Superficial and structural behaviour of activated carbon, obtained from bamboo, as adsorbent of mercury ions

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Abstract

Activated carbon was preparing by means of design of experiments starting from three bamboo species. The results show wide area superficial values (280 – 1500 m^2/g), pH average of 9.91, yields from 20 to 85 % and high content of functional superficial oxide acid groups. Scanning electron microscopy analysis suggest the evolution of the porosity in the material as result of the activation time where is possible to observe the increase in the radii of the porous channels. Adsorption studies by Freundlich isotherm indicates the formation of single layer, the kinetic behavior is described by Fleming's empirical model and diffusion studies indicates the superficial diffusion as controlling stage.

Introduction

Due to activated carbon (AC) is a widely used material[1,2,3], starting materials to obtain it must have enough carbon content such as wood, tar, coconut shells, fruit's nuts, anthracite and more. AC production mainly involves the next stages: raw material preparation, carbonization and activation. Physical activation, usually includes carbonization and activation in combined processes. Activation was done starting 400 ºC in a partial gasification with an oxidant agent (water steam, air, CO_2 and oxygen) with the purpose of developing porosity and an expected area superficial. At this conditions steam water reacts creating CO and gas hydrogen, described by the next reaction[4]:

$$C_{(s)} + H_2O \longrightarrow CO_{(g)} + H_{2(g)}$$
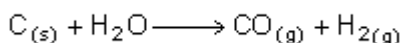
Depending of reaction conditions between raw material, activation atmosphere, temperature, oxidant agent and even raw material presentation, functional superficial oxygenated acid groups (FSOAG) are created on the AC surface. Bamboo in Mexico , has been designated mainly to the furniture elaboration and rural constructions nearby to the place where the bamboo species grow[5].

The purpose of this work is the use of bamboo species *Guadua Angustifolia, Bambusa Vulgaris Striata* and *Bambusa Oldhammi*, in the production of AC by means of physical activation and the use of statistical design of experiments (DOE) for activation, with the purpose of studying the effect of initial conditions on the AC production.

It is also the purpose of using these materials as adsorbents of Hg ions in water solution, describing the kinetics and diffusional aspects, by means of empiric models, in order to know the behaviour of the porous structure of AC, from the chemical and structural point of view and the nature of these processes by means of adsorption isotherms. Due to the amount of carbon available in the lignocellulosic bamboo structure, this natural resource represents a continuous source of raw material and it is an attractive material for AC production.

Experimental

DOE factorial 2^4 showed in table 1, was done in order to activate the selected carbons obtained in the previous stage. Four factors in a matrix arrange were analysed: carbon precursor (A), particle size (B), temperature (C) and activation time (D). Answer variables were the superficial area, measured as iodine number, and the SOAG content.

Table 1. DOE nomenclature for activation stage

		550 ºC		650 ºC	
		2 h	4h	2h	4h
C_{BV}	0.25 cm	CA11	CA12	CA13	CA14
	0.55 cm	CA21	CA22	CA23	CA24
C_{GA}	0.25 cm	CA31	CA23	CA33	CA34
	0.55 cm	CA41	CA42	CA43	CA44

Carbon sample with know weight, precursor carbon, particle size and indicated by DOE, was deposited in a quartz tube reactor heated by Thermolyne 21100 furnace (Di = 4.5 cm y L= 40 cm) in horizontal position. Steam water known flow was injected as activating agent and then the heating was increased in order to reach the temperature according to DOE. This temperature was kept, the time marked by DOE; and finishing this time, by natural convection the reactor was cooled to room temperature. The activated carbon obtained was washed, dried, and labeled according to DOE.

Properties of CA were measured; humidity (ASTM D 2867-99), pH (ASTM D 3838-80), density (ASTM D 2854-96), iodine number (ASTM D 4607-94), surface oxygen functional acid or basic groups by Boehm's method[6]. To analyse structural superficial features, X-ray diffraction pattern (XRPD) in the range $5 \leq 2\theta \leq 90$ has been taken on a Siemens D501 diffractometer (Cu $K\alpha_1$ radiation $\lambda = 0.15406$ nm). To analyse structural superficial features scanning electron microscopy (SEM) micrographs have been obtained with a JSM 6335 F electron microscope, operating at 10 kV and a working distance of 15 mm.

Adsorption capacity of mercury ions in water solution was made in static way under optimal conditions determined experimentally (AC dose of 0.6 g, initial concentration of Hg(II) of 10mg/L, pH of 9 and contact time of 16 h) and by means of ASTM 3500 Hg D.

Table 2 shows physical-chemical properties of the AC. Seven of them present area superficial, measured as iodine number, above commercial value (550 m^2/g AC). DOE analysis my means of Daniel's method[7] had shown that the second order interaction (carbon precursor and time) modified the growth of the porosity and area superficial, obtaining the best results with the carbon provided by *B. Vulgaris Striata* and activation time of 4 h.

The third order interaction (carbon precursor, temperature and time) is the responsible of the FSOAG (fig. 1) development on the AC surface, resulting in higher proportion (58.57%) carbonyl groups, these kind of oxides groups modified some properties of the AC, such as pH (average of 9.91) and surface polarity; responsible of the interchange of the surface oxygen by chemical compounds with polar affinity and lightly polar. The increase of these groups was reached with *B. Vulgaris Striata* carbon, 650 ºC and 2 h.

Table 2. Physic and chemical properties of the activated carbons

AC	Density g/mL	Humid %	pH	Yield %	Iodine number	SOAG meq/g
CA11	0.40	14.80	9.98	85.32	1500	1.03
CA12	0.35	11.00	9.87	84.14	364	1.04
CA13	0.32	31.32	9.91	74.49	502	1.25
CA14	0.33	50.96	9.95	67.39	421	0.93
CA21	0.35	9.81	9.82	85.04	590	1.01
CA22	0.33	7.71	9.81	82.34	1000	1.08
CA23	0.33	5.34	10.02	66.65	480	1.09
CA24	0.26	60.30	9.97	67.69	600	0.93
CA31	0.33	39.16	9.76	77.07	490	1.23
CA32	0.30	10.72	9.95	60.82	1340	0.86
CA33	0.29	48.71	9.97	54.26	440	0.92
CA34	0.23	67.02	9.85	20.98	1000	1.09
CA41	0.22	60.49	10.03	84.48	420	0.87
CA42	0.22	24.11	10.01	83.70	820	0.93
CA43	0.20	66.94	9.94	58.00	280	1.00
CA44	0.19	52.77	9.86	31.79	320	1.21
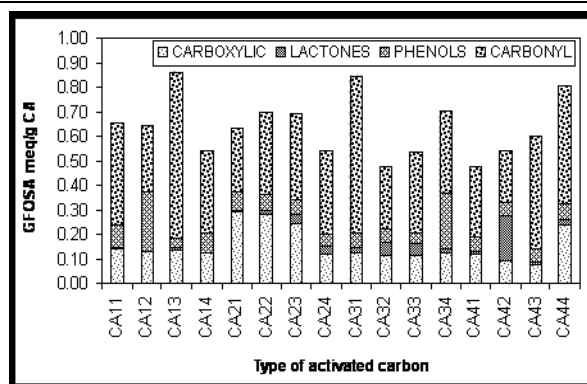
The appearance of a broad peak centered at the 2θ angle of 28º, obtained by means of X-ray powder diffraction (fig. 2a), suggest the presence of silica[8] as remnant material after the processes of carbonization and activation, this can be due to the lignocellulosic nature of the bamboo and the relative low temperatures of thermal treatment which ones doesn't permit the complete elimination of theses siliceous materials with high boiling point. The presence of the 002 and 101 (~ 24º and 43º respectively) of the graphite reflections show the amorphous nature of the AC containing a high disordered structure with carbon atoms randomly arranged.

The resulting structure of the AC has been acquire and studied by SEM. In figure 2b, it can be observed that, even after thermal treatment the micelle shape of the cellulose present in the bamboo remains and that it is possible to find it, this kind of structure, surrounded by layers of amorphous carbon and other small pieces of fragmented layers by the long time of exposition to the activation atmosphere. It is possible to assume that in this carbon layers the resulting porosity has been developed in a perpendicular direction to the water steam flow, breaking some of the micelles and producing holes trough the walls as it can be observed in the figure 2c. Some of these holes, are not completely created due to inorganic compounds that have not been removed in the carbonization-activation stages.

From the SEM images can be observed the area superficial created in the AC, as an arrange lightly ordered among the distribution of porous size (fig. 2d). The rise in the activation time, provides the growth of the micropores until creates mesopores and eventually "small macropores" developing this ones in the treatment of 4h. These macropores, will allow the easy access of the adsorbing species inward of the macropores channels where the micropores lie.
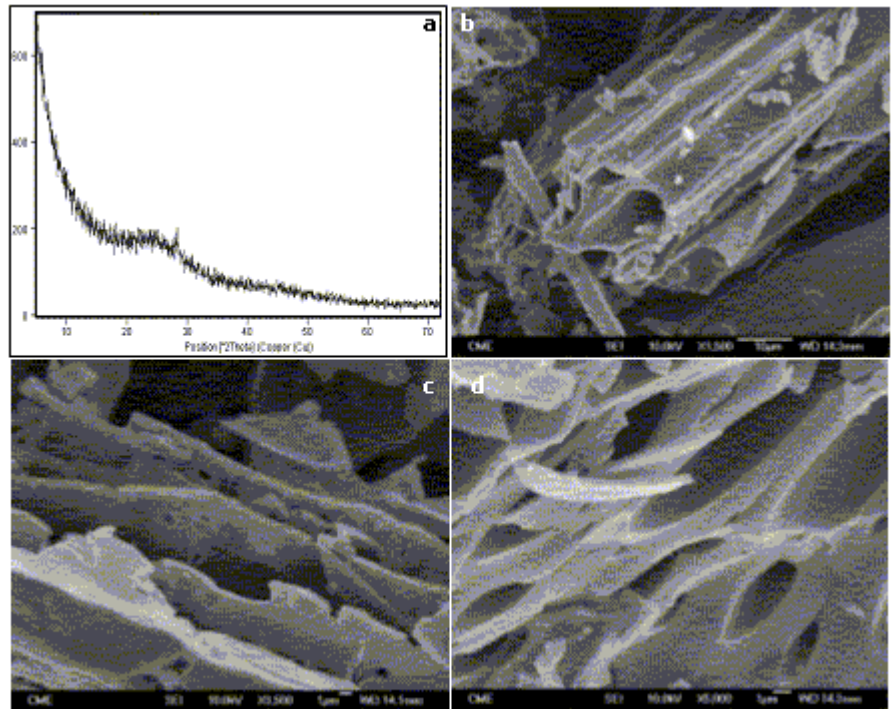

Figure 2. (a) X-ray powder diffraction analysis. SEM images showing: (b) micelle structure (c) pore structure on layered AC (d) pore size distribution.

Kinetic adsorption behaviour was adjusted to Fleming's empirical model (fig. 3a). The nature of this process follows the isotherm described by Freundlich. The shape of the isotherm (fig. 3b) shows that over the heterogeneous and amorphous surface of the material the ions do not compete by the available vacancies and suggest the formation of single layer adsorption where it can be observed the interaction between the mercury ions and the lightly polar surface of AC, the bonding energy of the ions with the FSOAG becomes in the controlling force making of this process a physical interaction between differential of electrical charges and so the diffusion process is not significant.
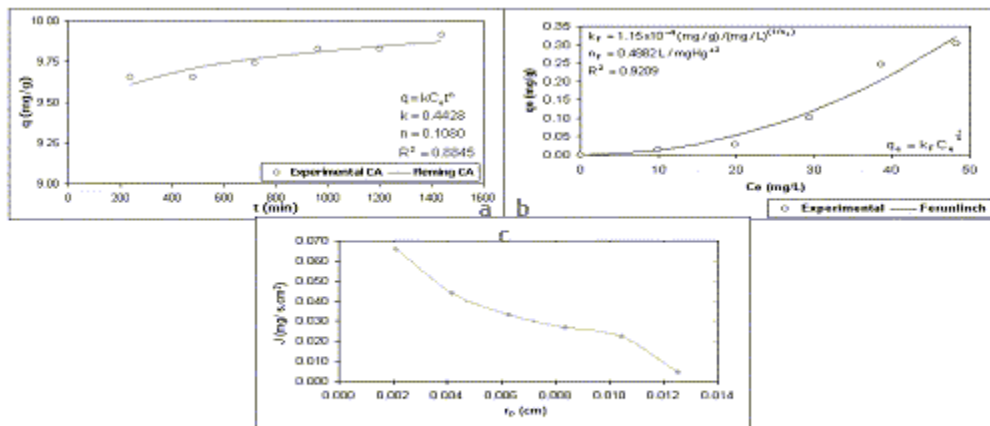

Figure 3. Experimental data adjusted to (a) empirical kinetic model (b) adsorption isotherm model (c) diffusional pore behaviour

The diffusion of the mercury ions inward of the microspores (fig. 3c) is limited by the radii of this ones, producing the filling of the internal channels. The access of the ions to the porous network can be attribute and controlled by the superficial diffusion. Due to the size and shape of the macropores network its permissible that in the free middle path of the ions the unique interaction with the AC had been physically by means of Van der Waals forces and this permit the desorption (by means of changes in the surface polarity) of the ions by chemical interchange giving the possibility of regenerate the AC and use it again in a continuous way even during five cycles more.

Conclusions

It was possible to produce AC by thermal treatment of the bamboo species *Bambusa Vulgaris Striata* and *Bambusa Oldhammi*, obtaining amorphous carbon with high area superficial and carbonyl groups content. The AC obtained shows by means of SEM the enlargement of the micropores into macropores due to the increase of the activation time, reason why the mercury process of adsorption-desorption was possible in an efficient way.

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