

Adsorption of Acetic Acid by Activated Carbons, Zeolites, and Other Adsorbent Materials Related with the Preventive Conservation of Lead Objects in Museum Showcases

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To test the suitability of adsorbents such as activated carbons, zeolites, and other materials to adsorb acetic acid vapors that are liberated inside museum showcases and may destroy lead objects, the adsorption capacities at the saturation pressure and the isotherms of adsorption at lower pressures were determined. The results obtained show that the NaX zeolite in pellet form and the RB4 activated carbon are the best adsorbents. Additionally, they show that materials with sodium content exhibit an exchange process that may be very important, particularly in the case of NaX zeolite. Some of the parameters determined (saturation capacity, Henry constant, kinetic parameter) seem to be related in a simple manner (although there are adsorbents that do not agree with the general trend). However, a simple relation was not found between the specific surface area previously determined with nitrogen at 77 K and the acetic acid saturation capacity at room temperature.

1. Introduction

Lead was a metal with a great importance in antiquity¹ and has been used ever since in coins, medals, documents seals, statues, stained-glass windows, and toys, among other works.

Although many lead objects exist for more than two thousand years in excellent conditions, in some situations works made with that metal may suffer very significant alterations in a small interval of time, including total loss.² This problem occurs when the objects are placed in closed spaces, namely, museum showcases, and the container is made from materials that liberate volatile organic compounds (VOCs) such as vapors of acetic acid. Among the materials that contain such volatile compounds are synthetic materials that make up paint layers, stickers, and coatings as well as natural materials such as wood. Even if the released amounts of VOCs are low, significant concentrations of these compounds can be reached inside showcases because of the small closed space.³ As shown in Table 1,^{2,4–9} inside museums, especially in showcases, the acetic acid concentration may attain values several times greater than that generally found outside (on the order of 0.001 mg/m³ or less).⁶ It must be noted that lead objects must not be exposed to concentrations of acetic acid greater than 0.43 mg/m³.²

The problem is not specific of lead works, as several other objects of different nature, such as paper documents, films, ceramics, and stones, among others, are also subject to degradation by the action of VOCs, particularly acetic acid vapors.^{4,10–14}

Obviously, a good selection of the materials from which showcases are made is the principal measure that can be taken to prevent such problems.^{4,15} Nevertheless, the removal of the pollutants inside showcases should be done also because unsuspected sources of VOCs may exist. With this goal, adsorptive materials can be placed near the objects in exhibition.^{9,16–18}

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Table 1. Maximum Concentration of Acetic Acid Detected in Museum Atmospheres and Used in Tests Related to the Conservation of Museum Objects

location or essay	CH ₃ COOH (mg/m ³)
British Museum, London, cupboard ^{4,5}	2.745 ± 0.043
British Museum, London, showcases ⁴	2.094 ± 0.060
Musical Instrument Museum, Brussels, showcases ⁶	0.604
Musical Instrument Museum, Brussels, gallery ⁶	0.082
Plantin-Moretus Museum, Antwerp, showcases ⁶	3.215
Plantin-Moretus Museum, Antwerp, gallery ⁶	0.106
Museums in Glasgow, Edinburgh, London, and Amsterdam, showcases and storage cabinets ⁷	1.8 ^a
tests with lead objects ²	105
tests with calcareous materials ⁸	1950 ^a
tests with calcareous materials ⁹	245 ^a

^a Calculated from the value expressed in ppm (or ppb) by the equation $c = 2.45x$, where c is the concentration expressed in mg/m³ and x the concentration in ppm. The equation does not consider deviations from the ideal gas model.

To test the suitability of adsorbents such as activated carbons, zeolites, and other solids to the utilization explained above, we have undertaken a study on the adsorption of acetic acid vapors on these materials at room temperature, since literature data on the acetic acid adsorption is lacking.

2. Experimental Section

2.1. Adsorbents. 2.1.1. Textural Characterization of Adsorbents. Samples of activated carbons, zeolites, silica gel, and a clay pillared with aluminum oxide pillars (PILC) were used in this study. Textural characteristics of the samples, obtained by nitrogen adsorption at 77 K after outgassing at 573 K for 2 h in a dynamic vacuum better than 10⁻² Pa, are given in Table 2. For these adsorbents, the BET surface area values (A_{BET}) are between 270 and

Table 2. Characteristics of the Adsorbent Materials Previously Determined and Acetic Acid Adsorption Properties Determined in the Present Study^a

sample label	type and origin	form	A_{BET} (m ² /g)	V_{DR} (cm ³ /g)	m^{max} (g _{vapor} /g _{sample})	$V^{\text{max}}/V_{\text{DR}}$ (%)
CarbTech	Carbon Tech	pellet	977	0.41	0.50	117
RB1	carbon RB1, Norit	pellet	985	0.44	0.47	103
RB3	carbon RB3, Norit	pellet	1305	0.53	0.44	80
RB4	carbon RB4, Norit	pellet	1320	0.54	0.54	95
NaX	zeolite 13X, BDH	powder	613	0.26	>1.25	>456
NaX(P)	zeolite 13X, BDH	pellet	533	0.22	>0.77	>335
NaY	zeolite Y, Aldrich	powder	835	0.34	0.48	135
Al-WYO	pillared clay	powder	270	0.10	0.28	264
SG60	silica gel 60	powder	490	(0.72) ^b	0.07	(9) ^c

^a Key: A_{BET} , specific surface area determined by nitrogen adsorption at 77 K;²³ V_{DR} , microporous volume determined by Dubinin–Radushkevich plots applied to the nitrogen adsorption data;²³ m^{max} , saturation capacity for acetic acid at room temperature; V^{max} , ratio between the acetic acid volume correspondent to m^{max} and V_{DR} . All samples were previously outgassed. ^b Total porous volume determined at relative pressure of 0.95. ^c Ratio calculated to the total porous volume.

1320 m²/g, the microporous volume calculated through the Dubinin–Radushkevich model (V_{DR}) for 8 of the 9 materials is between 0.10 and 0.54 cm³/g, and for the mesoporous silica gel the total porous volume is 0.72 cm³/g.

The activated carbons, zeolites, and silica gels are commercial products (see Table 2 for details), and the pillared clay (Al-WYO) was prepared in our laboratory from a Wyoming commercial clay, according to a procedure described elsewhere.^{19,20} The parent material was a montmorillonite with a cation exchange capacity of 118.5 meq/100 g and an average particle size of 7.9 μm.¹⁹

2.1.2. Sodium Content of the Adsorbents. From the ideal formula,²¹ the two zeolitic materials, namely, NaX and NaY, have sodium contents of about, respectively, 15% and 10%, for the dehydrated forms, and 11% and 7%, for the hydrated forms. Accordingly to a previous analysis,¹⁹ the sodium content of the Al-WYO material is 1.8%.

To support the explanation proposed for several observations, that the content of sodium is modified during the process of adsorption, the determination of the sodium content of one sample [NaX(P)] was made before and after the adsorption process. For that, an amount of the adsorbent with approximately 0.02 g, previously dried at 373 K, was made to react with 2 cm³ of *aqua regia* and 3 cm³ of HF. The mixture was closed in an autoclave (ILC B240) and maintained at 393 K for 2 h. After cooling, 2 g of boric acid were added and the mixture was finally adjusted to 50 cm³ with deionized water. The concentration of sodium was determined by flame atomic absorption spectrometry (Pye Unicam SP9 spectrometer) after dilution of the original solution. The standards employed were prepared from a 1000 ppm standard solution (BDH) by dilution with water.

2.2. Saturation Capacity for Acetic Acid. The saturation capacity of the adsorbents at room temperature (between 295 and 297 K) was determined, exposing samples with approximately 1 g to the acetic acid saturated vapor (between 1.8 and 2.0 kPa, accordingly to the temperature) in a conventional Pyrex vacuum line. For such samples, the weight was periodically determined (to the nearest 0.00001 g) and the saturation capacity (m^{max}) was obtained when the mass increment of the sample changed less than 1% in a period of, at least, 7 h. The acetic acid (99.8%, Riedel-de-Haën) was purified in situ by freeze–vacuum–thaw cycles.

The solids were previously outgassed at 573 K for 2 h in a dynamic vacuum better than 10⁻² Pa, obtained by a combination of a rotary and an oil diffusion pump. The saturation capacity was expressed by weight of the outgassed sample. Samples of some adsorbents were also used

without previous outgassing. This was done considering the conditions of their possible use in a museum.

2.3. Isotherms of Adsorption of Acetic Acid. Isotherms of adsorption were obtained at low relative pressure, up to 0.06, in samples, with approximately 0.1 g, outgassed as described above. The temperature of adsorption was maintained with a water bath (VWR Scientific) at 298 K. The determination of the adsorbed quantities was made using the volumetric method. The pressure was measured with a capacitance transducer from Balzers Instruments (CMR 262). Nonideality was accounted by the use of the gas compressibility factor Z , expressed as function of the pressure P (in Pa), given by the equation $Z = 0.351 + 0.729P^{-0.176}$, which was obtained by fitting of data published elsewhere.²²

Results and Discussion

3.1. Studies at Saturation Pressure. 3.1.1. Saturation Capacity for Acetic Acid. The values for the saturation capacity at room temperature of the samples previously outgassed are shown in Table 2. In general, they were obtained when an equilibrium state was attained (in the sense described above), which happens, frequently, 2 days after the beginning of the essays. However, in the case of samples of NaX zeolite, regardless of the form of the adsorbent, the equilibrium was not achieved even after a week. Moreover, other phenomena unseen on other types of materials were observed here which were attributed to the presence of the Na⁺ ion (see section 3.1.4).

The NaY zeolite and the carbon materials, despite the differences between some of these adsorbents, have similar saturation capacities of about 0.5 g_{vapor}/g_{sample} (Table 2). For these samples, with the exception of NaY, the corresponding volumes of the adsorbed acetic acid, calculated through the liquid density of the adsorbate, within the experimental incertitude, are equal or less than the microporous volume determined by nitrogen adsorption at 77 K (Table 2). For the NaY sample, this value is greater than the microporous volume determined with N₂, but it is possible that in such a case, besides adsorption, occurred nonadsorption phenomena similar to those that took place with the NaX zeolite samples, although in a lesser extension, due to the sodium content.

Despite a saturation capacity for acetic acid smaller than that of the above-mentioned materials, the Al-WYO sample has an anomalously high value for the ratio of saturation capacity to the microporous volume. This fact must also be related with the presence of Na⁺. On the other hand, the low values reported in Table 2 for the SG60 sample may be due to the reduced microporosity of the solid.

Table 3. Parameters of the Kinetics Equations for the Adsorption of Acetic Acid at Room Temperature^a

sample	<i>n</i>	eq	<i>b</i> (g _{vapor} /g _{sample})	<i>c</i> (g _{vapor} /g _{sample})	<i>r</i> ²	<i>a</i> (g _{vapor} /g _{sample})	<i>α</i> (g _{sample} /g _{vapor})
CarbTech	6	1	8.03×10^{-2}	-0.49	0.971	1.91×10^{-4}	12.5
RB1	3	1	6.76×10^{-2}	-0.42	0.996	1.46×10^{-4}	14.8
RB3	4	1	4.20×10^{-2}	-0.026	0.978	2.28×10^{-2}	23.8
RB4	5	1	3.74×10^{-2}	0.093	0.997	4.45×10^{-1}	26.7
NaX	13	2	$1.59 \times 10^{-6} b$	0.28	0.993		
NaX(P)	7	2	$2.59 \times 10^{-6} b$	0.18	0.970		
NaY	10	1	7.33×10^{-2}	-0.44	0.960	1.79×10^{-4}	13.6
Al-WYO	5	1	1.18×10^{-2}	0.12	0.923	3.65×10^{-2}	84.7
SG60	6	1	1.11×10^{-1}	-0.92	0.975	2.67×10^{-5}	9.0

^a Key: *b* and *c*, parameters for eqs 2 (for NaX and NaX(P)) and 1 (for the other adsorbents); *n*, number of experimental points; *r*, correlation coefficient; *a* and *α*, parameters of the Elovich eq 3, calculated from *b* and *c*. ^b In g_{vapor}/g_{sample}.

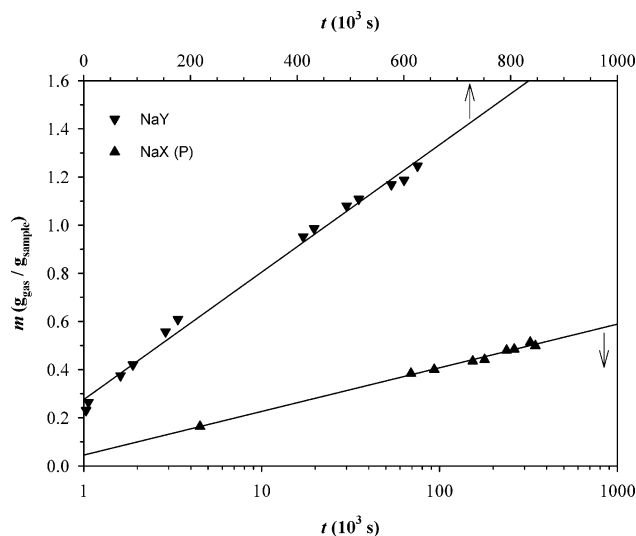


Figure 1. Mass of acetic acid adsorbed on NaY and NaX(P) samples vs the time of exposure of the adsorbent to the saturated acetic acid vapor. (Note, in the time axis, the arithmetic scale for the former sample and the logarithmic scale for the latter.)

Although the materials with the smallest saturation capacity (Al-WYO and SG60) have the smallest specific surface area, no simple relation was observed between the two parameters, as it could be expected, for the whole of the samples. Not even for a subset of materials with similar composition, such as RB1-, RB3-, and RB4-activated carbons,²³ it was disclosed any significant correlation between the adsorption capacity for acetic acid and the A_{BET} values. Generally, that absence of simple relationships can be related with other factors as the already mentioned influence of the sodium content or the possible dimerization processes that can be affected by the different superficial properties of the adsorbent materials.

3.1.2. Adsorption Kinetics. For all samples, the mass of acetic acid adsorbed (*m*) was plotted vs the time (*t*) and the equation that best described the relationship between these variables was singled out. As shown in Table 3, in the majority of cases, the equation has the form

$$m = b \ln(ft) + c \quad (1)$$

with *b*, *c*, and *f* as constants (see Figure 1, with the NaY zeolite example). *f* is a factor equal to 1 and has units of [time]⁻¹. For the NaX and NaX(P) samples (Figure 1), the equation has the form

$$m = bt + c \quad (2)$$

In the former situation, the relationship is in accordance with a process with a rate that decreases with time, whereas in the latter, the rate seems to be constant and in

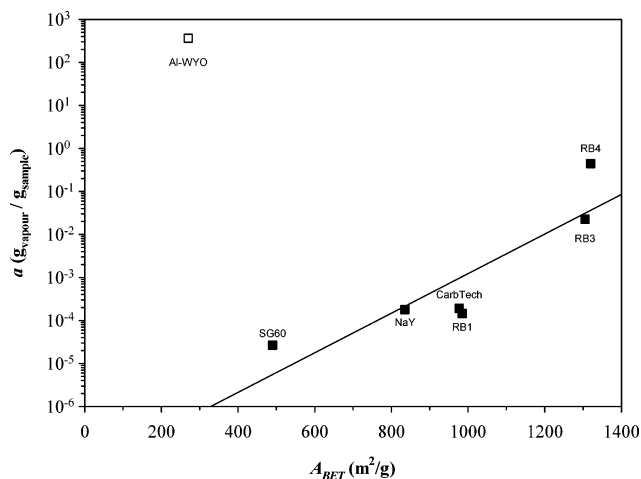


Figure 2. Elovich equation parameter *a* plotted against the specific surface area determined by nitrogen adsorption at 77 K. The point with an open mark was not considered for the calculation of the trend line.

agreement with the mentioned difficulty to reach the equilibrium.

In both cases, the data were not adequately represented, in general, by well-known models as the linear driving force (LDF) or the Fickian diffusion models.^{24,25} Only the data obtained for the NaY sample seem to be described by those models. In this case, the accordance with the last model is better than with the former, suggesting that the diffusion along the pores in the NaY zeolite is the rate-determining step and not the entry into the pores.²⁶

On the contrary, the Elovich model²⁷ seems to be useful for describing the majority of the studied systems. In fact, eq 1 has the form of the equation

$$q = \frac{1}{\alpha} \ln(ft) + \frac{1}{\alpha} \ln(a\alpha) \quad (3)$$

which is a simplified form of the Elovich equation, obtained when the amount adsorbed *q* at time *t* = 0 is zero and $t \gg (1/a\alpha)$, where *a* and *α* are constants and *f* is the same factor that appears in eq 1. The *a* constant is regarded as the initial rate, and of course, $a = b e^{c/b}$, where *b* and *c* are the two constants of eq 1. The *a* values calculated this way were presented in Table 3. Overall, the values follow the same trend as the correspondent values of A_{BET} , except for the Al-WYO sample (Figure 2). It is also noticed that, for the adsorbents that obey eq 1, the *b* constant obtained by regression, in general, is directly related with the saturation capacity for the acetic acid (Figure 3). The principal exception is the silica gel material, but this situation is probably due to the mesoporosity characteristic of this solid unlike to what happens with the other materials that are mainly microporous solids.

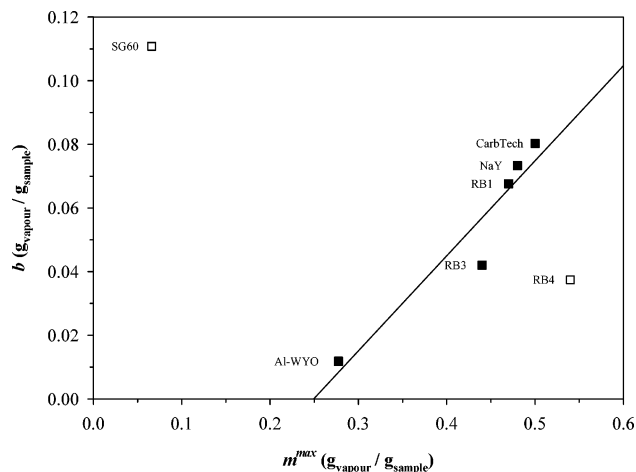


Figure 3. Saturation capacity for acetic acid plotted against the parameter b of eq 1. The points with open marks were not considered for the calculation of the trend line.

Table 4. Adsorption Capacity of Acetic Acid at Room Temperature (m^{\max}) of Samples without Previously Outgassing

sample	m^{\max} ($g_{\text{vapor}}/g_{\text{sample}}$)	
	uncorrected ^a	corrected ^b
RB1	0.47	0.49
RB3	0.45	0.47
NaX(P)	>0.85	>0.95

^a Expressed per unity mass of the adsorbent as is provided by the supplier. ^b Corrected per unity mass of the outgassed adsorbent.

3.1.3. Effect of the Previous Outgassing. The saturation capacity for acetic acid was determined for samples of NaX zeolite in pellets and RB1- and RB3-activated carbons not subjected to previous outgassing. The results are shown in Table 4 and are expressed both per unity mass of the adsorbent as provided by the supplier and per unity mass corrected from the weight loss observed in a different experiment with previous outgassing. This was made to allow the comparison with the results attained with the outgassed samples.

For RB1 and RB3, the obtained values are in accordance with the values reported in Table 2, within the experimental incertitude (deviation less than 10%). This suggests that the other substances that are adsorbed on the activated carbons when it arrives from the supplier, namely, the moisture, do not cause major prejudice to the adsorption of the acetic acid vapors. With the NaX(P) zeolite, an equilibrium state was not achieved, like in the essay performed with the outgassed sample. However, there are some differences in the observed phenomena, as described in the next section.

3.1.4. Nonadsorption Phenomena. The samples of the NaX zeolite previously outgassed (whether in pellet or in powder) acquired a dark color and showed a wet appearance after being exposed to the saturated acetic acid vapors for 48 h. After that time, but only in the case of pellets, it was observed that a liquid phase appeared in the contact points of the pellets with the cell glass and in the bottom of the cell.

With the samples not subjected to the previous outgassing, a similar situation arises, but after 24 h of acetic acid exposure, the formation of white crystals on the pellet's surface was observed (Figure 4), which dissolved several hours later. It was proposed that sodium acetate crystals

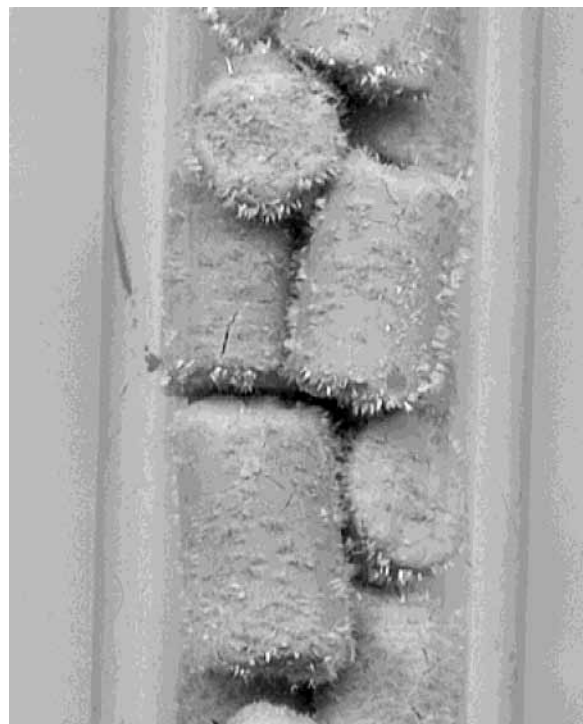


Figure 4. Crystals developed at the surface of the NaX(P) zeolite after exposure to the acetic acid, at saturation pressure, for about 24 h.

were formed by displacing the Na^+ ions of the zeolite by the acetic acid. To test this hypothesis, the sodium content of the zeolite was determined before and after the experiment. The results obtained, respectively, 10.9% and 6.3%, support our hypothesis.

The fact that the exposure of the NaX zeolite to the acetic acid vapors, unlike the other materials, does not conduct to an equilibrium state, as already described, is explained by sodium acetate formation.

From the chemical composition, one may expect that a similar process might occur with NaY zeolite, which, however, was not detected. This was most probably due to the fact that, on one hand, the sodium content of NaX zeolite is greater than that of NaY zeolite (about 88 Na^+ ions per unit cell in the former, against about 58 in the latter) and, on the other hand, the excess of ions in the NaX zeolite is mainly located in the zeolitic supercavities and, so, are more labile and easily exchanged than the Na^+ ions presented in other cavities of the NaX or NaY structures.

3.1.5. Reversibility of the Adsorption. After the adsorption experiments, several adsorbents have been subjected to a desorption process, exposing the samples to a dynamic vacuum better than 10^{-2} Pa, at room temperature. The results are shown in Figure 5 in the form of a plot of the fraction of the mass of the acetic acid that remains adsorbed vs time. They show that, despite the rapid desorption process that takes place in the beginning, a significant amount of acetic acid is not removed after 5 h (0.18×10^5 s) of exposure to vacuum. Either in absolute and relative terms, samples RB1 and NaY are those that retained high quantities of acid. In absolute terms, however, the differences between samples are small. Only the silica gel sample retained a much lower quantity of acetic acid, probably because of its predominantly mesoporous structure, which favors the desorption.

3.2. Isotherms of Adsorption for Acetic Acid. One of the main objectives of this work was to obtain detailed

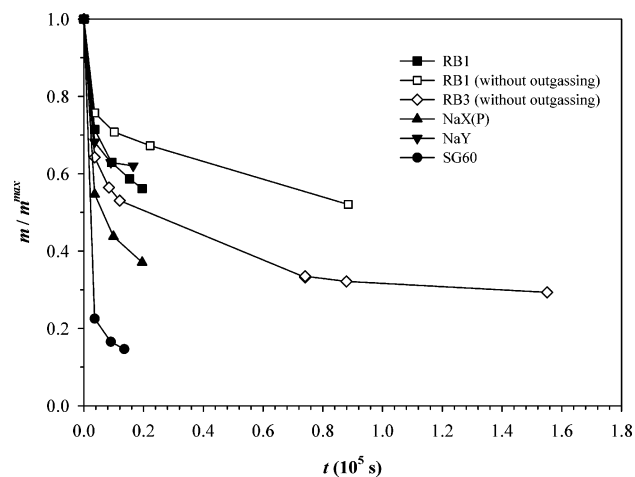


Figure 5. Fraction of the acetic acid that remains adsorbed on samples vs the time of exposure to vacuum.

isotherms of adsorption of acetic acid at low pressures since this situation is nearest to those that happens in museums. However, some experimental difficulties have led us to obtain only a few points per isotherm and no attempt was made to test the isotherms' reversibility. These difficulties, mostly due to the large amount of time that was necessary to attain an equilibrium state, probably are related with the reactions that acetic acid undergo, namely, the dimerization reaction.²⁸ Similar problems are probably in the origin of the lacking in the literature of thermodynamic data about the acetic acid and also of the acetic acid vapor adsorption studies. It can be noticed that of the several systems previously studied in the same vacuum line none put such significant experimental difficulties as the systems with the acetic acid.

The isotherms were obtained until values of relative pressures were about 0.06 (~0.13 kPa), although in the majority of cases the relative pressure of 0.02 (~0.04 kPa) was not exceeded. This second value corresponds to a concentration in atmosphere of about 400 ppm or about 1 g/m³, which is several hundred times the concentration found in most museum showcases, but comparable with the concentrations tested in other studies (Table 1). The isotherms were determined until the amount of the acetic acid adsorbed has a value that falls between ~13 and ~25% of the saturation capacity. The only exception is the SG60 material for which the quantity adsorbed at low pressure is comparable to the saturation capacity.

Within the experimental uncertainty, the isotherms are described by a straight line that passes through the origin (Henry isotherm), a situation which is expected due to the low-pressure range. As an example, Figure 6 shows the lines obtained in several essays. For each adsorbent, several determinations were made. Table 5 presents the number of experiments and the mean and minimum and maximum values obtained for the slope of each of the isotherms (Henry constant). According to these data, the NaX zeolite in pellet form and the RB4-activated carbon are the best materials for the removal of the acetic acid at reduced pressures since they present high values of the Henry constant.

3.3. Other Relations between the Adsorbents' Properties. The comparison of the results obtained at the saturation pressure with those obtained at reduced pressures shows that the saturation capacity for acetic acid and the Henry constants are correlated on the group of the activated carbon materials and NaY zeolite (Figure 7). The Henry constant is also related with another parameter

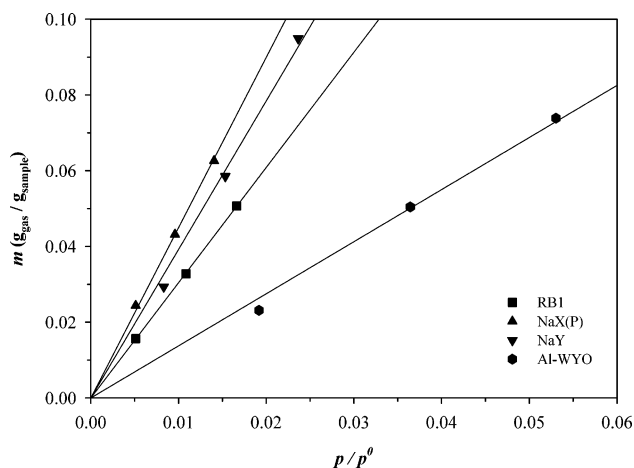


Figure 6. Isotherms of adsorption of acetic acid at 298 K in some adsorbents.

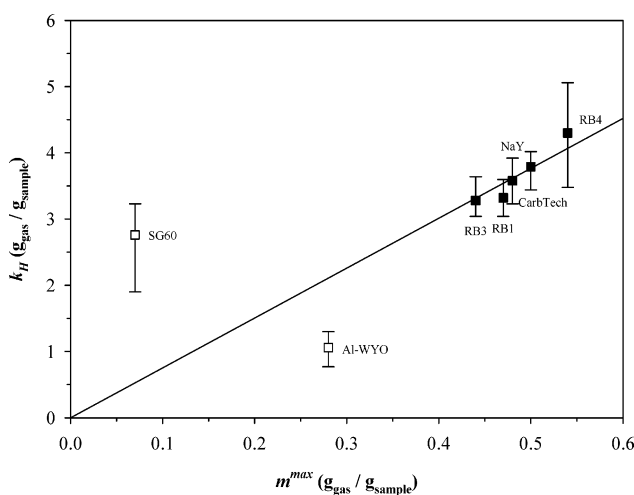


Figure 7. Relationship between the Henry constant and the saturation capacity of acetic acid. The points with open marks were not considered for the calculus of the trend line.

Table 5. Henry Constant (k_H) Obtained, from n Experiments, for the Adsorbents

adsorbent	k_H ($g_{\text{vapor}}/g_{\text{sample}}$)			
	mean	n	min	max
CarbTech	3.79	4	3.44	4.02
RB1	3.32	2	3.04	3.60
RB3	3.28	3	3.04	3.64
RB4	4.30	4	3.48	5.06
NaX	1.50	2	1.23	1.77
NaX(P)	4.26	3	3.95	4.49
NaY	3.58	2	3.23	3.92
Al-WYO	1.06	3	0.77	1.30
SG60	2.76	3	1.90	3.23

obtained at higher pressures (the Elovich parameter a), as it is shown in Figure 8. These observations are not obvious since at low pressures the adsorption could be primarily controlled by the nature of the interactions between the acetic acid molecules and the adsorbents' surface, while at high pressures, this factor is much less important. Therefore, it is not surprising that, for example, some points in the Figure 7, like those corresponding to the silica gel and PILC samples, stay away from the straight line.

However, a relation between the Henry constants and the adsorbent nature is not clearly visible. In fact, it can be noticed that materials with some similarities have different values of the Henry constant (RB3 and RB4, for example) and, conversely, some significantly different

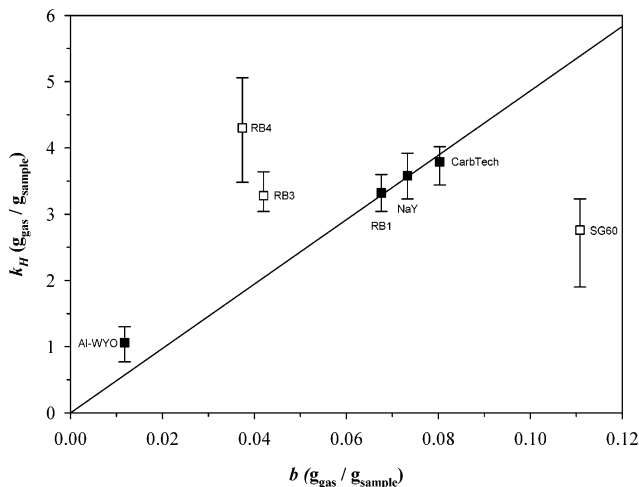


Figure 8. Relationship between the Elovich equation parameter a and the Henry constant. The point with an open mark was not considered for the calculation of the trend line.

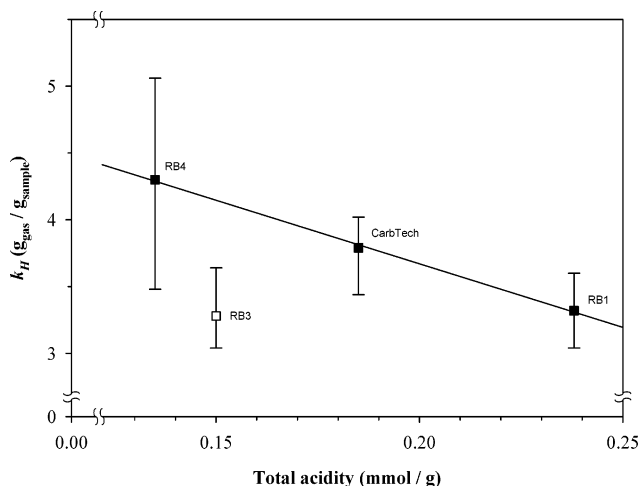


Figure 9. Relationship between the Henry constant and the total acidity of the activated carbon samples. The point with an open mark was not considered for the calculation of the trend line.

adsorbents have similar Henry constants (RB3 and NaY, for instance). In the same way, a general relationship was not found between the Henry constant and the acidic–basic properties of the activated carbons, previously determined by the Boehm titration,²³ although a trend seems to be noticed (Figure 9).

On the contrary, it seems that the Henry constants are dependent from the specific surface area, although the RB3 and NaX(P) samples deviate from the trend defined by the other materials, as shown in Figure 10.

It appears, therefore, that the adsorption process at lower pressures is a very complex process and it is significantly influenced by several factors that are also significant at higher pressures. Clearly, further experiments are needed to elucidate the details about the interaction between the acetic acid molecules and the surface of the adsorbents.

4. Conclusion

To our knowledge, the adsorption of acetic acid vapor in solids, particularly in activated carbons and zeolites, is a subject studied to a very limited extent. Probably, this situation is related to the experimental difficulties that arise from the reactions that acetic acid undergo in the vapor phase, namely, the dimerization. The data presented

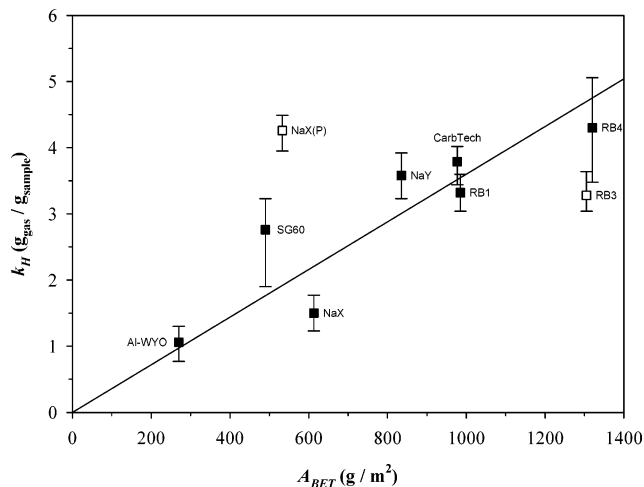


Figure 10. Relationship between the Henry constant and the specific surface area determined by nitrogen adsorption at 77 K. The points with open marks were not considered for the calculation of the trend line.

here suggest that the adsorption process is also a complex phenomena and can occur by mechanisms that, for some adsorbents, are beyond the physical adsorption.

Despite these problems, the results obtained at the acetic acid saturation pressure suggest that the NaX zeolite is the most efficient of the materials tested for the removal of this vapor from showcases. The data obtained at lower pressures showed that in such conditions the NaX zeolite in pellet form is comparable with the RB4 carbon. These two adsorbents are the best to be used in the display cases where the pressure of acetic acid usually do not exceed 1 mg/m³, that is, more than 1000 times less than the saturation pressure.

However, when we consider the competitive adsorption of other substances, such as the water vapor that also exists in the museum showcases, one must be very careful in the extrapolation of the results obtained with pure adsorbates. This effect is the subject of the work that is currently being done in our laboratory in which lead probes are exposed to a controlled atmosphere with acetic acid vapor and moisture with and without the presence of the adsorbents.

Literature Cited

- (1) Goffer, Z. *Archaeological Chemistry*; John Wiley & Sons: New York, 1980; p 207.
- (2) Tétreault, J.; Sirois, J.; Stamatopoulou, E. Studies of Lead Corrosion in Acetic Acid Environments. *Stud. Conserv.* **1998**, *43*, 17–32.
- (3) Tétreault, J.; Stamatopoulou, E. Determination of Concentration of Acetic Acid Emitted from Wood Coatings in Enclosures. *Stud. Conserv.* **1997**, *42*, 141–156.
- (4) Bradley, S.; Thickett, D. The pollution problem in perspective. In *Preprints of the 12th Triennial Meeting of the ICOM Committee for Conservation*; ICOM: Lyon, 1999; pp 8–13.
- (5) Thickett, D.; Bradley, S.; Lee, L. Assessment of the risks to metal artifacts posed by volatile carbonyl pollutants. In *Metal 98: Proceedings of the International Conference on Metals Conservation*; Mourey, W., Robbiola, L., Ed.; James & James: London, 1998; pp 260–264.
- (6) Kontozova, V.; Deutsch, F.; Godoi, R.; Godoi, A. F.; Joos P.; Van Grieken, R. Characterisation of air pollutants in museum showcases. In *Proceedings of art2002: The 7th International Conference on Nondestructive Testing and Microanalysis for the Diagnostics and Conservation of the Cultural and Environmental Heritage*; Van Grieken, R., Janssens, K., Van't dack, L., Meersman, G., Eds.; University of Antwerp: Antwerp, 2002.
- (7) Grzywacz, C. M.; Tennent, N. H. Pollution Monitoring in Storage and Display Cabinets: Carbonyl Pollutant Levels in Relation to Artifact Deterioration. In *Preventive conservation: practice, theory and research*; IIC: Ottawa, 1994; pp 164–170.
- (8) Brokerhof, A. W.; van Bommel, M. Deterioration of Calcareous Materials by Acetic Acid Vapour: A Model Study. In *Preprints of*

- the 11th Triennial Meeting of the ICOM Committee for Conservation; Bridgland, J., Ed.; ICOM: Edinburgh, 1996; pp 769–775.
- (9) Brokerhof, A. W. Application of Sorbents to Protect Calcareous Materials against Acetic Acid Vapours. In *Contributions to Conservation: Research in conservation at The Netherlands Institute for Cultural Heritage (ICN)*; Mosk, J. A., Tennent, N. H., Eds.; James & James: London, 2002; pp 16–24.
 - (10) FitzHugh, E. W.; Gettens, R. J. Calclacite and Other Efflorescent Salts on Objects Stored in Wooden Museum Cases. In *Science and Archaeology*; Brill, R. H., Ed.; MIT Press: Cambridge, MA, 1971; pp 91–102.
 - (11) Dupont, A.-L.; Tétreault, J. Cellulose Degradation in an Acetic Acid Environment. *Stud. Conserv.* **2000**, *45*, 201–210.
 - (12) Tennent, N. H.; Baird, T. Deterioration of Mollusca Collections: Identification of Shell Efflorescence. *Stud. Conserv.* **1985**, *30*, 73–85.
 - (13) Wegner, D. Lead Corrosion In Exhibition Ship Models. *Naut. Res. J.* **1998**, *43*, 32–41.
 - (14) Torge, M.; Jann, O.; Pilz, M. Simulating Pollution and Adverse Climatic Conditions: Sample Enamels Show Diverse Damage under Testing Conditions. *Restauro* **2000**, *106*, 436–441.
 - (15) Tétreault, J. Matériaux de Construction, Matériaux de Destruction. In *La Conservation Préventive: 3^e colloque international de IARAAFU*; ARAAFU: Paris, 1992; pp 163–176.
 - (16) Grosjean, D.; Parmar, S. S. Removal of Air Pollutant Mixtures from Museum Display Cases. *Stud. Conserv.* **1991**, *36*, 129–141.
 - (17) Parmar, S. S.; Grosjean, D. Sorbent Removal of Air Pollutants from Museum Display Cases. *Environ. Int.* **1991**, *17*, 39–50.
 - (18) Keneghan, B.; Martin E. Use of Molecular Sieve for Extending the Life of Cellulose Acetate Photographic Negatives. In *Care of Photographic Moving Image & Sound Collections*; Clark, S., Ed.; Institute of Paper Conservation: Leigh, 1999; pp 25–27.
 - (19) Carvalho, M. B.; Pires, J.; Carvalho, A. P. Characterization of Clays and Aluminium Pillared Clays by Adsorption of Probe Molecules. *Microporous Mater.* **1996**, *6*, 65–77.
 - (20) Pires J.; Carvalho, M. B.; Carvalho, A. P. Aluminum-Pillared Clays: Decomposition of the Intercalating Species and Textural Properties. *Zeolites* **1997**, *19*, 107–113.
 - (21) Breck, D. W. *Zeolite Molecular Sieves, Structure, Chemistry and Use*; John Wiley & Sons: New York, 1973; p 49.
 - (22) MacDougall, F. H. The Molecular State of the Vapor of Acetic Acid at Low Pressures at 25, 30, 35, and 40°. *J. Am. Chem. Soc.* **1936**, *58*, 2585–2591.
 - (23) Pires, J.; Pinto, M.; Carvalho, A.; Carvalho, M. B. Adsorption of Acetone, Methyl Ethyl Ketone, 1,1,1-Trichloroethane, and Trichloroethylene in Granular Activated Carbons. *J. Chem. Eng. Data* **2003**, *48*, 416–420.
 - (24) Reid, C. R.; Thomas, K. M. Adsorption of Gases on a Carbon Molecular Sieve used for Air Separation: Linear Adsorptives as Probes for Kinetic Selectivity. *Langmuir* **1999**, *15*, 3206–3218.
 - (25) Ruthven, D. M. *Principles of Adsorption and Adsorption Processes*; John Wiley & Sons: New York, 1984; p 167.
 - (26) Fletcher, A. J.; Thomas, K. M. Adsorption and Desorption Kinetics of *n*-Octane and *n*-Nonane Vapors on Activated Carbon. *Langmuir* **1999**, *15*, 6908–6914.
 - (27) Juang, R.-S. Preparation, Properties and Sorption Behavior of Impregnated Resins Containing Acidic Organophosphorus Extractants. *Proc. Natl. Sci. Counc. Repub. China, Part A: Phys. Sci. Eng.* **1999**, *23*, 353–364.
 - (28) Prausnitz, J. M.; Lichtenthaler, R. N.; Azevedo, E. G. *Molecular Thermodynamics of Fluid-phase Equilibria*; Prentice Hall: New Jersey, 1986; p 138.

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