

PREPARATION OF ACTIVATED CARBON FROM PULP AND PAPER MILL WASTES TO BE TESTED FOR THE ADSORPTION OF VOCS

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Introduction

Activated carbons are high-grade carbonaceous products, having a porous structure and a large internal surface area. Such properties enable them to adsorb a wide variety of substances, i.e. they are able to capture molecules of gases and liquids in their internal surfaces. Therefore, they are used in industry in several applications including those for purification, chemical recovery and environmental remediation.

The development of methods to re-use waste materials is greatly desired and the production of activated carbons from wastes offers a promising future [1-3].

Commercial grades of activated carbons are manufactured mostly from bituminous coal, peat and lignite, and they are generally expensive. A number of industrial residues, which are lignocellulosic and carbonaceous in nature, are available in abundance and could be suitable for the production of activated carbons. The utilisation of industrial wastes as raw material to produce activated carbons could result in a reduction of cost.

Activated carbons represent a family of carbonaceous substances manufactured by processes which specifically develop adsorptive properties of carbon. They normally have high surface areas and high adsorption capacities. They are often the material of choice for many environmental applications, as waste-water treatment processes, and are gaining increasing popularity for adsorbing volatile organic compounds, from gases and liquid phases [4-6].

The demand for activated carbon applications particularly in waste-water and polluted groundwater treatment is growing strongly, due to the greater awareness of the limited supply of water on this planet. As the values derived from gas-phase studies, may not be a true indication of the adsorption capacity in liquid-phase experiments, adsorption tests in aqueous solution have been designed with the purpose to check the behaviour

of the activated carbons produced, [1-3]. The organic compound selected for this work, was benzene, because it is a low molecular weight pollutant of high priority and is a good model for real world applications [1, 5].

In this study, the work involved the reuse of wastes from the paper industry to prepare low cost activated carbons, with high specific surface area and hence high adsorption capacities. The method of activation adopted was the chemical activation process with KOH. Different activated carbons have been prepared from this residue examining the effect of two process variables, on the development of the pore structure: temperature of the activation process and mass of sample to be activated. The activated carbons produced were tested for their adsorption capacity with respect to VOCs. This was done by producing adsorption isotherms using different concentrations.

Experimental

The residue utilised was a sludge obtained from a Portuguese Pulp and Paper company. This residue has a high content in carbon and volatile matter, as can be observed from Table 1, in which its proximate and ultimate analyse are presented.

Table 1: The proximate and ultimate analyses of the sludge from the paper and pulp industry (d.b., %Wt)

Moisture content	Ash	Volatile matter	Fixed carbon	Moisture content (%)	Higher heating value (MJ/kg)	C (%)	H (%)	N (%)	S (%)
10.0	10.8	62.0	17.2	83.3	19.8	43.7	5.88	3.97	2.12

The as-received residue was crushed and sieved, thus obtaining a particle size ranging between 0.1-0.2 mm. This fraction, without any previous treatment, except for the drying at 110°C, was mixed with an aqueous solution containing the activating reagent (KOH), using an alkali/residue ratio of 2/1 (in wt/wt). The volume of water employed to dissolve the potassium hydroxide depended on the mass of residue used, which was varied between 6 and 300 g. The mixture residue-KOH solution was stirred for 15 min and after dried at 110°C for 12 h. This mixture was then put inside a basket made of stainless-steel net and designed specifically for this purpose. This cylinder-shaped basket had a container in which the sample was situated, exactly, 1 cm below the thermocouple. The basket was placed in a reactor with a total height of 1.85 m and 0.1 m in diameter. The flow of the inert gas, N₂, was of 4 l/min, and was introduced through a gas distributor, which was a perforated plate situated at the bottom of the reactor. Prior to each run, a probe was introduced in the reactor through the upper part and the experiment was initiated when the reactor was totally purged. Then, the mixture was heated, using N₂ as inert gas, at the rate of 10°C/min, up to the process temperature at which it was held for 1 h. The process temperature was varied over a temperature range of 625-700°C. After the activation process, the sample was cooled under N₂ flow, and was washed sequentially five times with 5N HCl and finally with distilled water to remove residual chlorides. Then, the washed sample was dried at 130°C for 12 h [1].

The activated carbons were characterised using physical adsorption of gases (N₂ at 77K and CO₂ at 273 K). To calculate the apparent surface area and the micropore volume, (specifically micropore plus supermicropore volume), the BET and the Dubinin-Radushkevich (DR) equations were applied to N₂ isotherm data, respectively. To calculate micropore volume from CO₂ adsorption data, the latter equation was applied.

For the kinetic studies of benzene adsorption, a series of Erlenmeyer flasks containing 0.05 g of activated carbon and 50 ml of a 50 ppm solution of benzene were closed and placed in a shaking bath at 20±1°C. After different contact times (from 5 up to 120 min), the flasks were taken out and filtered for benzene analysis. The benzene analysis was performed by sampling the different liquid samples, using polydimethylsiloxane SPME fiber for analysis on a 6890 Hewlett Packard GC [1].

Results and Discussion.

Effect of the activation temperature.

Table 2 presents the data obtained from the activated carbons prepared at the four temperatures studied, employing a fixed chemical ratio of 2/1. For comparison purposes, an activated carbon prepared at 700°C, but employing the procedure of introducing the chemical agent by physical mixture (not dissolution) was also prepared. The corresponding results are also included in Table 2, which gives the corresponding yields of the process (difference between the initial amount and the amount determined after the washing step), the BET surface area, the micropore volume, the total pore volume (determined directly by the volumetric equipment used) and the Average Pore Radius.

Table 2: Characterisation of the activated carbons prepared at different temperatures.

CONDITIONS	S _{BET} (m ² /g)	V _{micropore} (cm ³ /g)	Total pore volume (cm ³ /g)	Average Pore Radius (nm)	Yield (%)
625°C (2/1)	1087	0.475	0.591	1.087	9.0
650°C (2/1)	1059	0.463	0.566	1.069	10.1
675°C (2/1)	1167	0.510	0.661	1.133	7.9
700°C (2/1)	1362	0.595	0.756	1.110	5.4
700°C _(physical mixture)	930	0.406	0.540	1.162	4.1

It can be observed from the results obtained that: the method of dissolution seems to be much more effective than the method of physical mixture, which involves mixing of KOH with the sludge. There is a moderate enhancement in the pore development with the temperature of activation, both in micropore and total pore volume and the temperature of activation seems not to affect the average pore radius.

Regarding the yield of the process, that is the amount of activated carbon produced for the amount of input material, this is not high, although values around 10% are acceptable, taking into account that, for example, in the case of agricultural by-products,

such as olive stones, the global yield of a process consisting of two steps: carbonization and activation in steam at 900°C in order to yield a surface area of 1300 m²/g was of only 9%. It should be noted that a much lower temperature and only one-step process are use in this study.

Reproducibility of the process.

Concerning the effect of the possible heterogeneity of this industrial residue, two identical experiments were repeated with the purpose to verify the reproducibility of the process.

Table 3: Reproducibility of the process.

CONDITIONS	S _{BET} (m ² /g)	V _{micropore} (cm ³ /g)	Total pore volume (cm ³ /g)
675°C (2/1)	1167	0.510	0.661
675°C (2/1)	1394	0.609	0.719

Results derived from the two experiences well in agreement reproducible, presenting a deviation in the surface area of around 16%, thus confirming the reproducibility of results.

Effect of the mass of sample.

The sample mass was varied in the range of 6-300 g. The conditions used were: 700°C and a chemical ratio of 2/1. The results derived from the characterisation in the pore structure are presented in Table 4.

Table 4: The characterization of the activated carbons produced as function of the initial mass

CONDITIONS (mass in g)	S _{BET} (m ² /g)	V _{micropore} (cm ³ /g)	Total pore volume (cm ³ /g)	Average Pore Radius (nm)
6	1362	0.595	0.756	1.110
12	1362	0.595	0.823	1.209
36	814	0.356	--	--
48	781	0.341	--	--
96	509	0.222	0.433	--

It can be seen that there is a substantial decrease in the surface area and micropore volume as the mass of residue to be activated increases from 12 to 96 grams. One of the reasons could be that the washing process became more inefficient because of a greater mass of sample (because in the laboratory there were not proper instruments to carry out this process, -such as great porous filters-). In spite of lack of more ideal conditions, the worst sample prepared still possesses the properties of a good-quality activated carbon, because the BET surface area obtained was higher than 500 m²/g.

Adsorption of benzene.

It has been previously observed that the preparation of activated carbon involving dissolution seems to be much more effective than the method of physical mixture and there is a moderate enhancement in the pore development with the temperature of activation. For this reason, two samples of activated carbons for the adsorption studies were selected, which were those prepared at 625°C (2/1) and the 700°C (2/1).

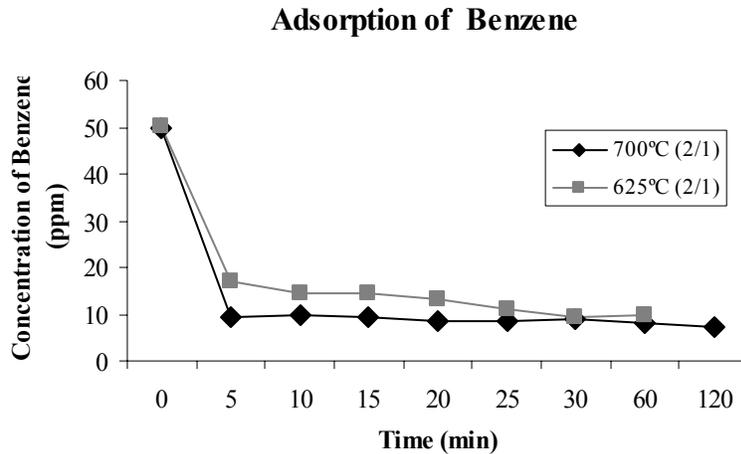


Figure 1: Kinetic curve of benzene concentration for the two samples. Experimental conditions: $C_0 = 50$ ppm; $V = 50$ ml; sample weight = 0.05 g.

Figure 1 illustrates the adsorption kinetic curve of benzene concentration for the two activated carbons. As clearly shown, the activated carbons were found to be effective in removing benzene from aqueous solution. Both activated carbons produced from pulp and paper mill waste show quite similar adsorption capacity. However, in the first 20 minutes, with the activated carbon prepared at 700°C (2/1) a small increase in the adsorption quantities of benzene was recorded, when compared with that of 625°C (2/1). Following this initial time, the adsorption of benzene within the two activated carbons was found to be similar. This fact could be due to the increase in micropore volumes of the samples.

Conclusions

The production of the activated carbon from pulp and paper mill waste has been proven to be very successful. The micropore development depends strongly on the method of dissolution utilized and on the temperature of activation. The activated carbon produced with largest adsorption capacity has a well developed porosity, providing a total micropore volume of $0.595 \text{ cm}^3/\text{g}$ and an apparent surface area, estimated from the DR method of $1362 \text{ m}^2/\text{g}$. The activated carbons prepared exhibit high benzene adsorption rates, due to their higher micropore volumes.

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