the production of activated carbon. In the literature there are no published studies on obtaining activated carbon from barley straw by the physical route (Loredo-Cancino et al. published a study on chemical activation of barley husks in 2013 [31]), which adds a special interest since this study extends the knowledge in the search for new, viable and low cost precursors. To this purpose, using an externally heated quartz reactor, the effect of final temperature, heating rate, hold time and gas flow rate of both CO_2 and steam in the production of activated carbon from barley straw have been investigated. Samples of the resulting activated carbon have been physically and chemically characterized for analysis and discussion.

2. Materials and methodology

2.1. Preparation and characterization of the precursor material

In this study, barley straw has been used as a precursor material for