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Optimization of preparation conditions of activated carbon from agriculture waste utilizing factorial design

Noemia Isoda, Raphael Rodrigues, Andreia Silva, Maraisa Gonçalves, Dalmo Mandelli, Flávia Camargo A. Figueiredo, Wagner Alves Carvalho *

Universidade Federal do ABC, Rua: Santa Adélia, 166, Bangu, Santo André, SP, Brazil

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ABSTRACT

In this work, activated carbon (AC) was prepared from rice husk by chemical activation. AC was prepared using factorial design as a statistical tool to facilitate the process and to reach results that would not be possible changing one variable at a time. AC characterizations were performed by N_2 adsorption/desorption and surface group titulation. Some AC was obtained with high surface area, up to 1593 $m^2 g^{-1}$, high mesopore volume, up to 1.22 $cm^3 g^{-1}$, and surface acids, up to 4.4 mmol g^{-1}. These characteristics are very important for AC application such as adsorption or acid catalysis. With this work, we were able to conclude that it is possible to prepare activated carbon from rice husk with high surface area, mesoporosity and surface acid groups, using factorial design as an efficient tool to plan the experiments.

1. Introduction

Brazil, for having an important agrarian economy, has an immense variety of agroindustrial wastes whose processing could be extremely advantageous with good economic and social interest. With the global population increase, the amount of wastes generated has also increased and consequently the environmental pollution. According to FAOSTAT (Food and Agriculture Organization of the United Nations Statistics), sugar cane, soybeans, maize, cassava, oranges, rice (paddy), bananas, wheat and seed cotton were the main crops produced in Brazil, in 2011, which generate more than 20 million tons of waste per year [1].

Rice husk (RH) is an interesting raw material owing to high rice consumption throughout the world. According to the statistical data of the Food and Agriculture Organization (FAO) of the United States, in recent years, more than 696 million tons of paddy grain (rice with husk) was produced in the world [2]. The RH represents about one-fifth of the annual production [3], thus, approximately 173 million tons of rice husk are produced each year worldwide. It is extremely important to develop technologies for the processing of these wastes into high-value added materials.

Biomass, from agriculture or forestry residues, can be used as a renewable source for bioenergy, when it is submitted to pyrolysis [4]. However, currently, an alternative use for this kind of waste is the production of materials with nobler application such as: bio-based composites [5], charcoal and activated carbon (AC) [6].

AC is an important material, mainly used as an adsorbent, catalyst and catalyst support. This importance can be attributed to its unique characteristics such as high "apparent" surface area, surface acid groups and micro and mesoporosity [7]. In the literature, several activated carbons (ACs) with high surface area and developed porosity from wastes are reported, including coffee residues [8], fruit seeds and shells [9–11], wood [12] and rice husks [13].

As described in the literature the conventional physical [7,14] and chemical [15,16] activation procedures, generally, provide materials with a well-developed porous structure [17,18], but most are restricted to the microporous range. There is some controversy with respect to the assignment of the conditions for mesoporosity development in AC. Several studies have reported that for mesoporosity development high temperature [19] or incorporation of inorganic species into the precursor with subsequent combination activation is necessary [20]. Nevertheless chemical agent, flow rate, precursor and the geometry of the experimental system used also are known to affect the porous texture of ACs [21–24].

The importance of mesopores for AC applications in adsorption and catalysis is even more controversial than the activation conditions for mesoporous AC preparation. However, a general trend has been established by several authors: the porous structural characteristic of AC greatly influences in the adsorption capacities for pollutants with bulky structures due to the presence of the size exclusion effect [25]. Thus, the environmental treatment process of a wide variety of

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* Corresponding author.
E-mail address: wagner.carvalho@ufabc.edu.br (W.A. Carvalho).

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substances, such as dyes or large organic molecules, requires a mesoporous AC.

Studies described in the literature by Al Bahri et al. present an AC from grape seeds obtained upon chemical activation with phosphoric acid, with high surface area (1139 m^2 g^{-1}) and developed mesopore volume (0.24 cm^3 g^{-1}). These authors evaluated diuron adsorption from water and then concluded that this AC was more suitable than other microporous activated carbons (ACs) [10]. In the Chen et al.'s review, some applications of mesoporous AC derived from rice husk were presented [26]. Levario et al. report that the influence of adsorption rate in ethanol and n-butanol, is enhanced by up to 1–2 orders of magnitude with the use of mesoporous carbons [27]. Galan et al. also obtained a higher and rapid adsorption process for several dyes using a mesoporous AC [28].

In order to prepare AC with high surface area and developed mesoporous volume, several tests are required with different variables, thus, in the process optimization (e.g., in a search of conditions for obtaining a material, such as AC, with better properties), applications of various combinatorial methods are very useful, such as factorial design (FD) [29–31].

Thus, to perform a general FD [29–31], an investigator selects a fixed number of ‘levels’ for each of a number of variables (factors) and then runs experiments with all possible combinations. If each variable occurs at only two levels we deal with the so-called factorial design at two levels measuring a response (for example the substrate conversion or/and selectivity). In the preparation of a material we can choose some of parameters as for example: temperature, pressure, concentration, etc. In the notation for the design matrix, 1 (or +) is used for the upper level of each factor and −1 (or −) for the corresponding lower level. In addition to the information about the effect of each variable on the response, the factorial design at two levels also provides the information about the so-called interaction (that is synergic or antagonistic) effects between 2 or more variables, that is impossible to obtain using the classical “one-factor-at-a-time” method [29]. It is clear, however, that if there are many variables, it is necessary to carry out a huge number of experiments, and the method becomes non-productive. For example, if there are 7 variables, it should be necessary to perform $2^7 = 128$ experiments. But, there are statistically smart ways to select experiments, building suitable fractions of the complete set, called fractional factorial design (FD). Application of FD [29] at two levels allows to reduce the number of experiments. For example, statistically choosing only $2^{7-3} = 16$ experiments from the complete set consisting of $2^7 = 128$ runs, the most important information can be obtained [30].

In the literature some authors have reported the use of FD for preparation and application of AC. Theydan and Ahmed used FD to prepare AC from date pits to remove phenol from aqueous solutions [32]. Fung et al. [33], described an FD application for AC preparation from tire waste, getting good results. These authors demonstrated that the yield, BET surface area and mesoporous volume of the AC are more sensitive to activation temperature and time. Rio et al. described a study for condition optimization for the preparation of a sorbent from sewage sludge using experimental design methodology [34]. Asenjo et al. described the use of FD to obtain the optimum conditions for the production of AC with controlled properties [35]. Annadurai et al. also studying Rhodamine 6G dye adsorption on AC used the FD to find factors that influence the adsorption process [36]. Recent publication shows that FD has been used as an important tool to optimize the use of AC for absorption process [37].

In this work we studied the preparation of AC from rice husk, using the FD statistical tool in order to carry out a lower number of experiments. The aim of this work was to obtain better activation conditions for AC preparation with high surface area, micro-mesoporosity and acid surface groups. As discussed in the literature, these properties are very important in the adsorption of a variety of compounds and in the catalysis of several organic molecules [38].

2. Methods

2.1. Preparation of AC

The inorganic components (SiO_2) were removed from the rice husk (RH) by washing with hydrofluoric acid (HF). For this, 30 g of RH were added in 14 mL of HF, for 12 h, at room temperature, followed by a washing for the removal of excess acid, drying at 100 °C.

To evaluate the influence of activating agent during the impregnation, impregnation in both materials, raw RH and carbonized RH, was also conducted. The RH (only washed) carbonization process was performed with a heating ramp of 5 °C min^{-1} from room temperature to 400 °C and kept at 400 °C for 4 h, under N_2 atmosphere (100 mL min^{-1}).

Impregnation of all material took place at 60 °C, for 6 h, with NaOH or $ZnCl_2$, at a rate of 1/3 and 2/3 (RH/activating agent) followed by drying for 24 h at 100 °C.

The activation treatment took place at two different temperatures 400 and 600 °C, and with two different activation times, 1 and 4 h, under N_2 atmosphere (100 mL min^{-1}). An intermediate level (dehydration) was carried out at 200 °C, for 1 h [16,39]. These variables that are used in the activated carbon preparation and their respective levels are presented in Table 1.

In this study, two levels (−) and (+) were used and all parameters were chosen based on the literature [15,16,40–42]. In order to obtain significant results all experiments took place in the same way and in a random sequence. In this work, fractional FD was studied with 2^{7-3} experiments. Table 1 presents all variables and parameters studied with levels (−) and (+).

2.2. Characterization

ACs were characterized by total acid groups using 25 mL of NaOH 0.1 mol L^{-1} and 0.7 g of activated carbon [42]. This mixture was stirred for 72 h, at room temperature, and then filtrated and titrated with HCl 0.1 M, in an automatic titrator (Metrohm 905 Titrando).

Table 1
Conditions, response and variables of experiments.

Exp.	β_1	β_2	β_3	β_4	β_5	β_6	β_7	Surface groups (mmol g^{-1})	S_{BET} (m^2 g^{-1})	V_{meso} (cm^3 g^{-1})
1	−1	−1	−1	−1	−1	−1	−1	0.00	0	0
2	1	−1	−1	−1	1	1	−1	1.09	1240	0.37
3	−1	1	−1	−1	1	1	1	1.88	130	0
4	1	1	−1	−1	−1	−1	1	1.25	920	0.08
5	−1	−1	1	−1	1	−1	1	0.00	500	0.06
6	1	−1	1	−1	−1	1	1	0.71	1300	1.12
7	−1	1	1	−1	−1	1	−1	1.76	840	0.02
8	1	1	1	−1	1	−1	−1	0.41	960	0.16
9	−1	−1	−1	1	−1	1	1	0.00	0	0
10	1	−1	−1	1	1	−1	1	2.29	1320	0.27
11	−1	1	−1	1	1	−1	−1	2.19	90	0
12	1	1	−1	1	−1	1	−1	0.98	770	0.09
13	−1	−1	1	1	1	1	−1	0.00	620	0.23
14	1	−1	1	1	−1	−1	−1	1.34	1090	1.22
15	−1	1	1	1	−1	−1	1	2.19	1590	0.10
16	1	1	1	1	1	1	1	0.98	950	0.05

Variables		Level	
		(−)/−1	(+)/1
β_1	Activating agent	NaOH	$ZnCl_2$
β_2	Carbonization	No	Yes
β_3	Activation temperature (°C)	400	600
β_4	Dehydration	No	Yes
β_5	RH/activating agent	1/3	2/30
β_6	Activation time (h)	1	4
β_7	Washing with HF	No	Yes