Granular activated carbons from avocado seeds

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Abstract

Avocado seeds have proven to be an excellent raw material for the production of Granular Activated Carbons (GAC). This residue, generated in large amounts in centralized facilities dedicated to the transformation of avocado fruit, has no commercial value at present. GAC have been produced by partial gasification of ground seeds under mildly oxidizing conditions (steam/nitrogen mixture). Optimum activation conditions were achieved at 1000 ºC and residence times between 120-150 min, resulting in burn off rates between 34-37 wt% and carbon yields between 12.4-13.0 wt%. These GAC exhibited type IV N_2 gas adsorption isotherm, characteristic of materials containing a mixture of micro and mesopores. Avocado seed GACs exhibited BET surface areas up to 700 m^2/g, CO_2 surface areas up to 900 m^2/g and micro-pore volumes up to 0.31 cm^3/g. This porous structure provided these GAC with a remarkable aqueous adsorption capacity for methylene blue (Langmuir qm = 153.8 mg/g and Freundlich Kf = 113.0 mg/g), which was greater than that determined for a range of GAC commercialized for the treatment of waste and drinking waters.

Keywords: Activated carbons; avocado seeds; adsorption; porosity; surface area

1. Introduction

Production of avocado (*Persea americana* Mill.) has been growing rapidly over the last decades to reach a global production of 5.0 million tons in 2014(FAO, 2017). Most of this is dedicated to human consumption, either directly as a fruit or processed in the form of guacamole, avocado oil, nutritional supplements and other foodstuffs (Bernal and Díaz, 2008, Cowan and Wolstenholme, 2003, Dominguez *et al*., 2014). The use of this fruit for the production of cosmetics is also growing rapidly. At present, Mexico is the world leader in avocado production (30% of the total) followed by Dominican Republic (8.5%), Perú (7%) and Indonesia (6%)(FAO, 2017). The avocado market is also expanding rapidly in Europe, primarily in countries of the Mediterranean basin such as Spain, Portugal, Greece, Bosnia and Herzegovina, and France (representing in total 2.3% of the world´s production) (FAO, 2017). The industrial transformation of this foodstuff in centralized plants generates large amounts of an organic waste consisting primarily of seeds and husks mixed with a small proportion of pulp (Bernal and Díaz, 2008). The seed itself represents around one fourth of the fruit mass (Weatherby and Sorber, 1931). Although rich in starch, this element is not used as forage because of its limited nutrient value and its unpleasant palatability due to the presence of bitter compounds (Bressani *et al*., 2006). In most cases, this waste is simply disposed of by landfilling and in some occasions composted for use as a fertilizer and soil conditioner with very limited economic revenue. Alternative uses for this residue have been investigated, primarily focusing on the energy valorization of avocado seeds (Sánchez *et al*., 2016). Additionally, preliminary investigations have also been dedicated to evaluate the potential of avocado seeds for the production of activated carbons for use in water treatment. These latter works concluded that activated carbons made from avocado seeds developed an extensive porosity and were effective adsorbents for the removal of phenol (Kassahun *et al*., 2016, Rodrigues *et al*., 2011) and ammonium (Zhu *et al*., 2016), as well as different dyes (Elizalde-González *et al*., 2007) in aqueous solutions, revealing a potential use for this residue that should be researched more extensively. This paper describes an investigation into the potential of using avocado seeds for the production of Granular Activated Carbon (GAC) via carbonization and partial steam gasification using a rotary furnace. Activated carbons produced to different burn off rates were characterized for their pore size distribution using gas (CO_2 and N_2) adsorption techniques and also for their capacity to remove dyes (methylene blue) from solution as an indication of potential use in wastewater treatment applications.

2. Materials and methods

2.1 Avocado seeds and commercial GAC

Avocado seeds from the Hass variety were supplied by a local restaurant (Punto MX, Madrid, Spain). The material was ground using a knife mill (Retsch GM 200) and tested for moisture content using a thermo-balance (PCE-MB Series). The ground seeds (with particle diameters between 2 and 4 mm) were subsequently oven dried for 24 h at 40 ºC in order to reduce moisture (<5 wt%) and then characterized for its chemical, physical and thermal properties using the procedures described in Sanchez *et al* (Sánchez *et al*., 2016). Four commercial granular activated carbons (GAC) used for wastewater treatment applications were also tested for comparative purposes. The characteristics of these materials are described as follows: MG1050 (*ChiemiVall*) is produced from bituminous coal with a highly mesoporous structure. Intended for the removal of medium molecular weight pollutants in wastewaters and in purification of drinkable water. GC1000 (*ChiemiVall*) produced from coconut shell with a highly developed micropore structure. Intended to for the removal of chlorine and volatiles from wastewaters and the purification of drinkable water. GMI1240/IS (*GalaQuim*) produced from bituminous coal. It is used for the removal of dyes and organic compounds, chlorine and volatile compounds from wastewaters. GCO 835/OS (*GalaQuim*) from coconut shell. It is used in the purification of drinkable water, as well as in the removal of chlorine, O_3 and volatiles from industrial gaseous emissions.

2.2 Carbonization and activation

Activated carbons were produced from ground and size fractionated avocado seeds using a laboratory scale rotary kiln set to rotate at 3 rpm. Each experiment involved loading the reactor with 250 g of avocado seeds and heating at 10 ºC/min to 900 ºC under a flowing (200 ml/min) nitrogen atmosphere. Volatiles generated during this stage were purged out of the furnace while the carbonized char remained inside the reaction vessel. When 900 ºC was reached, a peristaltic pump was activated to produce 400 ml/min of a steam/ nitrogen (50:50, v/v) mixture and the furnace was heated to a target temperature of 1000 ºC. Reaction times between 0 - 150 min were applied to generate activated materials with different degrees of burn off. At the end of each experiment, solid yields were determined gravimetrically. Activated carbon samples are codenamed using their activation temperature followed by their residence time in minutes.

2.3 Gas phase adsorption of activated carbons

Carbon samples were characterized for their surface and porosity characteristics using continuous volumetric gas adsorption. Nitrogen gas adsorption was performed at 77 K using a Coulter Omnisorb 610. Carbon dioxide adsorption was conducted at 273 K using an Autosorb-6 automatic adsorption analyser (*Quantachrome*). Total surface areas were determined by application of the BET equation in the p/p_o range 0.015 – 0.15, which generated correlation coefficients r^2 > 0.9999. External surface areas were determined by application of the t-plot model in the range 7–9 A, producing correlation coefficients r^2 > 0.9995. The Dubinin–Radushkevich (DR) was employed to characterize carbon microporosity. The DR equation was applied in the pressure range p/p_o 0.0005 – 0.1 generating correlation coefficients r^2 > 0.9995.

2.3.1 Aqueous phase adsorption characterization of activated carbons

Commercial activated carbons and those produced from avocado seeds were investigated for their aqueous adsorption characteristics using methylene blue (MB). Adsorption isotherms for MB were produced by contacting different masses of carbon (25–600 mg) with 100 ml of methylene blue (1000 mg/l) solution. In order to minimize the effect of pH on adsorption determinations, stock solutions contained 500 mg/ l of sodium bicarbonate and the pH was adjusted to pH 7.0 ± 0.2 by addition of concentrated hydrochloric acid. Carbon mixtures were shaken for 24 h at 20 ºC and filtered using 1238 Filter-Lab filter-papers. Residual concentrations were determined using a Pharmacia Biotech Ultrospec 2000 UV–Vis spectrophotometer at 661 nm (methylene blue). Adsorption results were modelled according to the Langmuir and Freundlich equations (Marsh and Rodríguez-Reinoso, 2006, Sing, 1982).

3. Results and discussion

3.1 Chemical, physical and thermal characterization

Ground and over dried avocado seeds had an average moisture content of 4.0 wt%. Table 1 describes the characteristics of this material regarding its chemical properties (proximate and elemental), fiber composition and energy content.

Table 1 Characterization of ground and dry avocado seeds

Proximate		**Fiber**	
Volatile	81.9	Starch	44.8
Fixed	15.9	Cellulose	6.1
Ash	2.2	Hemicellulose	13
Elemental		Lignin	10.9
Carbon	46.0	**Energy**	
Hydrogen	7.0	HHV_0	18.2
Nitrogen	0.8	LHV_0	16.7
Oxygen	44.0		

All values as weight percentage on a dry matter basis (wt %, dmb) except for higher and lower heating values (HHV_0 and LHV_0) which are expressed on a dry matter basis in MJ/kg

The characterization describes the avocado seed as a starchy non-proteinaceous biomass with a relatively low content of lignin when compared to conventional wood. Ash content (2.2 wt%) is also reduced compared to other plant tissues (e.g. cereal leaves and stems), exhibiting a high concentration of potassium (9500 ppm) and phosphorous (1380 ppm), as reported elsewhere (Sánchez *et al*., 2016). Elemental and proximate compositions, and energy values are typical of biomass products.

3.2 *Product yields and burn off rates*

As shown in Table 2, carbonization of avocado seeds at 900 ºC under inert atmospheric conditions (flowing nitrogen) generated 49.3 g of char, representing 19.7 wt% of the original biomass. This value has been set as 0.0 wt% burn off rate in the quantification of the degree of activation. In these conditions, oil fraction represents 56 wt% of the original mass and non-condensable gases represent 24.0 wt%.

Table 2 Processing conditions, solid yields and burn off rates of activated carbons produced from avocado seeds

Codename	Temp. (ºC)	Residence time (min)	Solid		
			mass (g)	Yield (wt %)	Burn off (wt %)
900_00	900	0	49.3	19.7	0.0
1000_15	1000	15	48.0	19.2	2.5
1000_60	1000	60	43.5	17.4	11.6
1000_90	1000	90	41.0	16.4	16.7
1000_120	1000	120	32.5	13.0	34.1
1000_150	1000	150	31.0	12.4	37.0

Activation at 1000 ºC under mildly oxidizing conditions (50/50 wt% steam/nitrogen) resulted in a progressive reduction in the solid fraction due to the oxidation of the solid fraction. The results in Figure 1 evidence a linear trend between activation time and degree of activation (*burn off*) throughout the entire process.

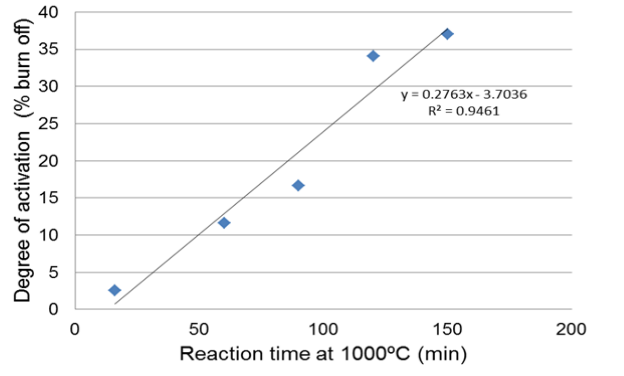

Figure 1 Burn off rates achieved by activated carbons produced from avocado seeds using different reactions times at 1000 ºC.

3.3 Pore size distribution and surface area

3.3.1 Nitrogen gas adsorption

Figure 2 illustrates the N_2 adsorption isotherms exhibited by the GAC produced from avocado seed under different experimental conditions. The adsorption capacity of the samples produced at very low degrees of activation (900_00 and 1000_15) was very limited. The isotherms showed a linear relationship between adsorption capacity and relative pressure (P/Po), as described by Henry's law. This behavior suggests a very limited degree of interaction between the solid surface and the adsorbate molecule (N_2), typical of solids with an insignificant pore structure. Activation at reaction times of 60 min and above generated solids with superior adsorption capacities, particularly at burn off rates above 20 wt%. These solids exhibited type IV isotherms with a type H2 hysteresis loops (Sing, 1982), suggesting the predominance of mesopores and a comparatively lower contribution of smaller micropores. However, it should be noted that, owing to the low temperatures involved (77 K), diffusional issues may also play a role in the adsorption of nitrogen in very small micropores, which may be generated during the initial stages of activation. This aspects is further investigated below using carbon dioxide adsorption at 273 K. Figure 3 describes the surface areas exhibited by the activated avocado seeds, as determined by applying the Brunauer–Emmett–Teller (BET) model to the adsorption branch of the nitrogen gas adsorption isotherm. The results show an almost linear relationship between BET surface area and the degree of activation. Activated carbons produced at very low burn off rate (< 12 wt%) exhibited negligible BET surface areas (below 10 g/m^2), while a *burn off* value of 16.7 wt% (GAC 1000_90) resulted in a BET value of 133 g/m^2, comparable to values previously reported in the literature for activated avocado seed carbons (e.g. 206 g/m^2) (Rodrigues *et al*., 2011). Carbons activated to burn off rates between 34-37 wt%, resulting in yields around 12-13 wt%, exhibited significantly higher BET surface areas in the range between 600-700 g/m^2. Commercial activated carbons tested in this investigation showed comparatively higher BET surface areas as follows: MG1050 (1100 g/m^2) and GCO 835/OS (900 g/m^2).

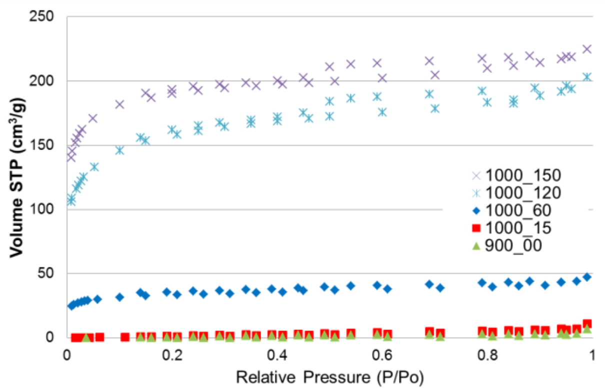

Figure 2 N_2 adsorption isotherms of activated carbons from avocado seed produced under different conditions

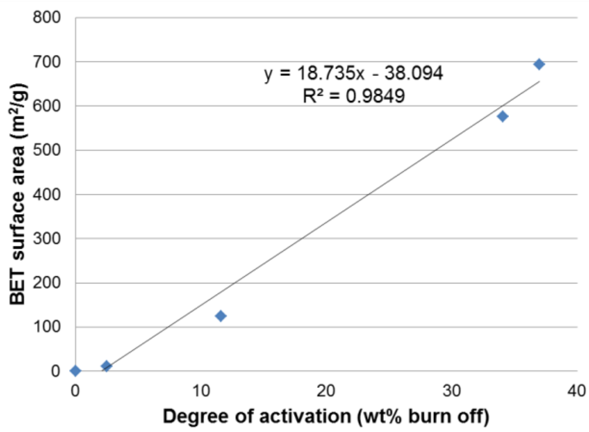

Figure 3 BET surface area of GAC from avocado seeds as a function of the degree of activation

3.3.2 CO_2 gas adsorption

Figure 4 illustrates the CO_2 adsorption isotherms exhibited by the avocado seed´s GAC produced at different experimental conditions. The shape of the isotherm in the relative pressure range covered (P/P_o < 0.03) is characteristic of Type I, describing an asymptotic approximation of the gas adsorbed (volume STP) to the monolayer capacity. In the absence of activation, the adsorption capacity of the samples produced at 900 ºC (0 min) was close to zero, suggesting a negligible degree of interaction between the solid surface and the adsorbate molecule. The results evidence a rapid increase in CO^2 adsorption capacity in solids produced at very low burn off rates (1000_15, equivalent to 2.5 wt% burn off). This improved capacity is attributable to diffusional hindrances that take place in N_2 gas adsorption tests, due to the lower temperatures involved (77 K compared to 273 K in the case of CO_2 adsorption). Hence, these results evidence the formation of an extensive microporosity during the initial stages of the activation of avocado seed chars. The experimental results show a progressive increase in the adsorption capacity of the carbon samples due to the development of their pore structure during the partial gasification.

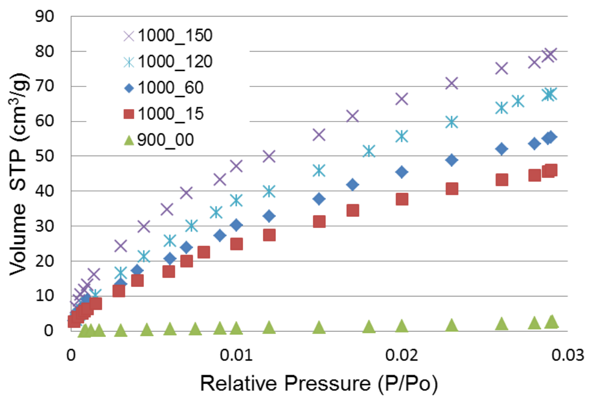

Figure 4 CO_2 adsorption isotherms of avocado seed GAC produced at different conditions.

Figure 5 illustrates the evolution in surface area and micropore volume of the avocado seed carbons as determined using the Dubinin-Radushkevitch equation. The results evidence the rapid expansion in micropore volume at very low degrees of activation (0.18 cm^3/g), while the external surface area only grows at higher burn of rates. Thus, the sample produced at 1000 ºC and 90 minutes residence time (1000_90) (*burn off* rate 16.7 wt%) exhibited a surface area of 628 g/m^2. Degrees of activation above 30 wt% resulted in carbons with DR areas close to 900 g/m^2, which are significantly higher to those reported by other authors for activated avocado seeds (Elizalde-González *et al*., 2007).

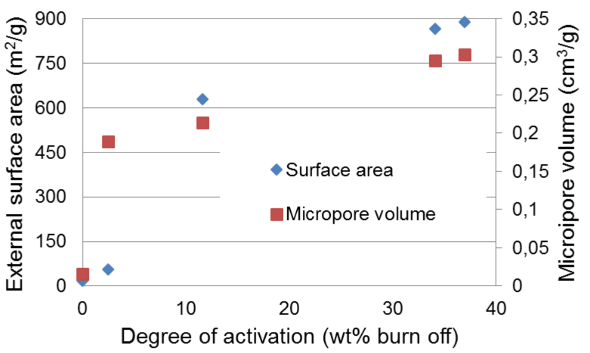

Figure 5 Degrees of activation of the avocado seed GAC vs their DR external surface areas and micropore volumes.

3.4 Aqueous adsorption

Figures 6 and 7 illustrate the methylene blue (MB) adsorption isotherms exhibited by the GAC produced from avocado seeds and also the commercial GAC, respectively. Table 3 shows the adsorption parameters determined by application of the Langmuir and Freundlich equations. The results show that non-activated carbons produced from avocado seeds (900_00) exhibited very limited adsorption capacity from solution.

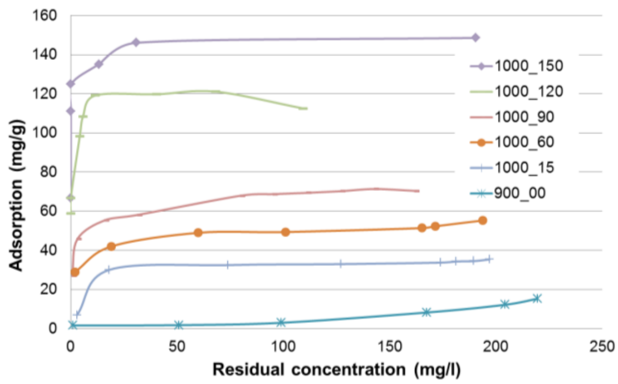

Figure 6 Methylene blue adsorption isotherms of avocado seed GAC produced at different experimental conditions.

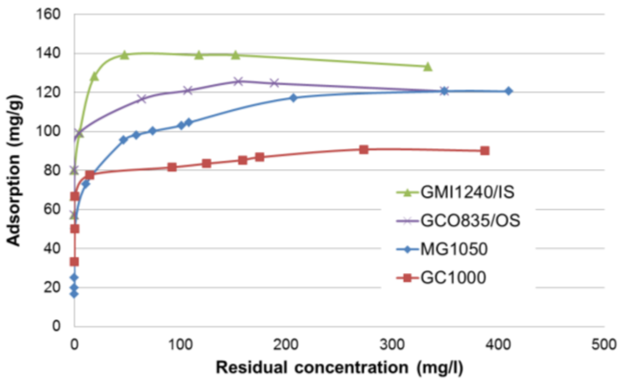

Figure 7 Methylene blue adsorption isotherms of commercial GAC.

Table 3 Adsorption properties exhibited by avocado seed and commercial GAC, as determined from application of Freundlich and Langmuir models to MB isotherms

	Freundlich			Langmuir		
Avocado	1/n	Kf	R^2	qm	Ka	R^2
900_00	0.20	4.3	0.92	4.4	0.56	0.83
1000_15	0.13	27.3	0.97	34.6	0.65	0.95
1000_60	0.06	35.1	0.93	50.7	0.35	0.85
1000_90	0.16	52.9	0.94	66.7	0.96	0.97
1000_120	0.09	85.1	0.91	112.3	29.7	0.91
1000_150	0.07	113.0	0.59	153.8	16.3	0.87
Commercial						
MG	0.20	40.3	0.92	114.9	2.90	0.96
CG	0.09	54.9	0.82	100.0	5.56	0.98
GMI	0.74	99.5	0.86	141.0	3.97	0.92
GCO	0.07	85.1	0.89	117.6	2.83	0.85

Aqueous adsorption capacity increased progresively as a result of activation. The best results where produced by avocado GAC 1000_150, produced at 37.0 wt% burn off rate (equivalent to 12.4 wt% carbon yield). Langmuir qm and Freundlich Kf for this sample were 153.8 mg/g and 113.0 mg/g, respectively. These values are around 10 % higher than those observed for the best performing commercial GAC (GMI) and between 30-50 % better than all the other commercial adsorbents.

4. Conclusions

High quality granula activated carbons (GAC) may be produced by partial gasification of avocado seeds. Optimum activation conditions were achieved at 1000 ºC and residence times between 120-150 min, resulting in burn off rates between 34-37 wt% and carbon yields between 12.4-13.0 wt%. These materials were essentially mesoporous with a lower contribution of micropores. GAC produced under optimized activation conditions exhibited N_2 BET surface areas up to 700 m^2/g, CO_2 surface areas up to 900 m^2/g and micro-pore volumes up to 0.31 cm^3/g. This combination of micro-mesopores provided avocado seed GAC with a remarkable aqueous adsorption capacity for methylene blue (Langmuir qm = 153.8 mg/g and Freundlich Kf = 113.0 mg/g), which was greater than that determined for the best performing commercial activated carbons

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