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Physical Adsorption of H_2S Related to the Conservation of Works of Art: The Role of the Pore Structure at Low Relative Pressure

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Abstract. The adsorption isotherms of H_2S in selected adsorbents were determined at 298 K, at relative pressures up to about 0.005, aiming the use of these materials in the removal of that pollutant from the museums atmosphere. The Dubinin-Astakhov equation adjusts very well the experimental results, although one cannot interpret the pre-exponential factor w_0 as the limiting adsorbed amount. The parameter E, related with the adsorption energy, and the parameter n, that can be associated with the surface heterogeneity of the adsorbents, are correlated and the first is also correlated with the adsorbed amounts. It was not found any expectable relationship between the adsorbed amounts and textural parameters of the adsorbents such as the specific surface area or the microporous volume. This points out that the adsorption of H_2S is highly specific. In general, 13X and Y sodium zeolites seem to be the most effective adsorbents, but at lowest tested pressures, near the concentrations found at museums, a pillared clay prepared from a Wyoming montmorillonite seems to be more efficient.

Keywords: adsorption, zeolite, activated carbon, pillared clay, hydrogen sulfide, museum, conservation

Introduction

The hydrogen sulfide present in the atmosphere is one of the factors that leads to the alteration of works of art conserved in museums or shown in exhibitions in other places. One well-known problem is the silver tarnishing that gives a dark gray color to silver works due to the formation of the black silver sulfide on its surface (Costa, 2001). Another problem, less frequent but with major consequences, is the blackening of paintings and drawings as a result of a reaction between H_2S and some pigments of copper or lead and the consequent formation of the black coppers and lead sulfides, respectively (Smith and Clark, 2002). Copper resinate (a transparent green pigment composed mainly of the copper salts of resin acids) and white lead (a basic lead carbonate) are the pigments more susceptible to this changes but other examples are also known. Although copper resinate is not one of the pigments most used in paintings, white lead is, undoubtedly, the most important pigment in easel painting until the beginning of the 20th century. At least until the middle of 19th century, it is rare to find an easel painting without it (Gettens and Stout, 1966). Silver and pigments are examples of materials that may suffer specific attack by the H_2S in the atmosphere; but several others materials, namely those that are more sensitive to the pH, like paper, can suffer damages due to the acidic properties of this atmospheric pollutant.

Contrary to what happens to other museum pollutants, such as organic volatile compounds, the H_2S found in a museum gallery generally has its principal origin outside the building. Some materials may be a significant source inside, but just in special circumstances: when these materials are in closed environments, that is, in showcases or in rooms with

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poor gaseous exchange to outside. Wool is one of these materials, as H_2S may be released from sulphur amino acids, particularly cystine, that makes wool proteins (Brimblecombe et al., 1992). This potential source of problems is already identified in the literature related to museology and preventive conservation and, accordingly, it can be expected that wool materials are not to be used in the museums equipment or in the museums buildings, for instance in floor carpets. Mineral specimens, namely sulfide minerals (Waller et al., 2000), may represent another possible source of H_2S inside showcases. Of course, this is a specific problem of museums with mineralogical collections.

Therefore, the H_2S concentration in the museum atmosphere is usually related with its concentration in the museum surrounding, the gaseous exchange between inside and outside, and the air purification systems that may exist. The first of these factors is not controlled by the museum, as soon as the building is already established in one location. The second factor is linked to the architecture and the air circulation system and, at the best, only occasionally can be improved. The last variable, that is, the air purification, may be associated to an air-conditioned system, but can also be independent of that. In this case, in principle, it is the variable more easily managed, a situation that relies on the possibilities provided by adsorbent materials.

In fact, solids with adsorbent properties are used in museums, or they can be used, for the removal of pollutants from the atmosphere and, consequently, to protect the collections. With that purpose, adsorbents may be employed in one of two ways: in active mode, the air is forced through the adsorbent; in passive mode, the air is diffused naturally across the adsorbent. In the former situation, with the adsorbent embedded in an air-conditioned filter, for example, it is possible to control the atmospheric composition in a space like a room. The passive mode is more adequate for smaller spaces such as the interior of a display case. It has the advantage that results from the fact that it does not involve any equipment, since it is enough to place the solid inside the space that one wants to purify or near the works that can be attacked by the pollutants. This advantage is really important as many museums or, at least, many rooms in museums, do not have air-conditioned systems (Bradley, 1996). In the specific case of the H_2S, the passive solution is much more important since this gas, accordingly to some studies, does not seem to be controlled by the filtration system associated to the air-conditioned at all (Cassar et al., 1999). It must be pointed out, however, that other studies claim that some adsorbents, like activated carbon and zeolite 13X, have an excellent efficiency in the H_2S removal from atmosphere when used in active mode (Pasmar and Grojean, 1991). Probably, the opposite conclusions derive from the different pollutant concentrations involved on those studies, lower in the former, higher in the later.

The H_2S concentration in museum atmospheres varies significantly. On one side, it depends on the museum. On the other hand, for a certain museum, the concentration varies along the year. The measurements done in some museums seem to show lower concentration values in Summer and Fall than in Winter and Spring. Nevertheless, the values are frequently below the 0.1–0.3 ppb range, although they can go up to 1 ppb (Brimblecombe et al., 1999; Cassar et al., 1999; Ankersmit et al., 2000).

The studies done in museum contexts have been made with a H_2S source and a sample of the solid adsorbent on test in a closed space and through direct measurement of the pollutant concentration in this atmosphere (Pasmar and Grojean, 1991) or, indirectly, through the measurement of the tarnishing effect on a silver sensor also present (Bradley, 1985).

The problem of H_2S and its removal from atmosphere is not exclusive of museums. The same situation, although with other consequences, arises in relation with the air purification from odorous and toxic compounds in water treatment facilities (Bandosz, 2002). In this case, however, the levels of H_2S are much higher.

In spite of these diversified interests in the adsorption of H_2S by adsorbents materials and in spite of the value of several other methods and techniques used in studies with relation to that process, to our knowledge, a lack of some fundamental data exists about those systems, namely adsorption isotherms and parameters that can be obtained from these through the application of theoretical models. The principal objective of the work presented here is, precisely, to provide some fundamental data about the adsorption of H_2S at low pressures by selected absorbent materials, amongst them activated carbons and zeolites, which can be useful in the museum conservation contexts. Besides, the analysis of the isotherms was made in order to investigate the nature of the adsorptive process and to proceed to a useful generalization of the results. This study is related to a previous one focused on acetic acid adsorption (Cruz et al., 2004).

Experimental

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 1. For these adsorbents, the BET surface area values (A_{BET}) are between 270 and 1320 m^2/g, the microporous volume calculated through the Dubinin-Radushkevich model (V_{DR}) for 10 of the 11 materials is between 0.10 and 0.54 cm^3/g and for the mesoporous silica-gel the total porous volume is 0.72 cm^3/g. Because the nitrogen molecules and the access pores of the 4A zeolite have similar dimensions, the BET area value was not determined for that adsorbent and the microporous volume was calculated by water adsorption at 298 K.

Table 1. Characteristics of the adsorbent materials previously determined.

Sample label	Type and origin	Form	A_{BET} (m^2/g)	V_{DR} (cm^3/g)
CarbTech	Carbon Tech	Pellet	977	0.41
RB1	Carbon RB1, Norit	Pellet	985	0.44
RB3	Carbon RB3, Norit	Pellet	1305	0.53
RB4	Carbon RB4, Norit	Pellet	1320	0.54
FM4/250	Carbon cloth FM4/250, Long Life for Art	Carbon cloth	824	0.34
NaX	Zeolite 13X, BDH	Powder	613	0.26
NaX(P)	Zeolite 13X, BDH	Pellet	533	0.22
NaY	Zeolite Y, Aldrich	Powder	835	0.34
4A	Zeolite 4A, BDH	Pellet	–	0.25[a]
Al-WYO	Pillared clay	Powder	270	0.10
SG60	Silica-gel 60	Powder	490	(0.72)[b]

A_{BET}: specific BET surface area determined by nitrogen adsorption at 77 K; V_{DR}: microporous volume determined by Dubinin-Radushkevich plots applied to the nitrogen adsorption data. For the majority of samples, the values for A_{BET} and V_{DR} were previously presented by Pires et al. (2003).

[a] Determined by water adsorption at 298 K.

[b] Total porous volume determined by nitrogen adsorption at 77 K at relative pressure of 0.95.

The activated carbons, zeolites and silica-gel are commercial products (see Table 1 for details) and the pillared clay (Al-WYO) was prepared in our laboratory from a Wyoming commercial clay, accordingly to a procedure described elsewhere (Carvalho et al., 1996; Pires et al., 1997). 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 (Pires et al., 1997).

Isotherms of Adsorption of H_2S

Isotherms of adsorption of H_2S (Alpha gaz, Air Liquide) were obtained at low relative pressure, up to about 0.005, 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). Non ideality was accounted by the use of the virial equation of state with the second virial coefficient obtained by interpolation of the values presented by Dymond and Smith, 1980. However, this correction is inferior to 0.1%.

For the conversion of units, like the conversion of mmol/g to cm^3/g, was used the value of 0.778 g/cm^3 for the liquid density of the H_2S at 298 K, obtained from an equation published elsewhere (Perry and Green, 1999).

Results and Discussion

The isotherms obtained are presented in Fig. 1. In the most of the cases, the adsorption isotherms are concave in relation to the pressure axis, as it would be expected from the microporous nature of the adsorbents. The isotherm obtained for mesoporous SG60 silica-gel, however, is linear in the studied interval of pressures. The Henry isotherm obtained for this adsorbent has a Henry coefficient with the value of 30.0 mmol/g.

The isotherms obtained for the microporous solids present low-pressure hysteresis which is observed down to relative pressures as low as 1×10^{-4} (Fig. 2). This phenomenon is verified with some frequency in IUPAC type I isotherms and is due to processes that are different of those that occurs at higher pressures: at high pressures the hysteresis is a result of capillary condensation while at low pressures can be related with the distortion of the adsorbent structure (Gregg and Sing, 1982). However, other reasons may exist in the present

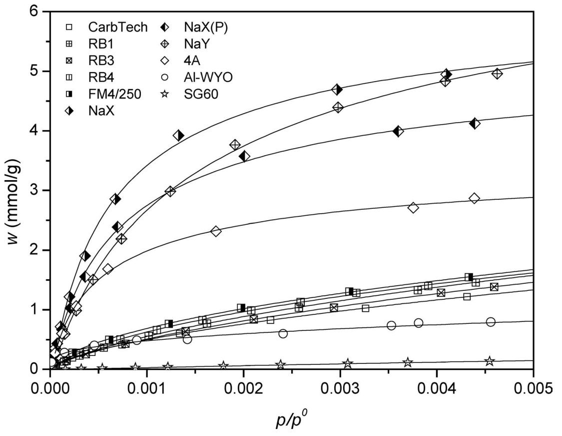

Figure 1. Adsorption isotherms of H_2S on select adsorbents at 298 K. The solid lines correspond to the Dubinin-Astakhov equation obtained by fitting of the data.

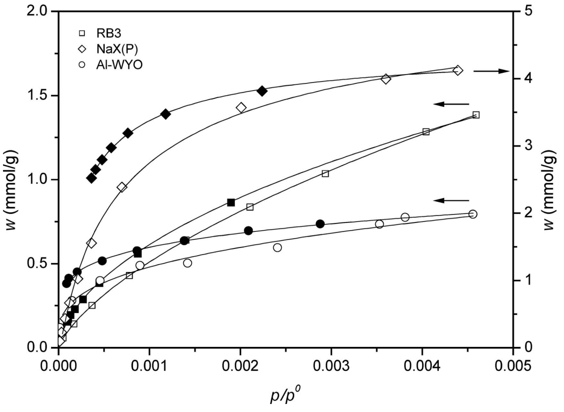

Figure 2. Adsorption isotherms of H_2S on three adsorbents of different nature at 298 K. The solid marks correspond to the adsorption process and the open marks to the desorption process. The solid lines show the Dubinin-Astakhov equation obtained by fitting of the data of each one of the branches.

case, as discussed below. The SG60 sample, which is predominantly a mesoporous solid, does not show such hysteresis.

Table 2. Parameters of the Dubinin–Astakhov equation (w_0, E and n) and amounts of H_2S adsorbed at relative pressures of 4.74×10^{-5} [w(0.1%)] and 4.74×10^{-3} [w(10%)].

Adsorbent	w_0 (mmol/g)	w_0 (cm^3/g)	E (kJ/mol)	n	w(0.1%) (mmol/g)	w(10%) (mmol/g)
CarbTech	23.5	1.03	5.1	1.12	0.071	1.28
RB1	12.9	0.56	8.1	1.53	0.052	1.53
RB3	16.6	0.73	6.8	1.36	0.054	1.41
RB4	7.8	0.34	10.2	1.79	0.061	1.57
FM4/250	12.6	0.55	7.9	1.38	0.101	1.62
NaX	6.1	0.27	19.2	4.75	0.230	5.11
NaX(P)	5.2	0.23	18.9	4.33	0.227	4.22
NaY	7.5	0.33	16.9	3.73	0.128	5.05
4A	3.5	0.15	19.7	4.23	0.254	2.86
Al-WYO	12.9	0.56	2.7	0.65	0.198	0.79
SG60	1.1	0.05	9.5	2.23	0.000	0.14

In a first glance, and according with Fig. 1, the tested adsorbents can be ordered according to the efficiency in the removal of H_2S, from the better to the poorest, in the following way: 13X and Y zeolites (NaX, NaX(P) and NaY samples); 4A zeolite; activated carbons (CarbTech, RB1, RB3, RB4 and FM4/250 samples); Al-WYO; and SG60. The last two materials are the solids with smaller values of BET area and with less microporosity. On the other hand, the superior efficiency of the zeolites compared to that of the activated carbons, not according to the mean values of the A_{BET} or microporous volume, could be explained because of the strong interaction that results from the greater polarity of the surface species in the formers with the polar molecules of H_2S [dipole moment = 0.97833 D (Lide, 2002)]. The fact that the materials with better capabilities for the adsorption, in the studied range of relative pressure, have been the large pore sodium zeolites, suggests that the presence of the extra-framework sodium cations is responsible for these favorable results obtained by the NaX, NaX(P) and NaY samples.

To elucidate these relationships in a quantitative manner, characteristic parameters for the isotherms were obtained using the Dubinin–Astakhov (D–A) equation, $w = w_0 \exp[-(A/E)^n]$. Here w is the amount of H_2S adsorbed, w_0 its limiting amount, E the characteristic adsorption energy, n a parameter related with the homogeneity of the adsorbent microporous structure, and A is the adsorption potential expressed by $A = -\mathrm{R}T \ln p/p^0$, where R is the gas constant, T the absolute temperature, and p/p^0 the relative pressure (Gregg and Sing, 1982; Bansal et al., 1988; Call, 1995). The equation was fitted to the experimental data using a non-linear least squares method and the obtained values for w_0, E and n are presented in Table 2. The curves obtained are plotted in Figs. 1 and 2. It must be noted that the D-A equation fits very well the experimental data.

The limiting amount, w_0, show a great variation, between 0.05 and 1.03 cm^3/g, and for some adsorbents it has values that are significantly greater than the microporous volume determined by nitrogen adsorption, which has a maximum value of 0.54 cm^3/g. In principle, having in mind only physical adsorption, this situation was not expected. One of the factors that can contribute to this is the use of a density value for the adsorbate inferior to the actual density. In fact, the value corresponding to the density of the liquid H_2S (0.778 g/cm^3) was used, as stated above, but it is possible that the H_2S in the filled micropores has a higher density, closer to that of the solid, as can be conclude from the discussion found in the literature about the correct density value to be used in nitrogen adsorption studies (Llewellyn et al., 1994). If we consider a density of 1 g/cm^3, inferior to the values that we found in the literature for the density of the solid H_2S (Blanc, 2002), only three adsorbents have a ratio w_0/V_{DR} significantly greater than 1, against the six obtained when is used the value of the liquid density. Another factor that can contribute to the apparent excessive value for the limiting adsorbed amount expressed in cm^3/g can be the occurrence of a chemical processes in addition to the physical adsorption. In fact, the occurrence of chemical reactions as result of the adsorption of H_2S is known in several solids, namely activated carbons, in the presence of oxygen (Bandoz, 2002). In these conditions, the oxidation of the H_2S, with the formation of sulfur, usually occurs. In the absence of oxygen it is also possible the occurrence of chemical adsorption, for instance in the zeolite 4A, which happens through dissociative processes (Garcia and Lercher, 1992). Another possibility is the formation of polysulfides (Bagreev and Bandosz, 2000). In the present case, the hysteresis at very low pressure can be interpreted as another consequence of some of those reactions. However, although the occurrence of chemical adsorption can not be excluded, this does not seem to be enough to explain the high value of the quotient w_0/V_{DR} since, for instance, the hysteresis does not seem to be more significant for the sample Al-WYO, the one that presents the higher value for that ratio, than for the generality of the other samples. A third factor that can contribute to the large value of the limiting amount can be the fact that the habitual interpretation of the value of w_0 involves an extrapolation for high pressures done from data obtained at very low pressures. Independently of the causes, it seems more correct in the present study to interpret that parameter just as a mathematical parameter of the equation of the curves that describes the isotherms, without special physical meaning. Besides, the comparison of the values obtained for w_0 with the plot in Fig. 1 shows that w_0 cannot be used as measure of the amount of H_2S adsorbed at low pressures.

For that reason, the amount adsorbed was calculated for two pressure values through the D–A equation. From the side of the highest pressures attained, it was selected the value of relative pressure of 4.74×10^{-3}, which corresponds to a concentration of 10% of H_2S in the atmosphere. From the side of the lowest pressures, it was chosen the value of 4.74×10^{-5}, in the limit of the experimental data, that is a concentration of 0.1%. These parameters were represented by $w(10\%)$ and $w(0.1\%)$, respectively, and their values are presented in the Table 2. In first place, these values clearly show that the relative efficiency of the adsorbents depends on the pressure, a fact that is not evident in the Figs. 1 or 2 due to the scale of the plots. Particularly important is the case of the Al-WYO pillared clay, which is one of the less efficient materials in the removal of the H_2S at the higher pressure, but it is one of the most efficient at the lower pressure. Again, this is most probably due to the specific interactions between the polar H_2S molecules and the surface groups, namely the OH groups of the clay sheets. These interactions are expected to be enhanced in the low coverage region.

The representation of $w(10\%)$ and $w(0.1\%)$ in function of BET area or, above all, microporous volume shows a relationship that is contrary to what is expected. In other words, the values of $w(10\%)$ or $w(0.1\%)$ do not increase with A_{BET} or V_{DR} but, on the contrary, they decrease, as can be seen in Fig. 3. Evidently, this implies that other factors are more important in the adsorption of H_2S. For the RB1, RB3, RB4 and CarbTech samples, for which we have data obtained by a Bohem titration, these factors are not related with the acidity or basicity of the adsorbents, as it is not visible any relation

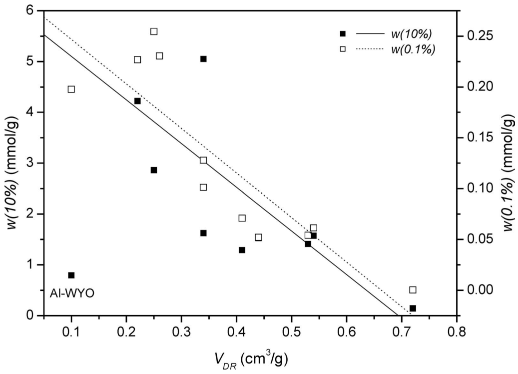

Figure 3. Relationship between the amounts of H_2S adsorbed at relative pressures of 4.74×10^{-3} [$w(10\%)$] and 4.74×10^{-5} [$w(0.1\%)$] and the microporous volume, V_{DR}. The lines show the respective trends. The point with a label (Al-WYO) was not considered for the minimum square adjust.

between $w(10\%)$ or $w(0.1\%)$ and the number of acid or basic sites. This is in accordance with studies that showed that it is not simple the relationship between the amount of H_2S adsorbed and the acid-basic characteristics of the adsorbent (Bandosz, 2002). Furthermore, it must be noted that the ratio $w(10\%)/V_{DR}$, with $w(10\%)$ expressed in cm^3/g, has values greater than 0.5 for the zeolitic samples and, consequently, most of the pores are filled at a relative pressure of H_2S about 0.005, particularly the zeolite 13X ($w(10\%)/V_{DR} = 0.91$ and 0.86 for the NaX(P) and NaX samples, respectively).

The second parameter of the D–A equation, the E parameter that can be related with the adsorption energy, is clearly dependent from the nature of the adsorbent: for the four activated carbons it varies between 5.1 and 10.2 kJ/mol; for the four zeolitic materials it has values from 16.9 to 19.7 kJ/mol. These highest adsorption energies obtained for the zeolites can explain the increase in the affinity of H_2S for those materials. In a general way, the $w(10\%)$ and the E parameters are correlated, being the samples SG60 and 4A the ones that deviate from the trend (Fig. 4). In the case of SG60 silica-gel the situation can be explained by its mesoporosity; in the case of the zeolite 4A the reason for it may be related with its small pore size (nominal pore diameter of 0.39 nm) compared with the diameter of the H_2S molecule [0.49 nm, calculated from the liquid density (Gregg and Sing, 1982)]. The parameter $w(0.1\%)$, likewise, depends on E, but the relationship is not so clear. The correlation between E and $w(10\%)$ suggests that, at the pressure for which was calculated the parameter $w(10\%)$, it is the adsorption energy that controls the amount of H_2S adsorbed more than any other factor.

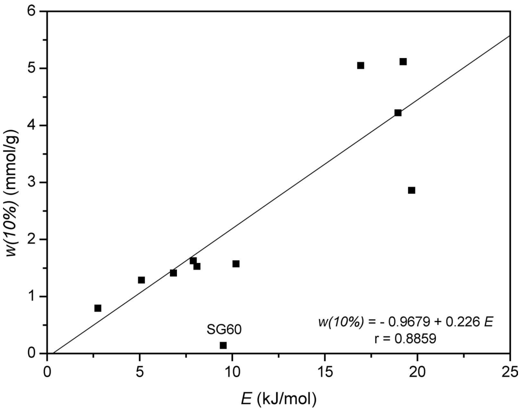

Figure 4. Relationship between the amounts of H_2S adsorbed at relative pressure of 4.74×10^{-3}, $w(10\%)$, and the Dubinin-Astakhov equation parameter E. The point with a label (SG60) was not considered by the trend line.

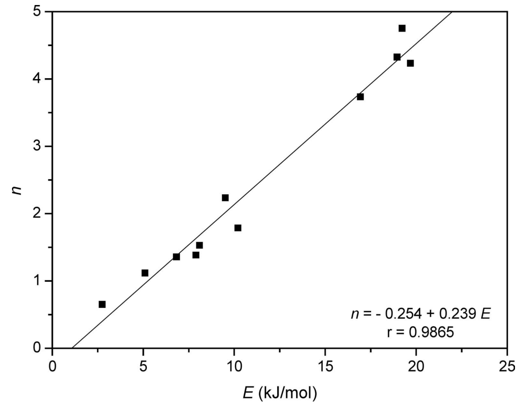

Figure 5. Relationship between the Dubinin-Astakhov equation parameters n and E.

The third parameter of the D–A equation, the n parameter that can be related with the surface heterogeneity, varies between 0.6 and 4.7, corresponding the smallest values to the Al-WYO clay and the activated carbons and the highest values to the zeolites. It is observed a positive correlation between n and E that is very significant (Fig. 5) which suggests that the heterogeneity of the adsorbent is a factor with great importance in the adsorption of the H_2S. This suggestion is in agreement with the results obtained in other studies, although in different conditions, that lead to conclusion that activated carbon materials with significant heterogeneity are more efficient in the adsorption of the gas than other more homogeneous solids with high superficial area (Bandosz, 1999).

In relation to the problem raised by the museums that was in the origin of the present study, it should be noticed that there is another factor that will affect the performance of the adsorbents tested: the composition of the atmosphere to which are exposed the objects to protect. In fact, the presence of water and other substances in the form of gas or vapor should have a significant effect in the amount of adsorbed H_2S and, as the its magnitude should be dependent on the nature of the solid, the relative efficiency of the tested adsorbents can be changed. Even if, the obtained results do not allow the anticipation of these effects in a complete way, we believe that the data in this work is a valuable contribution for the general problematic of H_2S removal in museum atmospheres and, given the importance of this type of information to the museum context, we intend to develop an experimental setup that allows the evaluation of the adsorbents performance regarding the adsorption of H_2S in the presence of other compounds.

Conclusions

The present study shows that adsorbents materials can be used in a passive mode with the objective of lowering the H_2S concentration in museums atmosphere. Although, in a general view, 13X and Y sodium zeolites, with large pores, seem to be the most effective adsorbents, at very low pressures, as it happens in museums, materials as the pillared clay tested (Al-WYO) can remove larger amounts of the pollutant, in spite that they have a small microporous volume and a small saturation capacity. It must be noted, however, that it is risky to do generalizations concerning the efficiency of other materials since the adsorption of H_2S seems to be highly specific and, therefore, the specific surface area, the microporous volume or other textural parameters cannot be used as indicators of the amounts of H_2S that can be adsorbed. On the other hand, it should be noted that in the real situation inside a museum the atmosphere has other substances in its composition that will have effects in the amount of H_2S adsorbed by each adsorbent material.

Nomenclature

A	adsorption potential (kJ/mol)
A_{BET}	BET surface area (m^2/g)
E	energy of adsorption calculated through the Dubinin-Astakhov equation (kJ/mol)
n	parameter of the Dubinin-Astakhov equation
p	H_2S pressure at 298 K (Pa)
p^0	H_2S saturation pressure at 298 K (Pa)
R	gas constant
T	absolute temperature (K)
V_{DR}	microporous volume calculated through the Dubinin-Radushkevich model (cm^3/g)
w	H_2S amount adsorbed at pressure p (mmol/g)
$w(0.1\%)$	H_2S amount adsorbed at pressure $p/p^0 = 4.74 \times 10^{-5}$ (mmol/g)
$w(10\%)$	H_2S amount adsorbed at pressure $p/p^0 = 4.74 \times 10^{-3}$ (mmol/g)
w_0	limit amount of H_2S adsorbed calculated through the Dubinin-Astakhov equation (mmol/g or cm^3/g)

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