Fuel Processing Technology 126 (2014) 476–486

Contents lists available at ScienceDirect

Fuel Processing Technology

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

Preparation of activated carbons from cocoa shells and siriguela seeds using H_3PO_4 and $ZnCL_2$ as activating agents for BSA and α-lactalbumin adsorption

Rúbner Gonçalves Pereira [a,*], Cristiane Martins Veloso [b], Neura Mendes da Silva [b], Lucas Farias de Sousa [b], Renata Cristina Ferreira Bonomo [b], Alexilda Oliveira de Souza [b], Marluce Oliveira da Guarda Souza [c], Rafael da Costa Ilhéu Fontan [b]

[a] Faculty of Food Engineering, State University of Campinas, CEP 13035-388, Campinas, SP, Brazil
[b] State University of Southwest Bahia, CEP 45700-000, Itapetinga, BA, Brazil
[c] State University of Bahia, CEP 41195001, Salvador, BA, Brazil

ARTICLE INFO

Article history:
Received 21 January 2014
Received in revised form 2 June 2014
Accepted 2 June 2014
Available online 21 June 2014

Keywords:
Chemical activation
Theobroma cacao L.
Spondias purpurea L.
Whey
Mathematical models

ABSTRACT

The aim of this work was to prepare activated carbons from cocoa shells and siriguela seeds and to evaluate the whey protein adsorption on produced activated carbon. The residues were impregnated with $ZnCl_2$ and H_3PO_4. DTA/TG and FTIR were performed with this material. Carbonization was performed under nitrogen flow for 40 min at 500 °C and the obtained activated carbons were washed, dried and stored. The resulting carbons were characterized regarding their textural properties. Additionally, an adsorption study was performed, using BSA and α-lactalbumin. The activated carbons showed surface areas higher than 642 $m^2 \cdot g^{-1}$. Impregnation with H_3PO_4 was more effective in modifying the structure of the precursors and carbon textural properties and this action was favorable for the adsorption of the protein α-lactalbumin. Impregnation with $ZnCl_2$ resulted in activated carbons which were more effective in the adsorption of BSA. In both cases, use of the siriguela seed as a precursor in the production of activated carbon was favorable. The pseudo second-order model was fitted satisfactorily to the time equilibrium experimental data, for both proteins. The Toth model represents most efficiently α-lactalbumin adsorption experimental data and the Langmuir model was considered the most satisfactory for the adsorption of BSA.

1. Introduction

Activated carbon is a material well-known for its complex pore structure, high specific surface area, and good chemical stability and for presenting various oxygen-containing functional groups on its surface [1]. Consequently, they are widely used as adsorbents, catalysts or in separation processes [2–6]. Among these applications its use as an adsorbent is highlighted because it is one of the most used on an industrial scale, as well as silica gel, activated alumina and molecular sieves.

Because of its large distribution of pore size and shape, activated carbons can be classified as microporous, mesoporous or macroporous, or even present a mixed structure, micromesoporous. The presence of micropores is predominant in conventionally prepared activated carbons, implying the need for specific production treatments which favor the formation of larger pores accessible by larger molecules. Such molecules require not only high surface area, but also a greater volume of meso and macropores on the activated carbon structure, whereas the diameter of the micropores enables exclusive access of small adsorbates, as in the case of gas molecules. This fact indicates that each type of pore has a key function on adsorption properties [7,8].

The preparation methods influence the textural characteristics of the activated carbons. There are two major activation methods in obtaining of activated carbons: physical and chemical. In physical activation, the precursor is heat treated in an inert atmosphere and the activation of the solid residual product (char) is realized at high temperatures (900–1000 °C), in slightly reactive atmosphere, such as steam or carbon dioxide [9]. Chemical activation involves impregnating the precursor material with chemical agents such as potassium hydroxide (KOH), sodium hydroxide (NaOH), sodium carbonate (Na_2CO_3), magnesium chloride ($MgCl_2$), phosphoric acid (H_3PO_4) and zinc chloride ($ZnCl_2$) [3]. All are dehydrating agents and influence pyrolysis of the precursor, inhibiting the release of volatile organic matter by aromatization and higher carbon sequestration, retarding the burning of the material and increasing the final product yield [10,11]. Though, activation with phosphoric acid is a well-established method for the preparation of activated carbon and presents characteristics that lead to more desirable textural properties. Some important advantages of chemical activation in

* Corresponding author. Tel.: +55 19 35214055.
E-mail address: rubnergp@gmail.com (R.G. Pereira).

http://dx.doi.org/10.1016/j.fuproc.2014.06.001
0378-3820/

relation to physical activation are: lower treatment temperatures, shorter treatment time, activated carbons with large surface area and well developed microporosity [9].

Although the processing conditions of activated carbon may have some influence on the structure and properties of the final product, these are primarily determined by the nature of the precursor material. Other factors that also heavily depend on the precursor material are productivity and ease of activation [12]. Carbon precursors used in the production of activated carbons are organic materials rich in carbon [13]. Agricultural residues are considered very important inputs for the preparation of activated carbons because there are renewable and low-cost materials [14]. Residues from agricultural activities have been employed as precursors to obtain activated carbons in order to enhance understanding of porous morphology of activated carbon, which is directly related to the preparation method and origin of the precursor [1,13–15].

From a technological standpoint, whey proteins have attracted a growing interest for industries as a raw material in food products, due to their versatility and functional properties including emulsifying and foaming capacity, hydration capacity and water retention, solubility, gelation, viscosity increase and oil absorption [16,17]. Development of techniques for fractionation, modification and preservation of whey proteins may contribute to recovery of this valuable nutrient, as well as improving the expression of their functional properties [18]. Efficient isolation and purification of these proteins is essential for commercial success since recovery often represents a large portion of the product cost [19].

Adsorption is often utilized in biomolecule separation processes through various interactions between the adsorbent and adsorbate, including ionic, affinity and hydrophobic. Activated carbons and synthetic adsorbents have been used to remove biomolecule from the liquid phase [20–23]. However, little data is available concerning the isolation of whey proteins by adsorption on activated carbon.

A key element for adsorption modeling is the understanding of data which describes the adsorption equilibrium of components in the system, considering the compound of interest (proteins, for example) and the components in the stationary phase. Kinetic studies are important in order to determine the time required to reach equilibrium, development of models based on adsorption rate, and use viability of the material as an adsorbent [24]. Moreover, in the equilibrium study the adsorption isotherms represent the solid–liquid equilibrium of a solute adsorbed in a given mass of the stationary phase in contact with a solution containing the solute [25].

Although the isotherm model most used to represent the solid–liquid equilibrium is the Langmuir model [25], other models can be effective and sometimes even better to describe these data. Models Toth, Freundlich and Jovanovic, are also used to explain the phenomenon [26].

Therefore, the objective of this study was to produce activated carbons from two agricultural residues (cocoa shells and siriguela seeds) using the chemical activation agents: zinc chloride and phosphoric acid. It was intended to investigate the mass losses during carbonization; the yield of activated carbon production; and the influence of the precursor material and methods of activation in the characteristics of materials impregnated with activating agents (before carbonization) and in the textural properties of activated carbons. In addition, were realized BSA and α-lactalbumin adsorption tests and were adjusted some non-linear models.

2. Material and methods

2.1. Preparation of the precursor material

The experiment was conducted at the Laboratory of Process Engineering, Campus of Itapetinga-BA of the State University of Southwest Bahia — UESB, where the raw materials (cocoa shell and siriguela seed) were titrated in a food processor, dried at 110 °C for 24 h in an oven (Tecnal TE 393/1), ground in a knife mill to obtain particles with sizes from 0.5 mm–1.70 mm and finally sieved through a 40 mesh sieve.

Moisture and ash contents were determined for the dried and sieved material in accordance with standards of the AOAC [27]. The lignin content was determined using sulfuric acid 72%[28]. Hemicellulose contents were calculated by the difference between NDF and ADF contents, and the cellulose content by the difference between FDA and lignin content [28]. The residue yield (R_r) was calculated as the percent mass ratio between the precursor material of the selected particle size (m_p) and the initial mass of fresh raw material (m_i) (Table 2 — eqn 01).

2.2. Preparation of the activated carbons

For production and activation of activated carbons, two methodologies were employed with modification of the agent activation. Yield of the activated carbon synthesis process from the two agricultural residues was calculated using eqn 02.

2.2.1. Chemical activation with zinc chloride — $ZnCl_2$

The residue was impregnated with zinc chloride (Merck, 98%) (1 g agent: 2 g of precursor) under manual agitation for 30 min, followed by drying at 110 °C for 24 h. Carbonization of the material was performed in a muffle furnace (Vulcan 3–550) with nitrogen flow for 40 min at 500 °C with a heating rate of 5 °C min^{-1}. The activated carbon obtained was immersed in a hydrochloric acid solution (Qhemis, 37%) for 20 min and washed with distilled water until reaching a neutral pH. This was followed by drying the material in an oven at 80 °C for 8 h, and storing it in hermetically sealed packages.

2.2.2. Chemical activation with phosphoric acid — H_3PO_4

The residue was impregnated with phosphoric acid (F. Maia, 85%) (1 g agent: 1 g of precursor) and heated to 80 °C under manual shaking for 30 min. It was then dried in an oven at 110 °C for 24 h. Carbonization of the material was performed in a muffle furnace (Vulcan 3–550) under nitrogen flow for 40 min at 500 °C with a heating rate of 5 °C min^{-1}. The activated carbon obtained was immersed in a hydrochloric acid solution (Qhemis, 37%) for 20 min and washed with distilled water until reaching a neutral pH. This was followed by drying the material in an oven at 80 °C for 8 h, and storing it in hermetically sealed packages. According to the processing stage, the materials used were coded as described in Table 1.

2.3. Characterization of the precursors and impregnated materials

The materials were characterized by the following techniques: differential thermal analysis and thermogravimetry to study the transformations occurring in the material during carbonization, and Fourier Transform infrared spectrophotometry to obtain information on the presence of functional groups.

Table 1
Codification of the samples obtained during synthesis of the activated carbons.

Code	Material
SBI	Siriguela seed biomass (*Spondias purpúrea* L.) in natura
TBI	Cocoa shell biomass (*Theobroma cacao* L.) in natura
SBP	Siriguela seed biomass (*Spondias purpúrea* L.) impregnated with H_3PO_4
TBP	Cocoa shell biomass (*Theobroma cacao* L.) impregnated with H_3PO_4
SBZ	Siriguela seed biomass (*Spondias purpúrea* L.) impregnated with $ZnCl_2$
TBZ	Cocoa shell biomass (*Theobroma cacao* L.) impregnated with $ZnCl_2$
SCP	Siriguela seed activated carbon (*Spondias purpúrea* L.) activated with H_3PO_4
TCP	Cocoa shell activated carbon (*Theobroma cacao* L.) activated with H_3PO_4
SCZ	Siriguela seed activated carbon (*Spondias purpúrea* L.) activated with $ZnCl_2$
TCZ	Cocoa shell activated carbon (*Theobroma cacao* L.) activated with $ZnCl_2$