

SPHERICAL ACTIVATED CARBONS FOR LOW CONCENTRATION VOCs ADSORPTION

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Introduction

Volatile organic compounds (VOCs) are one of the most important air pollutants because of their harmful effects on the environment and human beings [1]. Generally, VOCs are produced in gas phase and at very low concentrations. Hence, implementation of techniques that involve high efficiencies is required to control such emissions, which is costly. This study analyzes the development of adsorptive properties of spherical activated carbons (SACs) obtained from commercial petroleum pitch (Kureha). From this precursor, two series of SACs were prepared by physical activation with CO₂ and steam, studying the effect of activation time on the textural properties of different materials. The ACs have been used in toluene adsorption at low concentration.

Experimental

The present work uses a commercial SAC from Kureha Corporation (BAC) [2]. For physical activation with CO₂, a horizontal quartz tube of 2 m long and 0.7 m diameter was used. A flow of 80 ml/min of CO₂, a temperature of 880 °C and times of activation between 3 and 24 h were used. For physical activation with steam a vertical quartz reactor with upward flow was employed, using a steam flow of 0.9 l/min, a final temperature of 840 °C and activation times between 0.75 and 6 h. At these flow rates, fluidisation of the bed takes place. The nomenclature of the different spherical activated carbons derived from BAC can be described as follows. Firstly, the precursor (BAC) is indicated, secondly the burn-off (BO) percentage and, finally, the type of activating agent used (C for CO₂ and S for steam). As an example, the sample BAC58C has been prepared from BAC with a BO percentage of 58 %, being CO₂ the activating agent used. The morphology of pristine BAC and its derived SACs can be easily seen with scanning electron microscopy (SEM). The bed (bulk or tap) density, ρ_b , is the key parameter when working with packed beds. This volume includes the volume of pores, both opened and closed, and the space volume between the solid particles. This magnitude was measured for each SAC bed by the use of a measuring cylinder. The textural characterization of all the samples was performed using N₂ adsorption at -196°C and CO₂ at 0°C in a volumetric Autosorb-6B apparatus from Quantachrome. Temperature-programmed desorption (TPD) experiments were done in a DSC-TGA equipment (TA, SDT 2960 Simultaneous) coupled to a mass spectrometer (Balzers, OmniStar) to characterize the oxygen surface chemistry of all the samples. In these experiments, 10 mg of sample were heated up to 950°C (heating rate 20°C/min) under a helium flow rate of 100 ml/min. The pristine BAC material and two selected SACs derived from it (those having the highest

porosities prepared by steam or CO₂ activation) have been tested for toluene adsorption. For comparison purpose, a commercial AC from Mead Westvaco (WVA1100, 10x25) is also characterised and tested. Adsorption studies were performed at laboratory scale in a reactor (0.06 m inner diameter) coupled to a mass spectrometer (Balzers, OmniStar). The weight of AC was in the range of 0.25 g and a flow of 90 ml/min with a toluene concentration of 200 ppmv in air was used. The adsorption temperature was 25°C. Before adsorption, the AC samples were outgassed in helium at 250°C for 4 h. Through the graphical representation of the outlet concentration of toluene versus time the breakthrough curves can be obtained, leading to the toluene adsorption capacity (g toluene/100 g AC) by numerical integration. Also, volumetric adsorption capacity (g toluene/l SAC bed) has been assessed using the bed densities.

Results and Discussion

Table 1 summarises the different ACs prepared from BAC using the experimental conditions described before. Both series of SACs have quite similar degrees of activation, although obtained at different activation rates. Thus, for similar activation times, steam gives higher burn-off (BO) percentages than CO₂ activation, despite its lower activation temperature (840 °C instead of 880 °C). As expected, Table 1 shows that BO percentages increase with the activation time. Particle size distributions for these samples (Fig. 1) show that the activation of leads to a decrease in the mean particle size for both activating gases. Additionally, for similar BO percentages, there is a larger decrease in the mean particle size when steam is used as activating gas (Fig. 1). Thus, the mean particle size is 0.75 mm for BAC, 0.63 mm for BAC58C, whereas it is 0.55 mm for BAC60S.

The bed densities for these samples are compiled in Table 1. It has to be noted that BAC density is remarkably high (higher than that for a commercial AC with similar adsorption capacity) and, as expected, decreases with the activation. Table 1 compiles the BO percentages, the apparent BET surface area, the total micropore volume (calculated by nitrogen adsorption) and the narrow micropore volume (calculated by carbon dioxide adsorption). As the BO percentage increases, the apparent BET surface area and the total micropore volume considerably increase for both activating agents, whereas the volume of narrow micropores remains essentially constant for steam activation and increases slightly for CO₂ activation. For low-moderate BO percentages (up to about 30%) similar porosity developments are obtained for the two activating agents, showing that at these low-moderate BO percentages, steam activation has the advantage of producing SACs with higher bed densities than CO₂. For larger BO percentages much larger porosities are achieved with CO₂ activation than with steam (compare samples BAC60S and BAC58C). The bed density for WVA1100 is lower than the bed density for BAC and its derived adsorbents. WVA1100 has larger BET surface area than the pristine BAC, although its volume of narrow micropores is lower.

Table 1. Textural characterisation of the activated carbons

| Sample | BO | ρ_b | S_{BET} | $V_{N_2(DR)}$ | $V_{CO_2(DR)}$ | CO | CO ₂ |
|---------|----|----------------------|---------------------|----------------------|----------------------|-------------------|-------------------|
| | % | (g/cm ³) | (m ² /g) | (cm ³ /g) | (cm ³ /g) | (μ mol/g AC) | (μ mol/g AC) |
| BAC | -- | 0.59 | 1291 | 0.55 | 0.44 | 231 | 167 |
| BAC30S | 30 | 0.45 | 1654 | 0.72 | 0.46 | 339 | 192 |
| BAC40S | 40 | 0.44 | 1806 | 0.75 | 0.45 | 360 | 203 |
| BAC60S | 60 | 0.39 | 1880 | 0.77 | 0.45 | 392 | 171 |
| BAC31C | 31 | 0.39 | 1704 | 0.73 | 0.47 | 138 | 202 |
| BAC47C | 47 | 0.35 | 2232 | 0.82 | 0.56 | 226 | 264 |
| BAC58C | 58 | 0.31 | 2586 | 0.97 | 0.56 | 188 | 273 |
| WVA1100 | -- | 0.29 | 1757 | 0.67 | 0.36 | 1765 | 471 |

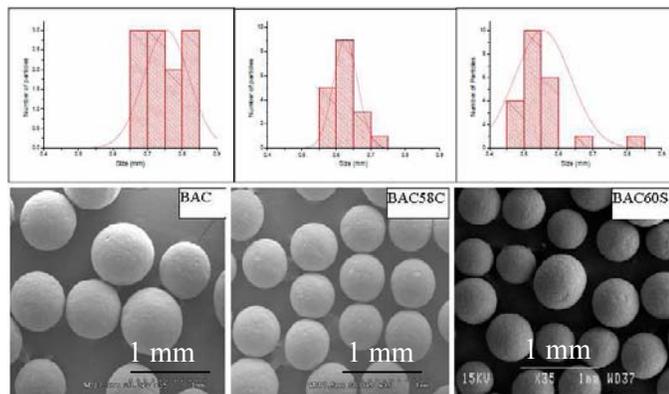


Figure 1. Particle size distributions and SEM images of BAC, BAC58C and BAC60S.

Regarding surface chemistry, Table 1 shows that surface oxygen is quite low for the different SACs. SACs activated in steam show a slight increase in surface chemistry with the increase in the BO percentage (there is an increase in the surface oxygen groups that decompose both as CO and CO₂). However, CO₂ activation leads to a small decrease in the content of surface oxygen groups that decompose as CO, and a more marked increase in the content of surface oxygen groups that decompose as CO₂. As a result, a small increase in the total surface oxygen contents is observed for samples activated with CO₂ in comparison to pristine BAC. Thus, it can be concluded that steam and CO₂ activation lead to some increase in the total surface oxygen contents of the AC. However, even for these BAC-derived activated carbons, the surface oxygen content, especially the content of those groups that decompose as CO, is much lower than that for the material used as a reference in the present work, WVA1100.

Fig. 2 shows the breakthrough curves obtained for toluene adsorption on these selected ACs. Table 2 compiles the adsorption capacities together with the narrow micropore volume and the oxygen content. Our results confirm that the apparent BET surface area does not control the toluene adsorption capacity and Table 2 shows that the highest toluene adsorption capacity corresponds to sample BAC58C, the one having the highest narrow micropore volume (0.56 cm³/g). Contrarily, sample WVA1100, the one having both the lowest

narrow micropore volume and the highest oxygen content, presents the lowest toluene adsorption capacity. Considering both the high adsorption capacity and the high density of the SACs used in this study, the volumetric adsorption capacities compiled in Table 2 for the pristine BAC and the SACs derived from it must be much higher than those achieved with commercial ACs. Thus, volumetric adsorption capacity for BAC60S is almost double than that for WVA1100 and, therefore, for the same volume of activated carbon, BAC60S adsorbs almost double quantity of toluene than WVA1100.

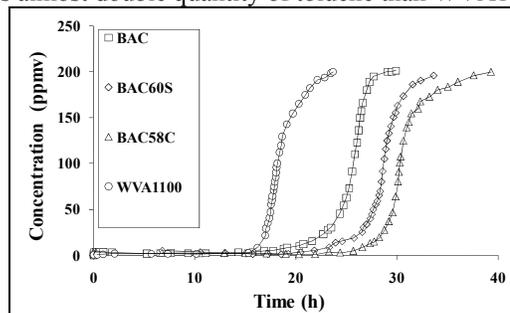


Figure 2. Breakthrough curves for toluene adsorption

Table 2. Adsorption capacities for toluene

| Sample | $V_{CO_2(DR)}$ (cm ³ /g) | total oxygen content (μ mol/g AC) | Adsorption capacities for toluene | |
|---------|--|--|-----------------------------------|----------------------|
| | | | (g toluene /100 g AC) | (g toluene/l AC bed) |
| BAC | 0.44 | 565 | 39 | 230 |
| BAC58C | 0.56 | 734 | 46 | 140 |
| BAC60S | 0.45 | 735 | 43 | 170 |
| WVA1100 | 0.36 | 2707 | 31 | 90 |

Conclusions

The SACs derived from BAC have high microporosity together with low surface oxygen groups content, positive for non-polar VOCs adsorption at low concentrations. Thus, SAC with high adsorption capacity have been prepared, leading to adsorption capacities as high as 46 g toluene/100g for BAC58C and 43 g toluene/100g for BAC60S, higher than those achieved with the commercial WVA1100 activated carbon. From the point of view of the volumetric adsorption capacity, it should be highlighted that the obtained values are quite high, especially for the pristine material (230 g of toluene/l), and decrease with activation. Considering the high gravimetric adsorption capacities and bed densities for these materials, their volumetric adsorption capacities are higher than that obtained with a commercial AC.

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References

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