INFLUENCE OF NITROGEN AND PHOSPHOROUS IN THE WATER VAPOR ADSORPTION ON ACTIVATED CARBONS

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Introduction

Desiccants are designed to control humidity and ambient moisture in a certain range. The traditional desiccants are silica gel and zeolites. The former has high adsorption capacities and it is easy to regenerate. The latter has similar adsorption capacities but its regeneration is very slow at room temperature [1]. Activated carbons, that can be obtained from many raw materials, including carbonaceous waste, present a high capacity for water vapor adsorption, due to their large specific surface area and high porosity. Unfortunately, it is well known that carbon surface is essentially hydrophobic; this results in a Type V isotherm for water vapor adsorption, with very low uptake at low relative pressures.

Despite of the strong influence of surface chemistry in water vapor adsorption, most of the work published in the technical literature is focused only in the effect of oxygen groups in the water vapor adsorption [2,3], however less attention has been directed to the behavior of activated carbons containing other elements. Mahajan et al [1] used oxidized carbons with high amounts of metal cations (Li, Na, K, Na) and show that the presence of these cations increases the water adsorption , especially, in the low relative pressure range, changing the isotherm shape from type V to type IV, and even to type I. Cossarutto et al [4] found that the presence of nitrogen on the carbon surface results in an enhancement of water vapor adsorption at low relative pressures and a decrease of the maximum amount of water adsorbed. More recently, our group have reported a paper [5] analyzing the presence of sodium on activated carbons obtained from Kraft lignin by means of CO_2 partial gasification. The sodium present on the carbon surface enhances the water adsorption capacities in the whole relative pressure range.
In this paper we investigate the contribution of phosphorous and nitrogen to water vapor adsorption on activated carbons.

Experimental

Different phosphorous containing carbons were obtained by chemical activation of Alcell lignin with H_3PO_4 as activating agent. Alcell lignin was mixed with H_3PO_4 and water and was stirred. An impregnation ratio of 3/1 (weight of activating agent/weight of lignin) was used in this research. The mixture was dried at 333 K during 24 hours and heated to 773 K, in a N_2 flow (150 cm^3 STP/min) at a heating rate of 10 K/min. The sample was held at this temperature for 2 hours and cooled down in N_2 flow. The carbonized sample was

submitted to different washing treatment in order to eliminate the activation agent progressively. P-UW denoted the carbon obtained without washing treatment (unwashed). P-W1 was obtained by washing P-UW with 100 ml of water at room temperature, P-W2 by washing P-W1 with 100 ml of water at 333 K and, finally, P-W3 by washing P-W2 with 100 ml of HCl and water until no Cl^- was found in the washing solution.

Two other activated carbons were obtained by means of physical activation of plywood with water vapor. The plywood samples were carbonized at 1073 K under N_2 atmosphere (150 cm^3 STP/min) in a conventional lab-scale tubular furnace. The carbonization temperature was achieved at a heating rate of 10 K/min. The gasification was performed in the same furnace with the char held in flat ceramic boats. Activation was carried out by partial gasification with water vapor. The activated carbons obtained were denoted by the letter 'N' and a number that correspond to the burn-off degree.
The porous structure of the chars and activated carbons was characterized from 77 K N_2 adsorption-desorption and 273 K CO_2 adsorption isotherms, carried out in a Coulter Omnisorp 100cx automatic adsorption analyzer and a Quantachrome Autosorb-1 respectively. Samples were previously outgassed during 8 hours at 423 K at 10^{-6} mtorr.
In order to know the surface chemistry of the samples X-ray photoelectron spectroscopy (XPS) analyses have been performed. XPS analyses of the samples were obtained using a 5700C model Physical Electronics apparatus with Mg Kα radiation (1253.6 eV).
Both water vapor adsorption-desorption equilibrium and kinetics studies were performed in a gravimetric termobalance (CI electronics). The termobalance automatically measures the weight of the sample as a function of time. Water adsorption isotherms were performed by setting pressure intervals relative to the saturation vapor pressure (p/p_o) at 298 K. Previously, the samples were outgassed under vacuum (10^{-3} Torr) in order to eliminate water physisorbed on the carbon surface, at 383 K during at least 24 hours.

Results and Discussion

The porous structural parameters obtained from N_2 adsorption-desorption isotherms, such as apparent surface area, A_{BET}, external area, At, micropore volume, Vt and narrow mesopore volume, Vme, and from CO_2 adsorption isotherms, such us narrow micropore area and volume, A_{DR} and V_D, are reported in Table 1. It can be observed, for the case of plywood-derived carbons, that the apparent surface area increases with burn-off and that almost no mesopores have been developed, indicating that the porous structure of these carbons is, mainly, microporosity. With respect to the P-containing carbons, the low A_{DR} and V_{DR} values obtained for P-UW carbon suggest that its porous structure is blocked, most likely, by the activating agent. The washing process removes the activating agent, opening up the structure of the carbon. It is remarkable the high values of micro and mesopore volume, Vt and Vme, respectively, observed for 'P' series carbons (except P-UW) in comparison with those observed for the 'N' series. This indicates that 'P' series carbons have a wider and more developed porous structure than 'N' series carbon. It is important to underline that the main difference between both sorts of samples is the much higher contribution of external area to the porous structure in the case of 'P' series carbons.

Table 1. Porous structure parameter values for different carbons.

Carbon	A_{BET} (m^2/g)	$At(m^2/g)$	Vt (cm^3/g)	Vme (cm^3/g)	A_{DR} (m^2/g)	V_{DR} (cm^3/g)
N-39	576	43	0.257	0.017	455	0.173
N-61	649	60	0.282	0.024	589	0.227
P-UW	2	-	-	-	80	0.030
P-W1	791	265	0.447	0.245	547	0.208
P-W2	815	260	0.465	0.239	437	0.166
P-W3	827	264	0.528	0.251	423	0.161

Once analyzed the porous structure of the carbons it is necessary to study the surface chemistry, because this is a critical factor in water vapor adsorption, especially, at low relative pressures. For this purpose, X-ray photoelectron spectroscopy (XPS) analysis of the surface of the carbons has been carried out. To obtain the atomic surface concentration a quantitative peak analysis was carried out. The results are reported in Tables 2 and 3 for 'N' and 'P' series carbons, respectively. In the former case, as gasification proceeds, carbon concentration decreases due to the addition of oxygen groups to the carbon surface. In the case of P-containing carbons, the washing process eliminates the phosphorous retained in the carbon matrix, as indicated by the decrease of the P2p atomic surface concentration. A decrease of the oxygen concentration and an increase in the carbon surface concentration takes place too.

Table 2. Atomic surface concentration determined by XPS quantitative analysis of N-containing carbons.

Sample	C1s (%)	O1s (%)	N1s (%)	Ca2p(%)
N-39	88.89	8.71	1.68	0.72
N-62	87.21	10.58	1.15	1.06

Table 3. Atomic surface concentration determined by XPS quantitative analysis of P-containing carbons.

Sample	C1s (%)	O1s (%)	P2p (%)
P-UW	31.63	50.95	17.42
P-W1	91.11	6.87	2.02
P-W2	91.43	6.60	1.97
P-W3	91.88	6.61	1.51

Figure 1 represents the water vapor adsorption isotherms of the carbons used in this study; the isotherm of a traditional desiccant like silica gel has been also included for comparison. Both plywood-derived carbons, N-39 and N-61, show a very similar water vapor adsorption isotherm, most likely, due to the little difference in their porous structure and surface chemistry. Both samples have lower adsorption capacities than silica gel in the entire relative pressure range. In contrast, the P-containing carbons adsorb much more water vapor than silica gel at high relative pressure. The adsorption behavior of these samples is almost exponentially, probably due to water clustering over the phosphorous located on the external surface and subsequent multilayer adsorption.

Figure 1 shows that water adsorption capacity decreases with washing treatment for the whole relative pressure range. It is noteworthy that P-UW carbon, despite of its porous structure is partially blocked by the phosphorous, adsorbs more water vapor than the silica gel in the whole relative pressure range. This behavior makes this carbon very suitable to be used as desiccant.
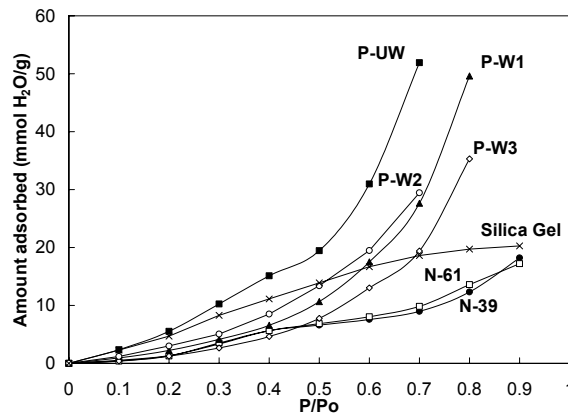

Figure 1. Water vapor adsorption isotherms for different carbons at 298 K.

However, not only the equilibrium values are important, adsorption-desorption kinetics play also a significant role in this process. The kinetic of water vapor adsorption on these carbons seems to follow a linear driving force mass transfer (LDF) model [6]. Figure 2 represents the kinetic rate versus relative pressure for the N- and P-containing carbons. The decrease of the adsorption rate at low relative pressure and further increase at medium relative pressures found for the N-containing carbons, not observed in the literature, suggests that after a fast adsorption of water vapor on the active adsorption centers (oxygen and nitrogen surface groups) at very low relative pressures, probably on the wider micropores, water clusters growth and a slow diffusion process of water molecules to fill the narrowest micropores seems to take place in the 0.2-0.4 relative pressure range. A further increase of the relative pressure (0.4-0.7) leads to an enhancement of the kinetic of water vapor adsorption, preferentially, on the wider micropores.

The results observed for the P-containing carbon are similar to those found in the literature. At low relative pressures the water molecules are chemisorbed on the active adsorption centers (oxygen and phosphorous surface groups), with the high adsorption rate. An increase of the relative pressure leads to water clusters growth, which reduces considerably the kinetic of adsorption. The washing treatment, clearly, increases the kinetic of adsorption at low relative pressures for the P-containing carbons, due to the enhancement of the porous structure during this process.
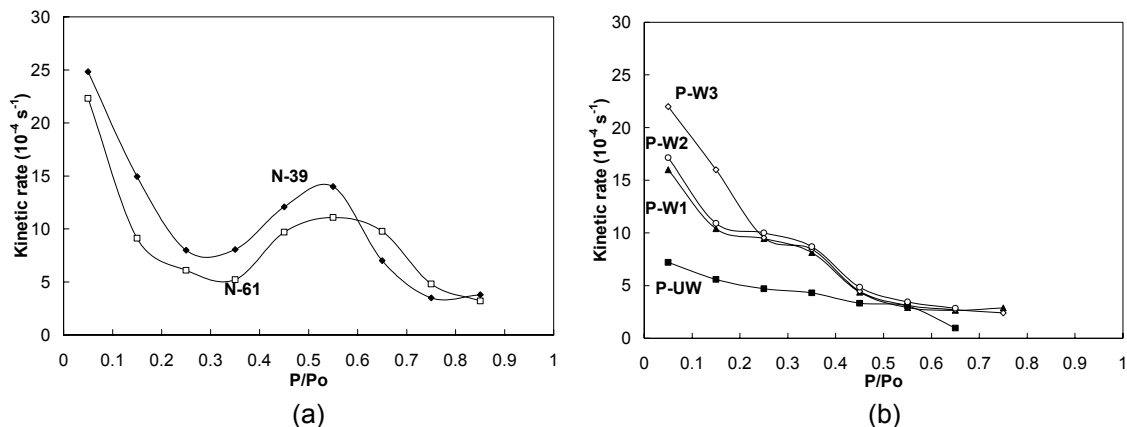
Figure 2. kinetics constants for water adsorption on different carbons at 298 K.

Conclusions

An activated carbon,P-UW, obtained from chemical activation with phosphoric acid of lignin show an important increase in water vapor adsorption in the entire relative pressure range, as compared with silica gel, a typical desiccant, which makes this carbon very suitable to be used as desiccant. The kinetics curves obtained for the P-containing carbons suggest that at low relative pressures the water molecules are chemisorbed on the active adsorption centers (oxygen and phosphorous surface groups), with the high adsorption rate. An increase of the relative pressure leads to water clusters growth, which reduces considerably the kinetic of adsorption. The washing treatment, clearly, increases the kinetic of adsorption at low relative pressures for these carbons, due to the enhancement of the porous structure during this process.

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