

PREPARATION OF ACTIVATED CARBON FROM GRAPE SEEDS BY CHEMICAL ACTIVATION AND APPLICATION TO THE ADSORPTION OF HERBICIDES IN WATER

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Introduction

Carbonaceous materials, especially activated carbons, are of great importance as adsorbents and catalytic supports, mainly because there is great flexibility for the adjustment of their porous structure and surface chemistry for each specific application [1]. The properties and behaviour of an activated carbon are closely linked to the starting material and the method of activation. The starting materials used for the preparation of activated carbons are diverse, having lignocellulosic materials a great weight in both industry and academy. The literature shows special interest in the preparation of granular activated carbons, which has led to the study of different starting materials of various kinds, with frequent use of seeds and waste biomass [2,3]. The use of grape seeds for the preparation of activated carbons shows relatively few references for both physical and chemical activation [4,5].

This work deals with the preparation of granular activated carbon by activation of grape seeds with phosphoric acid and the evaluation of their potential for the adsorption of diuron in water.

Experimental

Whole grape seeds were collected from a local winery. After air drying the seeds were pretreated with 5% (vol) sulfuric acid for 24 h in order to remove oils and improve wettability. The product was rinsed with water until neutrality and removal of sulfates, dried overnight at 120°C and stored for activated carbon preparation.

Chemical activation was carried using phosphoric acid as activating agent. Samples of 25 g of pretreated seeds were impregnated with 100 mL of phosphoric acid solution at 85°C for 2 h under stirring. The concentration of the solution was adjusted to provide phosphoric acid to pretreated seeds mass ratios of 1:1, 2:1, 3:1 and 4:1. After impregnation the samples were dried overnight at 120°C. Carbonization of impregnated samples was carried out in a horizontal furnace at temperatures ranging between 350 and 550°C for 2 h under a nitrogen flow rate of 100 mL/min, with a ramp of temperature of 10°C/min. Finally, carbonized samples were washed with water under reflux for 24 h. The nomenclature for the activated carbons prepared can be seen in Table 1.

The porous structure of the activated carbon and the catalysts was characterized by N₂ adsorption-desorption at 77

K (Autosorb-1 Quantachrome). The BET equation was used to obtain the surface area and the t-method for micropore volume. The external or non-micropore surface area was also obtained from the t method. The difference between the volume of N₂ adsorbed at 0.95 relative pressures (as liquid) and the micropore volume was taken as the mesopore volume. The morphology of the samples was studied by SEM with a Hitachi S-3000N apparatus.

Adsorption runs were carried out in 100 mL stoppered flasks placed in a shaking water bath (Julabo SW22) between 15 and 45°C. After the contact time programmed the liquid phase was filtered and diuron concentration was measured by UV spectroscopy (Shimadzu UV-1603) at 254 nm.

Table 1. Operating conditions for the preparation of activated carbons.

Sample	H ₃ PO ₄ /seed ratio	Carbonization temperature (°C)
PC-1-500	1:1	500
PC-2-500	2:1	500
PC-3-500	3:1	500
PC-4-500	4:1	500
PT-3-350	3:1	350
PT-3-400	3:1	400
PT-3-450	3:1	450
PT-3-550	3:1	550

Results and Discussion

Chemical activation provided activated carbons with a granular morphology since they maintained the shape of the starting material. SEM images of crushed activated carbons showed that they have an egg shell like structure with a wall thickness between 200 and 300 µm, thus Figure 1 shows PC-3-500 sample as a representative example.

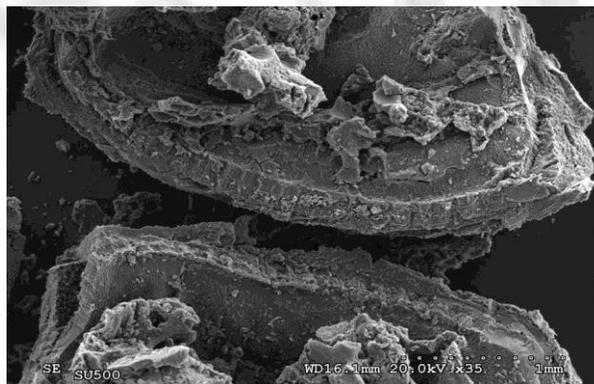


Fig 1. SEM image of crushed PC-3-500 sample.

The nitrogen adsorption-desorption runs revealed type I isotherms for samples PT-3-350 and PT-3-400, showing a mainly microporous structure. For the rest of the samples type II isotherms were obtained, which indicates the contribution of higher size pores. Table 2 summarized the main data about the porous structure of the activated carbons. The ratio of phosphoric acid to pretreated seeds used during the impregnation shows a limited influence in the surface area,

however it is an important factor for the development of mesoporosity, as it has been reported previously [6]. A ratio of 3 provides optimum results in terms of surface area (1139 m²/g), external area (269 m²/g) and mesoporosity (0.24 cm³/g). With regard to the influence of carbonization temperature, values above 450°C are needed to achieve relevant mesoporosity and external area, whereas beyond 500°C the development of porosity declines.

Table 2. Textural properties of activated carbons.

Sample	S _{BET} (m ² /g)	A _{EXT} (m ² /g)	V _{MICROPORES} (cm ³ /g)	V _{MESOPORES} (cm ³ /g)
PC-1-500	926	147	0.12	0.41
PC-2-500	957	215	0.19	0.54
PC-3-500	1139	269	0.24	0.49
PC-4-500	1026	202	0.18	0.51
PT-3-350	677	73	0.06	0.30
PT-3-400	657	98	0.09	0.28
PT-3-450	1111	258	0.23	0.48
PT-3-550	982	178	0.15	0.47

Activated carbon PC-3-500 was selected for the diuron adsorption study due to its higher porosity in terms of both BET surface area and mesoporous volume. Figure 2 shows that type S-3 isotherms (Giles classification) were obtained. The three consecutive regions of the isotherms fitted to Freundlich, Langmuir and Potential models. From these models the following values were calculated for each region for Gibbs energy, activation enthalpy and entropy according to Valenzuela [7]: $\Delta G^* = 4\text{--}89$ kJ/mol, $\Delta H^* = 26\text{--}42$ kJ/mol and $\Delta S^* = 0.16\text{--}0.36$ kJ/Kmol. The endothermic nature of the adsorption of diuron is the most relevant result, which is in agreement with literature on the topic [8].

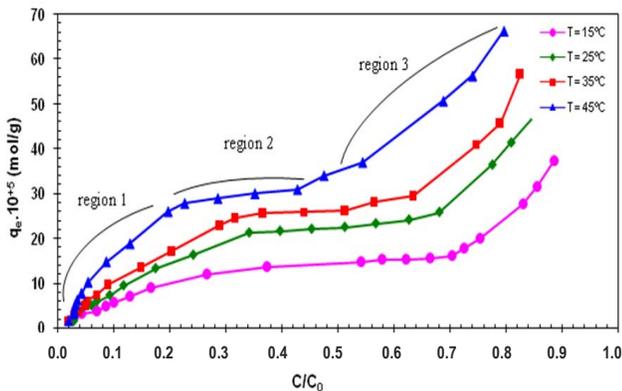


Fig 2. Diuron adsorption isotherms for PC-3-500 activated carbon ($C_0 = 6.5 \cdot 10^{-5}$ mol/L).

Figure 3 shows the kinetic data for the adsorption of diuron. It can be seen that at 25°C (a) the main uptake of diuron takes place during the first 8 hours; from that time much slower adsorption is observed. Optimum data fit was obtained for second order kinetic model. The rate constant increased by nearly two-fold when temperature was raised from 15 to 45°C, indicating enhanced mass transfer.

Thermodynamic functions were calculated according to the Eyring–Polanyi equation, yielding the following values: $\Delta G^* = 92\text{--}100$ kJ/mol, $\Delta H^* = 21$ kJ/mol and $\Delta S^* = -0.3$ kJ/Kmol. The endothermic nature of the adsorption of diuron calculated from kinetic data is in agreement with the behavior found in the equilibrium study.

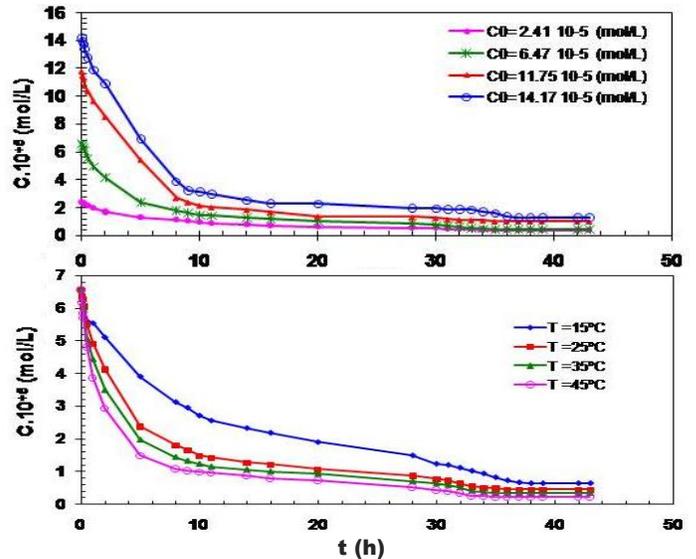


Fig 3. Diuron adsorption kinetic data for PC-3-500 activated carbon. a) $T = 25^\circ\text{C}$. b) $C_0 = 6.57 \cdot 10^{-5}$ mol/L.

Conclusions

Chemical activation of grape seeds with phosphoric acid provides activated carbons with well developed micro and mesoporosity. Optimum carbonization temperature and phosphoric acid to seeds ratio were 500°C and 3:1, respectively. Significant uptake of diuron in water was observed, showing as most relevant characteristic the endothermic nature of adsorption.

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References

- [1] Radovic LR, Sudhakar C. Introduction to Carbon Technologies. Universidad de Alicante (1997).
- [2] Georgova K, Petrov N, Eser S. Carbon 1993; 32(4):693-702.
- [3] Stavropoulos GG, Zabaniotou AA. Microporous and Mesoporous Materials 2005;82:79-85.
- [4] Kim HH, Yoon KS, Kim MN. Chawon Rissaikuring 2005;14(1):47-54.
- [5] Lupashku T, Nastas RV, Gonchiar V, Ghikavyi DU. Patent N° MD 2381 F1 (2004).
- [6] Lozano-Castelló D, Lillo-Ródenas MA, Cazorla-Amorós D, Linares-Solano A. Carbon 2001;39(5):741-749.
- [7] Valenzuela-Chamorro C, Navarete-Guijosa A, Stitou M, Cuerda-Correa EM. Physicochem. Eng. Aspects 2004; 237:7-13.
- [8] Fontecha-Cámara MA, López-Ramón MV, Álvarez-Merino MA, Moreno-Castilla C. Langmuir 2006;22:9586-9590.