

WATER SORPTION ISOTHERMS OF RESORCINOL-FORMALDEHYDE HYDROGELS, XEROGELS AND CARBON XEROGELS

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Abstract

The classical saturated salt solutions method was used for the study of water desorption-adsorption isotherms of resorcinol-formaldehyde hydrogels, organic xerogels and carbon xerogels. Ten different salts were chosen to achieve relative humidities ranging from 5 to 95%. The comparison of desorption and adsorption isotherms gives the critical humidity upon which samples shrink. The influence of the temperature as well as that of the synthesis conditions was considered. The reversible part of isotherms was modelled by both the Oswin and GAB models. Statistical analysis shows that Oswin equation is the most suitable to predict water desorption-adsorption isotherms of resorcinol-formaldehyde hydrogels, organic xerogels and carbon xerogels.

Introduction

A carbon xerogel can be synthesized by the sol-gel polycondensation of resorcinol (R) with formaldehyde (F) using sodium carbonate to control the pH of the pristine solution, followed by air subcritical drying and pyrolysis in an inert atmosphere (Leonard, Job et al. 2005). The resulting nanostructure is very sensitive to the synthesis and processing conditions (Matos, Fernandes et al. 2006). According to its tailorable pore texture, this carbon material can be used for many applications such as packing materials for high-performance liquid chromatography, electrode materials for electrical double layer capacitors, medical applications and materials for catalyst supports (Tonanon, Wareenin et al. 2006). In the case of carbon supported catalysts, diffusion limitations can be avoided by choosing a carbon containing pores large enough to overcome mass transfer limitations (Job, Heinrichs et al. 2006). For applications such as electrodes or supercapacitors the electrochemical properties probably depends on the pore texture of the final material (Job, They et al. 2005).

This study concerns the determination of the water desorption isotherms of resorcinol-formaldehyde hydrogel –and the adsorption isotherms of the corresponding dried hydrogel and carbon xerogel. Two motivations can be found to this study. The first one addresses the process whereby water is removed and is related to the desorption isotherm of the RF hydrogels. When the drying conditions are too severe, the mechanical stresses caused by differential shrinkage may lead to the cracking of the sample. The control of the drying step, upstream from the pyrolysis step, is thus essential. To resolve shrinkage and cracking problems during solvent removal in order to preserve the monolithic shape before pyrolysis, it is necessary to optimize the drying process by using a thermo-hygro-mechanical simulation model (Léonard, Crine et al., 2006). The development of such a simulation model requires the knowledge of the moisture desorption isotherms at different temperatures. Indeed, desorption properties have a direct impact on the drying boundary conditions: at any time, the equilibrium water content at the surface of the material depends on both the temperature and the relative humidity of the boundary layer. The desorption isotherms also allow to determine the final residual moisture content that can be reached for given drying conditions. The second motivation deals with the adsorption isotherm, because the presence of moisture around the material can affect either mass transfer or adsorption capacity. This is particularly important for the carbon material, after pyrolysis of the RF xerogel. For example, it is well known that the presence of pre-adsorbed water results in a decrease of the adsorption capacity of activated carbon beds (Lodewyckx and Vansant 1999). The knowledge of the water adsorption isotherm gives information about the amount of water that will be (pre-)adsorbed by the carbon material for given storage conditions.

Several methods can be used to determine moisture sorption isotherms. The gravimetric technique, using saturated salt or sulphuric acid solutions, has been considered preferable to obtain complete sorption isotherms and has been recommended as the standard method (Iguaz and Virseda 2007). In the present work, ten different salts were chosen to achieve relative humidities ranging approximately from 5 to 95%. The effect of the temperature was investigated between 20 and 80°C. The influence of the gel synthesis conditions was also considered. Isotherms were modelled by both the Oswin and GAB models.

Materials and Methods

Preparation of the RF hydrogels and pyrolysis

Hydrogels were produced by polycondensation of resorcinol and formaldehyde, solubilized in water, in the presence of sodium carbonate (C) as basification agent. The molar ratio of resorcinol/formaldehyde, R/F, and the dilution ratio, D, i.e., the Solvent/(R+F+C) molar ratio were fixed at 0.5 and 5.6, respectively. The total amount of solvent takes into account the deionised water added but also water and methanol included in the formaldehyde solution. Three different values of resorcinol/sodium carbonate molar ratio, R/C, were tested, chosen equal to 300, 500 and 1000, in order to modify the pH of the precursor's solutions.

Resorcinol (VWR International, 99 %) and sodium carbonate (UCB, 99.5 %) were put together in a flask with deionised water and magnetically stirred. After complete dissolution, formaldehyde (Aldrich, 37 wt. % in water, stabilized by 10-15 wt. % methanol) was added and 2 ml of solution was poured into glass moulds of the same size and shape (cylinders, diameter = 13 mm). Then, the samples were put into the oven for gelation and aging during 24 h at 70 °C (Job, Sabatier et al. 2006). Just after gelation, the wet RF hydrogels were put in the containers with the salt solutions for the desorption experiment. After equilibrium was reached, the samples were dried in an oven to determine the dry solid content, and then they were put back in the containers for the adsorption experiment.

Once the desorption-adsorption isotherms of the RF hydrogels were determined, the samples were pyrolyzed to get carbon xerogels. The pyrolysis was realized in a tubular oven at 800°C, under nitrogen at atmospheric pressure, following a temperature program fully described elsewhere (Job, Pirard et al. 2004).

Sorption isotherms determination

The water adsorption and desorption isotherms of the RF hydrogels were determined at 20, 50 and 80°C by static gravimetric method. This method is based on the use of ten saturated salt solutions which were selected to give different relative humidities ranging from 6 % to 97 %. The vapor partial pressure and the corresponding water activity (or equilibrium relative humidity) over each solution both depend on the temperature, as shown in **Table 1**. Analytic grade solutions were prepared in plastic containers that were put under partial vacuum in order to speed up the adsorption-desorption process. The moisture content of each sample was determined by weighing them periodically each 3 days. This procedure was continued until a weight change equal to or lower than 0.001 g was observed between each measurement. With this criterion, the longest experiment took 11 days. The dry solid content of the samples was determined by putting the samples in an oven at 105 °C during 24 h. The equilibrium moisture content W_{eq} was expressed on a dry basis, i.e., the amount of water divided by the amount of dried solid.

Table 1. Saturated salt solutions and corresponding relative humidity.

Solutions	% Relative Humidity at 1atm		
	20°C	50°C	80°C
LiBr	6.4	5.5	5.2
LiCl	11.3	11.1	10.5
KC ₂ H ₃ O ₂	22.5	18.9	15.1
MgCl ₂	32.8	30.5	26.1
K ₂ CO ₃	43.2	42.7	41.1
NaBr	58.0	50.9	51.4
CuCl ₂	67.0	67.0	67.0
NaCl	75.3	74.4	76.3
KCl	84.3	81.2	78.9
K ₂ SO ₄	97.3	95.8	95.8

Modelling

The data, consisting of equilibrium water contents reached at different relative humidity levels, were fitted using the Oswin (Eq. 1) and Guggenheim, Anderson, DeBoer (GAB, Eq. 2) models (Simal, Femenia et al. 2007). These models can be applied to describe water sorption isotherms between 1 to 90% of relative humidity.

$$W_{eq} = A \left(\frac{RH}{1 - RH} \right)^B \quad (1)$$

$$W_{eq} = \frac{W_m C_G K RH}{(1 - K RH)(1 + (C_G - 1)K RH)} \quad (2)$$

In these equations, RH is the relative humidity expressed in %, W_{eq} the equilibrium moisture content of the material expressed on a dry basis ($g_{water}/g_{dry\ solid}$), A and B are fitting parameters, W_m is the moisture content of the monolayer of adsorbed water ($g_{water}/g_{dry\ solid}$), K and C_G are parameters related to multilayer properties and to the heat of sorption, respectively. The parameter identification was realized using non-linear least square regression analysis. The root mean squared error (RMSE) (Eq.(3)) (Simal, Femenia et al. 2007) was used in order to evaluate the accuracy of the simulation provided by the proposed models.

$$RMSE = \sqrt{\frac{\sum_{j=1}^N (W_{j\text{cal}} - W_{j\text{exp}})^2}{N - np}} \quad (3)$$

In Eq. 3, $W_{j\text{cal}}$ and $W_{j\text{exp}}$ are the calculated and experimental value of W_{eq} , respectively. $N - np$ represents the degrees of freedom of the fitting equation. These statistical parameters have also been used by other authors (Jamali, Kouhila et al. 2006; Iguaz and Virseda 2007). The differences between the experimental and calculated data ($W_{j\text{exp}} - W_{j\text{cal}}$) are defined as residuals. A model is considered acceptable if the residuals are uniformly scattered around zero.

Results and Discussion

Water desorption isotherms of RF hydrogels

All the experimental data obtained during water desorption from RF hydrogels are presented in **Table 2**, for the three investigated temperatures and the three R/C ratios. In the range of the temperatures tested, for a same relative humidity, the equilibrium moisture content decreases with increasing temperature and, at the same temperature, the equilibrium moisture content decreases with increasing R/C ratio. The effect of the temperature and the R/C ratio is illustrated in **Figure 1** and **Figure 2**, respectively. **Figure 1** shows that, for R/C = 300, desorption data are close from each other at the lowest temperature in all the RH range, whereas data are quite different from each other at 80°C, in particular for large RH. This results are in good agreement with previously reported sorption studies (Jamali, Kouhila et al. 2006). **Figure 2** shows that, for the same temperature, the curves are superimposed for RH lower than 50 % and then completely split. In the split zone, the higher the R/C, the lower the equilibrium water content. The impact of the R/C ratio is related to sample textural changes. Indeed, a decrease of the R/C ratio leads to a decrease of the maximum pore size in the wet gel, which will undergo a larger shrinkage during water removal (Job, Sabatier et al. 2006). For each sample, the breaking of the curve roughly corresponds to the end of shrinkage.

Table 2. RF hydrogels desorption isotherms data.

T=20 °C				T=50 °C				T=80 °C			
RH	R/C=300	R/C=500	R/C=1000	RH	R/C=300	R/C=500	R/C=1000	RH	R/C=300	R/C=500	R/C=1000
	Weq	Weq	Weq		Weq	Weq	Weq		Weq	Weq	Weq
6.4	0.065	0.062	0.065	5.5	0.044	0.042	0.045	5.2	0.032	0.033	0.032
11.3	0.068	0.066	0.071	11.1	0.044	0.043	0.044	10.5	0.027	0.028	0.028
22.5	0.097	0.098	0.106	18.9	0.052	0.053	0.056	15.1	0.030	0.030	0.032
32.8	0.126	0.125	0.134	30.5	0.079	0.075	0.077	26.1	0.049	0.047	0.044
43.2	0.142	0.136	0.143	42.7	0.111	0.101	0.102	41.1	0.071	0.068	0.061
58.0	0.224	0.167	0.169	50.9	0.143	0.119	0.120	51.4	0.080	0.074	0.070
67.0	0.455	0.192	0.183	67.0	0.470	0.231	0.164	67.0	0.315	0.144	0.121
75.3	0.545	0.218	0.194	74.4	0.497	0.211	0.164	76.3	0.348	0.132	0.116
84.3	0.747	0.304	0.218	81.2	0.668	0.458	0.201	78.9	0.397	0.150	0.124
97.3	1.595	1.609	0.472	95.8	1.819	1.860	2.084	95.8	0.900	0.900	0.275

Water adsorption isotherms of RF xerogels

The experimental data obtained for water adsorption of RF xerogels are indicated in **Table 3**. The results present the same tendency with regards to the influence of the temperature and the R/C ratio as the desorption isotherms. Nevertheless, **Figure 3** clearly shows the existence of an hysteresis when both the adsorption and desorption branches are plotted. The hysteresis is located in the range of relative humidity higher than 0.5. The hysteresis region is indicative of the changes occurring in the solid structure due to drying shrinkage. Indeed, the dried material can not recover the volume lost during the desorption phase.

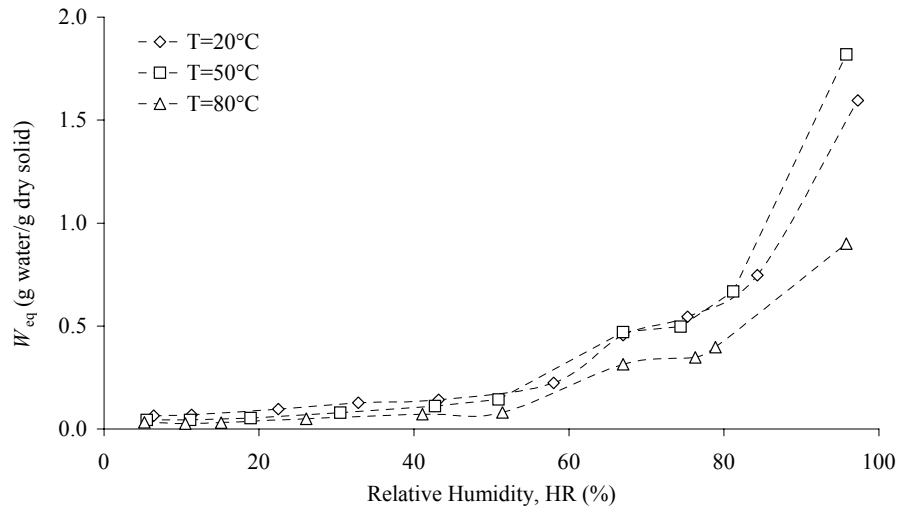


Figure 1. Moisture desorption isotherm of RF hydrogels for R/C=300, at 20, 50 and 80°C.

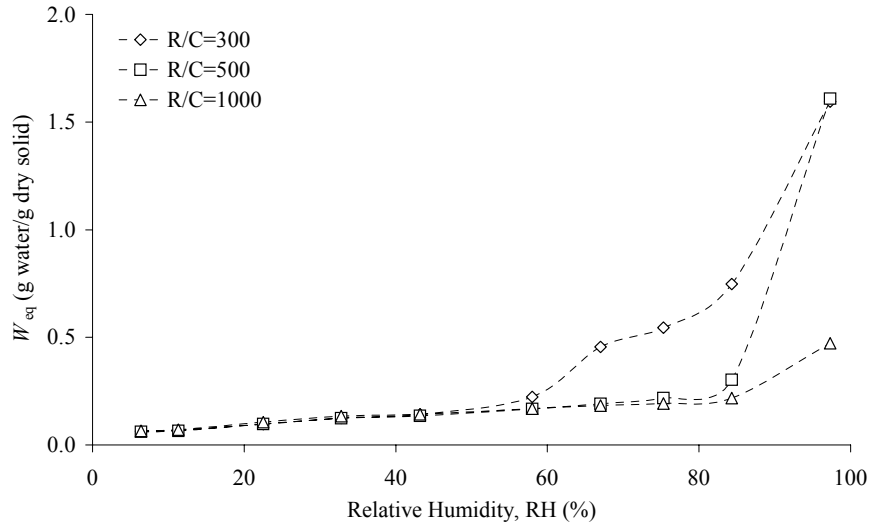


Figure 2. Moisture desorption isotherm of RF hydrogels at 20°C for R/C = 300, 500 and 1000.

Shrinkage behaviour was studied by Job, Sabatier et al (2006) under various convective drying conditions. They observed a volume reduction of about 10-15 % for R/C=1000, while the final shrinkage reached 45 % and 60 % for R/C=500 and 300, respectively. In the case of an ideal shrinkage, i.e. the volume reduction corresponding exactly to the volume of removed water, Equation 4 and 5 can be applied. From these equation, it is possible to find back the water content corresponding to the end of shrinkage, taking into account the above volume reduction data.

$$\frac{V}{V_0} = \varphi_0 \left[1 + \left(\frac{\rho_s}{\rho_w} \right) W \right] \quad (4)$$

$$\varphi_0 = \frac{1}{1 + W_0 \frac{\rho_s}{\rho_w}} \quad (5)$$

In the two latter equations, φ_0 is the initial solid concentration, W_0 is the initial water content and ρ_s and ρ_w are the skeletal density of the resin and the density of the water, respectively. Applying these equations for R/C=300, 500 and 1000 gives water contents corresponding to the end of shrinkage near to $W_{eq} = 0.43$, 0.84 and 1.66, respectively. These values correspond to the beginning of the hysteresis, at around RH = 67 %, as seen in **Figure 3**.

Table 3. RF xerogels adsorption isotherm data.

T=20°C				T=50°C				T=80°C			
RH	R/C=300	R/C=500	R/C=1000	RH	R/C=300	R/C=500	R/C=1000	RH	R/C=300	R/C=500	R/C=1000
	Weq	Weq	Weq		Weq	Weq	Weq		Weq	Weq	Weq
6.4	0.057	0.060	0.064	5.5	0.048	0.049	0.053	5.2	0.058	0.055	0.052
11.3	0.038	0.041	0.057	11.1	0.033	0.036	0.035	10.5	0.036	0.037	0.036
22.5	0.059	0.063	0.047	18.9	0.041	0.044	0.045	15.1	0.044	0.043	0.046
32.8	0.102	0.127	0.207	30.5	0.057	0.058	0.058	26.1	0.058	0.057	0.051
43.2	0.111	0.111	0.110	42.7	0.079	0.075	0.071	41.1	0.086	0.087	0.070
58.0	0.124	0.097	0.111	50.9	0.092	0.085	0.082	51.4	0.083	0.078	0.076
67.0	0.158	0.121	0.114	67.0	0.206	0.143	0.121	67.0	0.160	0.120	0.114
75.3	0.181	0.133	0.121	74.4	0.192	0.143	0.124	76.3	0.149	0.111	0.101
84.3	0.321	0.172	0.141	81.2	0.265	0.182	0.140	78.9	0.162	0.121	0.106
97.3	0.397	0.879	0.278	95.8	0.509	0.998	0.388	95.8	0.630	0.695	0.261

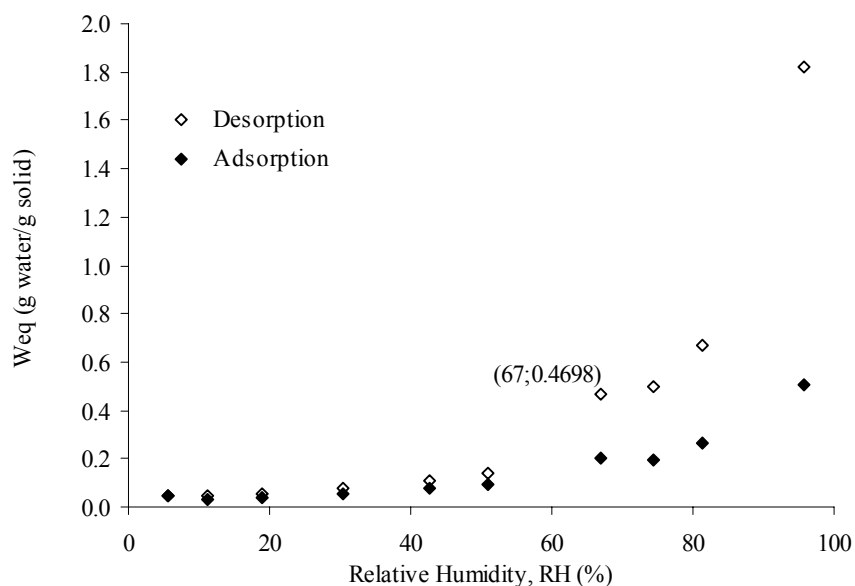


Figure 3. Water adsorption-desorption isotherms of RF hydrogels, at R/C=300 and T=50°C.

Modelling of RF hydrogels water isotherms

To estimate the parameters of Equations 1 and 2, only the desorption data in the range from RH = 5 to 67 % were considered. Indeed, for higher RH the desorption mechanism corresponds to the elimination of water by structure shrinkage.

Table 4. Fitting parameters of Oswin equations for RF hydrogels adsorption-desorption.

Isotherm Models	T (°C)	R/C	Desorption			Adsorption		
			A	B	RMSE	A	B	RMSE
Oswin	20	300	0.18	0.48	0.0129	0.13	0.33	0.0384
		500	0.15	0.35	0.0055	0.07	0.68	0.0471
		1000	0.16	0.33	0.0074	0.11	0.23	0.0449
	50	300	0.13	0.54	0.0100	0.12	0.48	0.0254
		500	0.11	0.45	0.0066	0.06	0.88	0.0323
		1000	0.11	0.43	0.0068	0.08	0.50	0.0164
	80	300	0.08	0.45	0.0065	0.11	0.56	0.0647
		500	0.07	0.39	0.0066	0.08	0.69	0.0772
		1000	0.07	0.36	0.0052	0.10	0.28	0.0611

On the contrary, the full humidity range was used for the adsorption branch. **Tables 4** and **5** show the parameter estimates and the RMSE obtained after fitting of the equations. The equilibrium moisture content was taken as the variable dependent.

Table 5. Fitting parameters of GAB equations for RF hydrogels adsorption-desorption.

Isotherm Models	T (°C)	R/C	Desorption				Adsorption			
			Kg	Wm	Cg	RMSE	Kg	Wm	Cg	RMSE
GAB	20	300	3.26	4.25	0.03	0.0306	0.45	0.58	0.55	0.0365
		500	2.53	6.97	0.02	0.0349	0.28	0.08	0.91	0.0738
		1000	0.27	8.04	0.26	0.0250	0.07	81.67	0.75	0.0532
	50	300	3.33	3.93	0.02	0.0190	0.47	0.28	0.69	0.0285
		500	3.42	4.80	0.02	0.0195	0.28	0.09	0.92	0.0492
		1000	3.50	4.55	0.02	0.0211	0.39	0.16	0.74	0.0390
	80	300	1.53	2.37	0.05	0.0150	0.39	0.14	0.82	0.0897
		500	1.69	2.46	0.04	0.0168	0.22	0.13	0.90	0.0961
		1000	1.66	2.44	0.04	0.0174	4.25	4.61	0.01	0.0758

From **Tables 4** and **5**, it can be seen that Oswin equation gives the lowest values of RMSE for both the water desorption and adsorption isotherms of RF Hydrogels, in the range of temperature studied. According to these results, Oswin model was considered as the best model for predicting the equilibrium moisture content in all the RH range for adsorption and from 5 to 67 % RH for desorption. **Figure 4** shows, as an example, the experimental data and predicted values obtained by Oswin equation for R/C=300 samples at 80 °C. It is seen that Oswin equation is the most appropriated to predict the moisture isotherms for RF hydrogels, especially for in the range from 5 to 80 % RH.

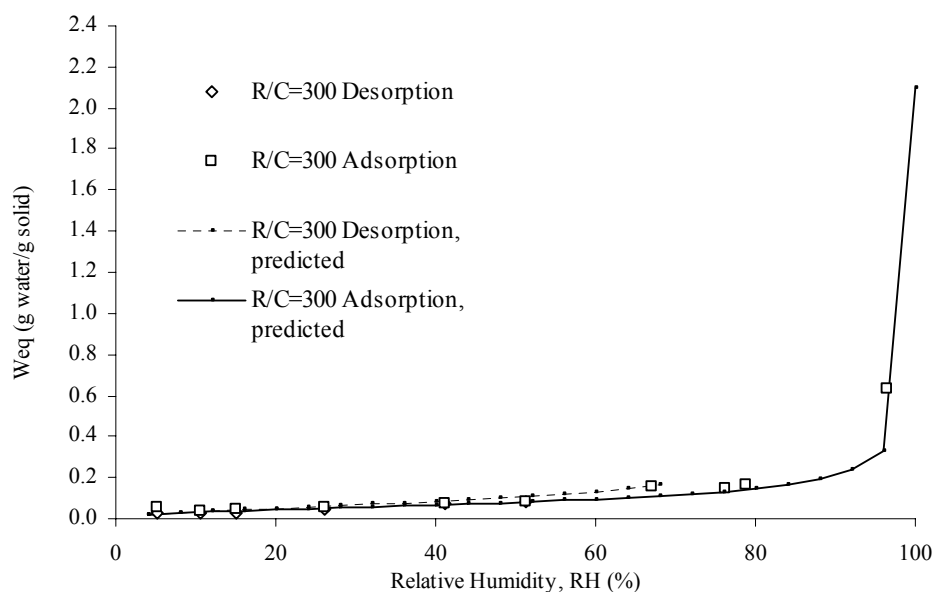


Figure 4. Experimental and Oswin model predicted water adsorption-desorption isotherms of RF hydrogels, at R/C=300 and T=80 °C.

Sorption isotherms of carbon xerogel

The experimental data obtained at 80°C for water adsorption isotherms of carbon xerogels are plotted on the **Figure 5**. It can be observed that the adsorption isotherms are superimposed for the whole of RH, independently of the molar ratio R/C. This indicates that, after pyrolysis, the affinity of the carbon materials for water is the same, whatever the initial pore texture. This can be related to the textural modifications occurring during pyrolysis. All the samples shrink and their specific surface increases through the formation of micropores. According to previous works, nitrogen adsorption-desorption shows that the microporosity is quite the same for the three R/C ratios, while the maximum pore diameter increases with R/C, due to increasing mesoporosity (Job, They et al. 2005). This would suggest that the mechanisms underlying water adsorption only involve the microporosity. **Figure 5** also shows that the amount of water adsorbed at 80°C is not negligible. This will be even worse at lower temperatures. This confirms that the control of carbon material storage conditions is crucial. **Table 6** contains the parameter estimates and the RMSE obtained after fitting of the Oswin

and GAB equations for the water adsorption isotherms of carbon xerogels. This table shows that Oswin equation gives the lowest values of RMSE, similarly to the results obtained with RF gels.

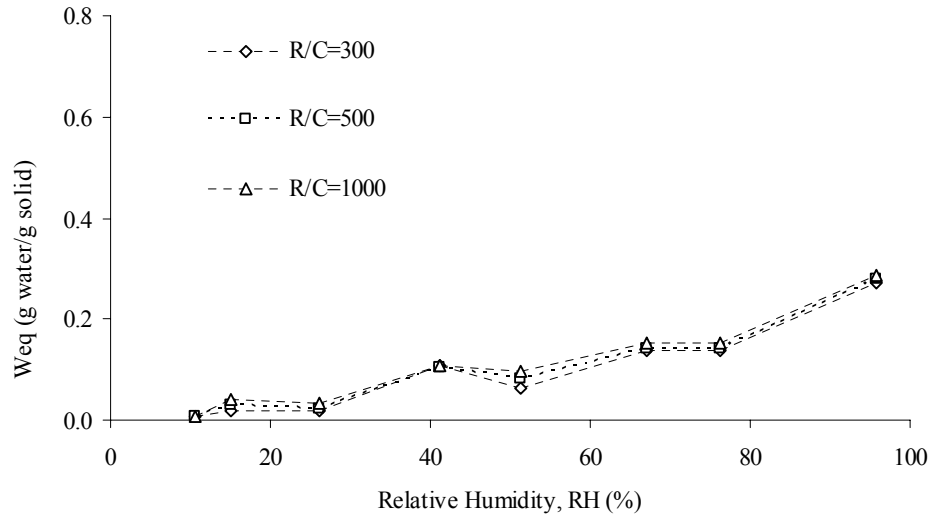


Figure 5. Moisture adsorption isotherm of carbon xerogels at 80°C for R/C = 300, 500 and 1000.

Table 6. Fitting parameters of GAB and Oswin equations for carbon xerogels adsorption.

Isotherm Models	R/C	Adsorption			
		K	W_m	C_G	RMSE
GAB	300	0.54	0.32	0.52	0.0262
	500	0.62	0.33	0.49	0.0235
	1000	1.06	0.29	0.40	0.0248
Oswin	R/C	A	B	RMSE	
	300	0.08	0.41	0.0266	
	500	0.08	0.40	0.0232	
	1000	0.09	0.38	0.0246	

Conclusions

Water desorption isotherms of RF hydrogels were determined for various molar ratio R/C and at three temperatures. It was shown that, for a same relative humidity, the equilibrium moisture content decreased with increasing temperature and that, at the same temperature, equilibrium moisture content decreased with increasing R/C ratio. The comparison of the desorption and adsorption isotherms obtained on the same material showed that for low RH both isotherms superimpose whereas for high RH a hysteresis loop is observed. This hysteresis is attributed to shrinkage occurring during the drying process. Oswin and GAB isotherms were used to model the reversible part of desorption data and the whole adsorption isotherms. Statistical calculations showed that Oswin model provides the best fit to predict equilibrium moisture contents. Finally, water adsorption isotherms of the carbon xerogels were also determined. For these samples, Oswin model fits on all the RH range.

The desorption data obtained on RF hydrogels will be introduced in a thermo-hygro-mechanical model used to simulate the stresses induced during the convective drying (Léonard, Crine et al., 2006). The non-reversible part of the desorption isotherms will be analysed in terms of shrinkage stress (Brinker and Scherer, 1990). Finally, the adsorption data relative to carbon xerogels will be collected at lower temperatures in order to define optimal storage conditions at room temperature. The results will also be compared to nitrogen adsorption-desorption isotherms, to get a better understanding of the underlying mechanisms of water adsorption on carbon xerogels.

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