ACTIVATED CARBONS PREPARED FROM PINE WASTES FOR THE UPTAKE OF ORGANIC COMPOUNDS FROM AQUEOUS SOLUTION

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Introduction

Activated carbon is a highly porous material which has various applications in adsorption of both gases and solutes from aqueous solution. Coals and ligno-cellulose materials are commonly used as the starting raw material for preparing activated carbons. Recently, numerous attempts to prepare activated carbons from solid wastes have also been undertaken. The development of methods to re-use waste materials is greatly desired and the production of activated carbons from wastes offers a promising future.

Biomass wastes obtained from cleaning of forests and industrial use may play an important role in finding new alternative fuels. Biomass gasification, performed in a fluidised bed in the presence of air and steam mixtures, has proven to be a viable method of converting environmentally hazardous wastes into economically valuable products, which can be used as fuels to produce energy. Biomass gasification, using mainly pine wastes in Portugal, leaves some unconverted char which can have further use through upgrading. In fact, the characterisation of this char has shown that it could be converted into a suitable activated carbon of high value because of its intrinsic porosity and low ash content.

As the production of an active carbon must satisfy economical viability with high performance, cheap precursor materials readily available and convertible to an active carbon using a minimum of resources could become very attractive raw materials. Among the two classical methods of preparing activated carbons, physical and chemical activation, the latter has been chosen, because it is performed in a single-step (in the presence of chemical reagents), the process normally takes place at temperature lower than that used in the physical activation process, and the yields of carbon are usually high.

The demand for activated carbon is growing, particularly for its use for waste water and contaminated groundwater treatment due to the greater awareness of the limited supply of water of 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 has been designed with the purpose to check the behaviour of the activated carbons produced. The organic compound chosen for this preliminary adsorption assessment was benzene, because it is a low molecular weight pollutant of high priority and is a good model for real world applications. Two sets of experiments were undertaken: kinetic studies as a function of the time of contact between the activated carbon and the organic pollutant and equilibrium studies for different benzene concentrations.

Therefore, the main objectives of this work were to study the feasibility of preparing chemically-activated carbons from a char obtained by the gasification of pine wastes, finding the optimised conditions in making activated carbons with well-developed porosity and testing their ability in benzene adsorption. The influence of the preparation conditions, such as, the activating agent to char ratio, and the temperature and the duration of the process were all investigated. Additionally, a new design of the stainless-steel basket in which the sample to be activated is inserted, was also studied for selected cases.

Experimental

The char, obtained from pine wastes in a pilot gasifier, without any previous treatment, was physically mixed with the activating reagent (KOH), using different alkali/char ratios (from 1/1 to 4/1 in wt/wt). This mixture was then put inside a basket made of stainless-steel net and designed specifically for this purpose. This cylinder-shaped basket has 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, N_2, was of 4 l/min, and it 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 N_2 as inert gas, at the rate of 10°C/min, up to the process temperature at which it was held for 1 h. Other residence times were tested, ranging from 30 min to 3 h. The process temperature was varied over a temperature range of 725-800°C. After the activation process, the sample was cooled under N_2 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 110°C for 24 h.

The activated carbons were characterised using physical adsorption of gases (N_2 at 77K and CO_2 at 273 K). To calculate the apparent surface area and the micropore volume, (specifically micropore plus supermicropore volume), the Dubinin-Radushkevich (DR) equation was applied to N_2 isotherm data.

For the kinetic studies of benzene adsorption, a series of Erlenmenyer 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. For the equilibrium studies, a series of Erlenmeyer flasks containing the same amount of activated carbon and 50 ml of benzene solutions ranging from 0.5 up to 500 ppm of pollutant were kept in contact for 48 h to assure that equilibrium was reached. For all the cases, batches containing the model compound but not AC were also sampled to verify the loss of compound from causes other than AC adsorption. The benzene analysis was performed by sampling the different liquid samples, using polydimethylsiloxane SPME fiber for analysis on a 6890 Hewlett Packard GC.

Results and Discussion

The chemical agent to char ratio was found to be the most important parameter in the process studied in the present work. This is clearly demonstrated in Figure 1 which illustrates the N_2 adsorption isotherms for the different activated carbons prepared with different KOH to char ratios, ranging from 1/1 to 4/1, at 775°C (temperature that was verified to be optimum for the process). The parent char has been also included for comparison. The materials prepared have the type I N_2 adsorption isotherms corresponding to essentially microporosity, as shown in Figure 1. Activated carbons prepared using the procedure described above has been found to develop very high porosity, thus improving, for all the ratios studied, the adsorption capacity of the original char. Isotherms with continuous lines correspond to mixtures activated in the stainless-steel basket with a rigid solid support (made also of stainless-steel) as bed. If this support was not used, and the mixture was placed directly on the net, thus allowing N_2 to flow through the sample and hence improving the gas-solid contact, the adsorption capacity of the resulting activated carbon was found to be increased even further (comparing the isotherm in dashed line with the corresponding in continuous line for the ratio 3/1).

The variations in the total micropore volume (expressed per unit weight of activated carbon) with the KOH to coal ratio are shown in Figure 2. The amount of total micropore volume developed increased linearly from the original char up to a ratio of 3/1. From then on, the enhancement was not linear because it corresponded mainly to enlargement of micropores and not to the generation of further microporosity, as observed with CO_2 isotherms (not shown). Under these conditions, the best activated carbon prepared resulted in a micropore volume of 0.678 cm^3/g.

Concerning the kinetic studies of benzene adsorption, Figure 3 illustrates the adsorption kinetic curves of the activated carbons prepared from different alkali/char ratios, including also the original char. As shown clearly, the set of activated carbons prepared are effective in removing benzene from aqueous solution, the initial slope of the adsorption curve being more pronounced as the alkali/char ratio increases. From the original char to the best activated carbon prepared under the conditions used, there is a progressive and important enhancement in the adsorption capacity of the samples, consistent with the increase in the micropore volume. From the Adams-Bohart-Thomas equation, the initial adsorption coefficients were computed from the initial slopes of the kinetic curves by:

$$\gamma = -V/C_o m (dC/dt)_{t \to 0}$$

where C_o: solute concentration (mg/L); V: volume of solution and m: mass of the activated carbon in the batch reactor (g), as described in the literature [1].

Th kinetic coefficients of the different samples tested varied from $2.4 \cdot 10^{-5}$ (corresponding to the original char) to $17.3 \cdot 10^{-5}$ $Lmg^{-1}min^{-1}$ (corresponding to the best activated carbon prepared). Such a large variation can be attributed to the presence of a high proportion of micropore volume [1] (around 90% of micropore volume with regard to mesopore volume) present in the samples. Concerning the equilibrium studies, carried out after 48 hours of contact between the pollutant containing liquid and the AC, as given in Figure 4 which gives the adsorption capacity in equilibrium for some samples tested at two different benzene concentrations (200 and 500 ppms, respectively). The adsorption capacity in equilibrium seems also to be related to the amount of micropores present in the samples, as illustrated in Figure 4. Activated carbons prepared from pine wastes can reach a benzene adsorption capacity as high as 370 mg/gC, which could be encouraging for commercial use.

Conclusions

In conclusion, the production of the activated carbon from char obtained during the gasification of pine wastes has been proven to be very successful. The micropore development depends strongly on the KOH to char ratio. The activated carbon produced with largest adsorption capacity has a well developed porosity, providing a total micropore volume of 0.678 cm^3/g and an apparent surface area, estimated from the DR method of 1908 m^2/g. The activated carbons prepared exhibit high benzene adsorption rates, increasing with the enhancement of their micropore volumes.

References

1. Le Cloirec P, Brasquet C and Subrenat E. Adsorption onto fibrous activated carbon: applications to water treatment. Energy Fuels 1997; 11(2): 331-336.
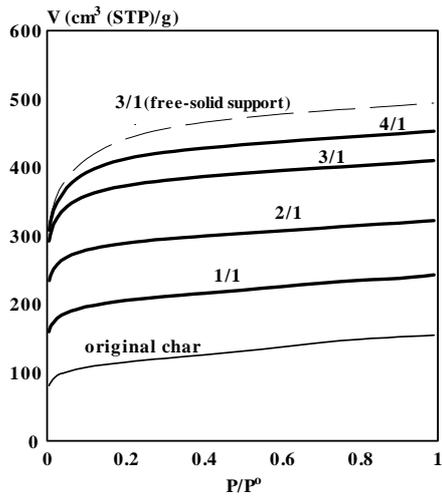
Acknowledgements

Figure 1. N$_2$ adsorption isotherms at 77K.
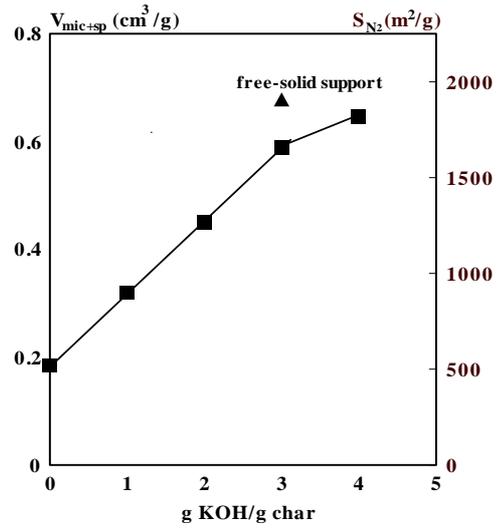

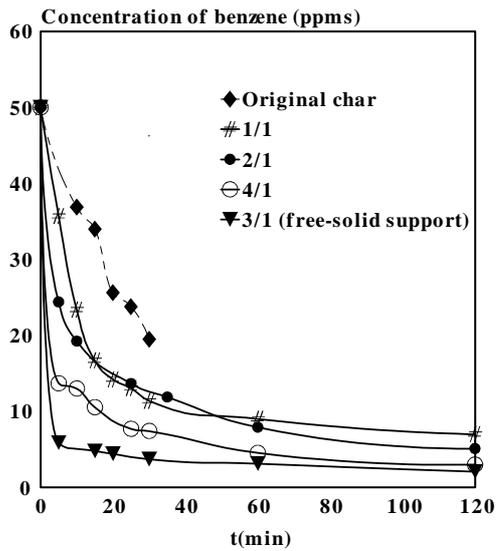**Figure 2.** Effect of KOH to char ratio on total microporosity development.

Figure 3. Kinetic curves of benzene concentration for different samples. (C$_o$=50 ppms; V=50 ml; weight of sample=0.05g).
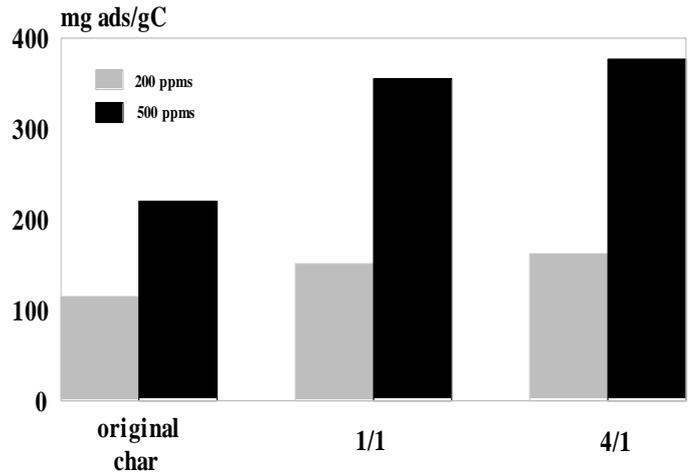

Figure 4. Amounts of benzene adsorbed at two different concentrations (200 and 500 ppms) for some of the samples studied.