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Original article

Comparison of adsorbent materials for acetic acid removal in showcases

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Abstract

The effect of selected adsorbents in the preservation of objects of cultural value was studied. For this, two adsorbents that, in previous studies, revealed to be effective in the adsorption of acetic (ethanoic) acid vapors (activated carbon RB4 and NaX zeolite), were used in tests where lead sensors were exposed to the vapors of an acetic acid aqueous solution (corresponding to a concentration of acetic acid in atmosphere of about 160 mg m^{-3}). The protection provided by the adsorbents was measured through the comparison of the increase of the sensor mass in the presence and in the absence of the adsorbents. The RB4 activated carbon has shown to be the most advantageous adsorbent. With amounts corresponding to 3.3 kg per m^3 of the volume showcase, it originated a decrease of the lead alteration of 50–70% for some months. It was verified that it is possible to recycle the RB4 with good yield by heating it at 120°C during 24 h. It was not detected any decrease of efficacy after one cycle of use. The extension of the regeneration suggests that it will be possible to reuse the material several times.

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1. Introduction

Acetic (ethanoic) acid is one of the atmospheric pollutants that can be found inside museums in concentrations that can produce significant effects in the objects on exhibition. Several materials can suffer fast alteration by exposition to acetic acid vapors, but, probably, it is the lead and the lead alloys that can show more serious consequences. Significant problems have been reported with coins [1], document seals [2], weights [3], sculptures [1] or Oriental lacquer objects [4], among other objects made of lead or with lead components. Between the lead and the acetic acid a specific interaction exists, which does not occur with mineral acids and, that is responsible for an exceptional conservation problem. It is interesting to notice that one of the painting pigments with greater historical importance, the white lead, traditionally was prepared, precisely,

exposing lead pieces to vapors of acetic acid released by vinegar, corresponding the pigment to the alteration product formed at the metal surface [5]. Besides, this pollutant can also attack other materials, such as, for example, copper alloys [6,7], paper [8], shells [9] or other calcareous materials [10]. It was already stated that, at least in some European museums, acetic acid is the more significant cause of the deterioration [11].

While some of the atmospheric pollutants in museums have its origin outside, the main source of acetic acid is, usually, inside, where it can be released by the building materials or the furniture. The wood, especially wood not aged, wood panels and synthetic polymeric materials used in the museum equipment, namely adhesives and other plastics, are among the materials that can release larger amounts of volatile organic compounds, like acetic acid [12–16]. Even if the amounts of acetic acid released by these materials are low, when they are used in closed spaces, as inside showcases, relatively high concentrations can be reached. In fact, values higher than $3000 \mu\text{g m}^{-3}$ were already detected inside museum showcases, when outside the buildings the concentration of the acetic acid in the atmosphere usually is between 0.1 and $100 \mu\text{g m}^{-3}$, depending on the pollution degree [17]. It must

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be noted that the “no observable adverse effect level” of acetic acid on lead was determined to be $430 \mu\text{g m}^{-3}$ and, in consequence, was suggested that the pollutant concentration should be maintained below $100 \mu\text{g m}^{-3}$ [7,18], although this is a matter of dispute [19,20].

Obviously, a good selection of the materials from which showcases must be made is the principal measure that can be taken to prevent such problems. Another is the removal of the pollutants from inside showcases, because unsuspected sources of pollutants may exist. That removal can be done by means of adsorbent materials, which can be employed in a passive mode (simply putting the adsorbent close to the objects to protect) or in an active mode (forcing the air to pass through the adsorbent) [21,22].

Zeolites and activated carbons are the types of adsorbent materials that, in general, have larger application for the removal of pollutants. In the specific case of acetic acid vapors, there is definitely a lack of reported studies concerning the adsorption of this pollutant, although many museums and conservators employ adsorbents within showcases and other containers (e.g., archival storage boxes). Above all, in spite of the works already published, there is the need for systematic studies, conducted specifically for museum atmospheres, on the relative efficiency of the available adsorbent materials. It was in this context that we have initiated a study with the objective of comparing the efficiency of several zeolites, activated carbons and other adsorbent materials, namely silica gel and a clay pillared with aluminum oxide pillars (PILC), for the removal, in a passive mode, of acetic acid vapors from the atmosphere [23,24]. In a first stage, nine adsorbents were studied and for each one the adsorption capacity at the saturation pressure of the acetic acid and the adsorption isotherm at low pressures were determined at room temperature. Accordingly to the obtained results, the best adsorbents are the NaX zeolite in a pellet form and an activated carbon from Norit (RB4). Those studies were conducted in atmospheres constituted only by acetic acid and therefore they do not consider the possible interaction with other substances usually present in the museum atmospheres as, for instance, the water vapor. Besides, such studies do not show the conservation consequences in the lead objects from the use of the adsorbents. Likewise, they do not consider the effect of certain variables such as the amount of adsorbent that should be used in a certain space or the time that should not be exceeded without the substitution of the adsorbent. Therefore, in a second phase of the study, tests with the two more efficient adsorbents (NaX zeolite and the activated carbon RB4) were done with recourse to lead sensors that were weighed from time to time. The sensors were maintained in a closed space where a source of acetic acid vapors was present and several variables that could influence the process were considered. The results obtained in this second phase are presented here.

2. Experimental

2.1. Adsorbents and lead sensors

Adsorbents were characterized and selected in previous studies [24]. RB4 is an activated carbon in pellet form (from

Norit, Holland) with a specific surface area of $1320 \text{ m}^2 \text{ g}^{-1}$ and a microporous volume of $0.54 \text{ cm}^3 \text{ g}^{-1}$. NaX is a zeolite X, also in pellet form, from BDH, with a specific surface area of $533 \text{ m}^2 \text{ g}^{-1}$ and a microporous volume of $0.22 \text{ cm}^3 \text{ g}^{-1}$. In previous publications was labeled as NaX(P) or NaXP [23,24].

In a way to tentatively approach the final use of the adsorbents, these were used as received, that is, without any previous cleaning. Consequently, they had substantial amounts of adsorbed compounds, namely water. From the results obtained during the experiments, we can estimate this adsorbed amounts as 4.2 and 12.8% of the degasified mass for the RB4 and the NaX adsorbents, respectively. The adsorbents were used as received because we wanted to simulate, as close as possible, the conditions available in some museums. However, in one set of experiments, adsorbents regenerated from the materials used in the previous set were tested also. The regeneration was made by heating the used adsorbents in a sand bath at 120°C during 24 h.

Small pieces of lead (with about 4 cm^2 and 3 g), cut from a lead plate (from V. Reis, Portugal, 98%), were used as sensors. Immediately before use, the lead was cleaned in a solution of hydrochloric acid 10%, washed with deionized water and acetone, and air dried.

2.2. Experiments

The experiments were done in glass flasks with a polyethylene lid and a total capacity of about 600 cm^3 . In each flask, as shown in Fig. 1, a goblet with the lead sensor was put together with a test tube with 5 cm^3 of a solution of acetic acid 2% (v/v), and, except in the flasks used as reference, another goblet with the adsorbent. The experiments were done in three sets (Table 1), each one involving 10 flasks simultaneously. The flasks were kept at room temperature, exposed to similar light conditions. The tests were always made in duplicate and therefore in each group of 10 flasks, eight were used to test four



Fig. 1. Experimental setup: goblet with adsorbent (left), test tube with the acetic acid solution (center), and lead sensor at the top of a goblet (right).

Table 1
Experiments and experimental conditions

Experiments	Adsorbents	Adsorbent mass/g	Time/ days	Remarks
Set 1	NaX, RB4	0.5; 2	45	—
Set 2	NaX, RB4	2	77	In some experiments, the adsorbent was regenerated from the material used in set 1
Set 3	RB4	0.2; 1; 2; 3	55	—

different conditions and two, without any adsorbent, were used as references.

The concentration of acetic acid in the atmosphere inside the flasks can be estimated through the Henry's law. However, there is no agreement among the values published for the Henry's law constant for the aqueous solution of acetic acid. The best available values are between 4.1×10^3 and 9.3×10^3 mol dm $^{-3}$ atm $^{-1}$, at the temperature of 25 °C [25]. If we do not consider deviations from the ideal gas model, the concentration of acetic acid in the flasks atmosphere, in accordance with those limits, was between 98 and 222 mg m $^{-3}$ or was about 160 mg m $^{-3}$ (mean value).

Similar experiments were also made with a solution of acetic acid 0.08%, corresponding to a concentration in the atmosphere of about 6.4 mg m $^{-3}$. In those conditions, the minute variation of sensor mass (determined with an analytical balance Mettler mod. H54 with a precision of 0.01 mg) did not allow us to obtain the same type of results and, therefore, those tests are not registered in Table 1.

In both conditions the relative humidity was expected to be high due to water vapor from the acetic acid solution, and near constant due to approximately unchanged temperature.

The experiments were monitored through the weight variations of both, the adsorbents and the lead samples. In each set, the weight of the lead sensors in the presence of the adsorbents was compared with the weight of other sensors exposed to the same conditions but in the absence of adsorbents. A parameter of the protection proportioned by an adsorbent was calculated through the equation:

$$\text{Protection} = \left(1 - \frac{\Delta m_{\text{Pb}}}{\Delta m_{\text{Pb}}^0} \right) \times 100$$

where Δm_{Pb} and Δm_{Pb}^0 are the average percentage of the mass increase of the lead sensors in the presence and in the absence of the adsorbent, respectively. The values of Δm_{Pb} and Δm_{Pb}^0 were calculated from two sensors. A value of 0% for the Protection parameter implies that the adsorbent cannot offer any protection to the lead and a value of 100% mean that the adsorbent prevent any change of the metal.

The mass increase of a given adsorbent was expressed by Δm_{ad} , corresponding to the mass increase (in %) obtained from the samples used in two flasks.

The results obtained for the lead sensors are presented as a plot of the *Protection* parameter against the exposition

time to the vapors of the acetic acid solution. Similar plots are presented for the adsorbents but with the parameter Δm_{ad} against the time.

2.3. Thermal analysis

Thermal analysis of the adsorbents before and after the experiments and of the alteration products formed at the surface of the lead sensors was made in a Setaram TG-DSC 111 apparatus. Samples with 10–20 mg were heated in an aluminum crucible from room temperature up to 400 or 700 °C, at a rate of 5 °C min $^{-1}$, in a nitrogen atmosphere with a flux of 0.5 cm 3 s $^{-1}$. The mass loss and the heat flow were registered simultaneously.

2.4. Scanning electron microscopy

The surface of some lead sensors, before and after use, was observed with a JEOL JSM-5200LV scanning electron microscope (SEM). The sensors were gold coated by sputtering.

2.5. X-ray diffraction

With the objective of characterization the alteration products formed at the surface of the lead, the X-ray diffraction (XRD) pattern was obtained for the products removed from the sensors. The powder diffractogram was obtained in a Philips PX 1820 diffractometer using the K α copper radiation.

3. Results and discussion

3.1. Lead alteration

As a result of the exposition to the vapors liberated by the acetic acid solution, the lead samples used as sensors began by being matte and had darkened and were iridescent. Those changes were already significant in some samples after the first day. Later, they began to exhibit products of alteration with white color that in some cases, particularly in the case of the samples exposed without adsorbents, developed very significantly (Fig. 2). In the flasks without adsorbents, the amount of the white compounds formed after 10 days was already meaningful. At the end of the tests, the lead plates had attained a mass increase of about 1%, at most.

The observation of the samples surface with SEM at a magnification of 500 times show significant differences between the dark gray and the white surfaces. However, at higher magnifications the same structures are visible in the two cases: aggregates of tabular particles with a diameter in the order of 10 μm and random orientation, and more compact aggregates of particles apparently more spherical in the order of 1 μm. At the lower magnification, it is possible to see the original surface behind the crystals developed in the dark surfaces, but not in the lighter.

The X-ray diffraction pattern obtained for the white material formed at the surface of some samples is of difficult



Fig. 2. Lead sensors with alteration products of gray (left) and white color (right).

interpretation probably due to the preferential orientation of the crystals — a very significant problem, for instance, with the lead carbonates [26]. Some of the peaks can be attributed to plumbonacrite (ICDD 19-680), a black lead oxide carbonate hydroxide ($6\text{PbCO}_3 \cdot 3\text{Pb}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$). One of the lead acetate oxide hydrates (ICDD 18-1739 and 18-1740) with white color, probably the former, with the formula $\text{Pb}_3(\text{CH}_3\text{CO}_2)_6 \cdot \text{PbO} \cdot \text{H}_2\text{O}$, may also be present.

The same material was subject to thermal analysis (Fig. 3). It was observed an endothermic peak centered at 230°C accompanied by a decrease of mass of 3.1% between 215 and 242°C . A succession of three or four endothermic peaks, not resolved but successively more endothermic, was observed between 260 and 350°C . In this range of temperature the mass loss was 8.3%. The last peak was centered at 331°C . The lacking of systematic reference data about the thermal processes suffered by the lead salts prevents the detailed

interpretation of these data. However, it is possible to do some observations based on the data presented in some reference works [27,28]. It is known that the lead acetate trihydrate had undergone several successive transformations at 204°C , between 230 and 270°C , between 275 and 325°C , and between 325 and 380°C [29], but the pattern obtained, shown on Fig. 3, can not be due to such a compound, because it is not observed any peak at lower temperatures, between 30 and 110°C , due to the melting and the dehydration process. For the lead acetate trihydrate, the processes between 230 and 380°C correspond to the transformation of acetate groups in to oxide groups and do not involve the lead acetate trihydrate, which in the meantime was transformed, but involve the resulting compounds. Probably, the processes shown in the thermogram are similar to those and they can have origin in a compound like the lead acetate oxide hydrate that, according to the XRD pattern, seems to be present. The peak at 331°C can also be related with the decomposition of the lead carbonate, which, according to the tabulated data, occurs at about 315°C [28] even if, in practice, that process is only concluded at about 350°C [26,30]. Although the lead carbonate was not identified by XRD, the lead oxide carbonate hydroxide should also undergo decomposition of the carbonate group at comparable temperatures. Due to the mass decrease observed, that peak should not result from the melting of lead at 327°C (which, moreover, should not be present in the analysed sample because only the alteration product was collected).

It should be noticed that the number of possible alteration compounds formed at the lead surface is very large and depends significantly on the acetic acid concentration and the time of exposure [18].

3.2. Effect of the nature of the adsorbents

In the experiments done with equal amounts of zeolite and activated carbon (experiment sets 1 and 2), the protection

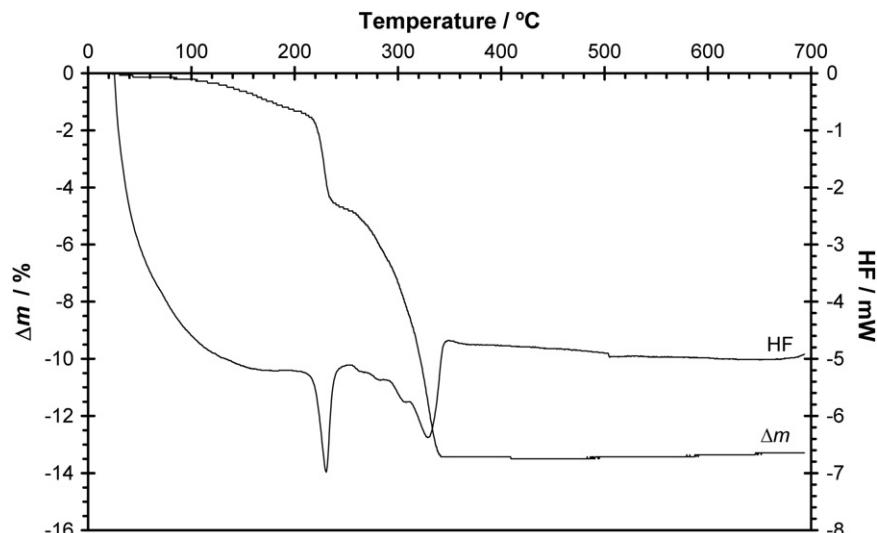


Fig. 3. Thermogram of the white alteration product removed from a lead sensor. Δm = mass loss; HF = heat flow.

provided by the adsorbents, in general, was comprised between about 30 and about 50% and was not clearly dependent of the nature of the adsorbent (Figs. 4 and 5). In the experiment set 1, after 45 days, the protection parameter had a value of 32 and 35% for 0.5 g of RB4 and NaX, respectively, and 56 and 48% for 2 g of the same adsorbents. In experiments set 2, after 77 days, the values of 54 and 48% were obtained for 2 g of RB4 and NaX, respectively. If at the beginning of the experiments the zeolite provided a superior protection than the activated carbon, at the end, this situation only occurs with the lower amount of the adsorbent. With an amount of 2 g, the activated carbon revealed a better efficiency than the zeolite after the first days, succeeding that at the end the values obtained in the two sets are notably consistent. However, it should be noticed that the experimental uncertainty is greater at the beginning of the experiences than at the end. In fact, due to the smaller amount of the alteration products formed, the errors in the weighting are more significant in the first days because the protection parameter is expressed in percentage, which can account for the larger oscillations of the curves (Figs. 4 and 5) observed for short times.

The mass increase of the adsorbents in the experiment set 1 is plotted against the time in Fig. 6. As expected, it shows that after some time, here called saturation time, the mass variation of the adsorbents is insignificant. That time is different for the two adsorbents: the zeolite is saturated faster than the activated carbon. This happens not just because the value of maximum adsorption for the zeolite is smaller, but also because the adsorption process is initially faster for this adsorbent, as revealed by the highest slope of the curve before the saturation time. Therefore, the zeolite protects more the lead probe in the beginning of the experiments, but, from a certain moment, it becomes the less efficient protector material. Because of the more polar character of the zeolite surface, a stronger interaction can be predicted between this solid and the polar molecules of the acetic acid than between these molecules and the activated carbon surface. This different interaction is

clearly visible in the thermogravimetric curves in the Fig. 7 which shows that the removal of the adsorbed compounds is much easier in the case of the activated carbon than in the case of the zeolite. So, the superior efficiency of the zeolite in the beginning of the experiments can be explained by the stronger interaction between the adsorbent and the adsorbate, although this polar factor did not seem to have great importance in the conditions employed in the previous studies [24]. The fact that, for any of the adsorbents, the adsorbed amount in percentage is greater when a smaller amount of adsorbent is used can be explained by the easier diffusion of the acetic acid in the goblet with a reduced amount of the adsorbent.

The time to reach the saturation capacity is higher for the RB4 carbon than for NaX zeolite and, as expected, increases with the mass of the adsorbent. According to the results obtained in the experiments set 3, there is a direct relation between the saturation time for the activated carbon and its mass. From the plots like those in Fig. 6, we can estimate the values of the mass increase of the adsorbents corresponding to the plateau which are 35% (standard-deviation, $s = 2\%$; number of determinations, $n = 14$) for RB4 and 16% ($s = 3\%$, $n = 6$) for NaX. These values, however, do not take into account the compounds already adsorbed before the experiments and, on the other hand, were calculated with the mass of the adsorbent not previously desorbed. Considering these facts and the data provided by the thermograms, we can estimate the value of maximum adsorption for the RB4 carbon, at the conditions employed, as 41%. This value is significantly inferior to the value of 54% obtained in a previous study, by another method, for an atmosphere of pure acetic acid at its saturation pressure [24]. Therefore, due to the moisture in the atmosphere or the lower concentration of the acetic acid vapors, the maximum capacity of adsorption of the activated carbon, as determined with an atmosphere of pure acetic acid, the present case is not completely available. A similar situation occurs for NaX zeolite: the value of maximum

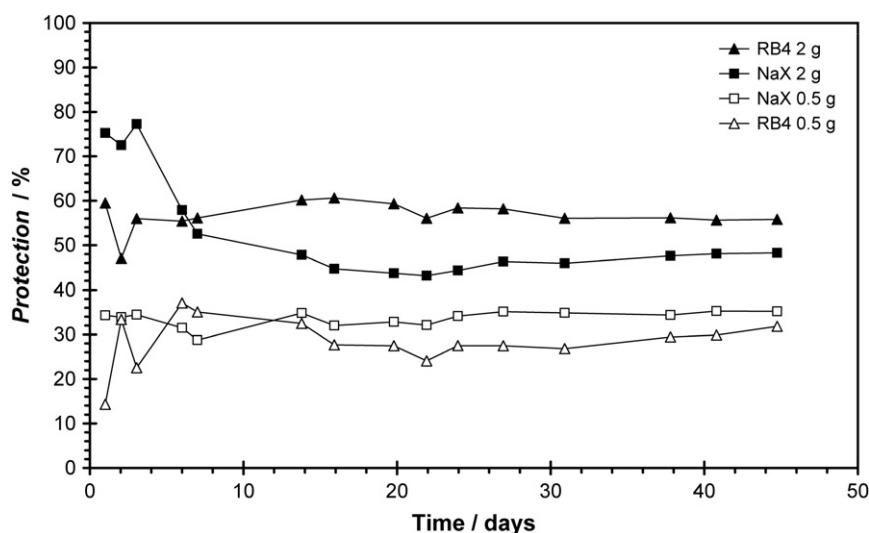


Fig. 4. Protection provided to the lead sensors by the adsorbents in experiment set 1, which intended to compare the efficiency of the two adsorbents.

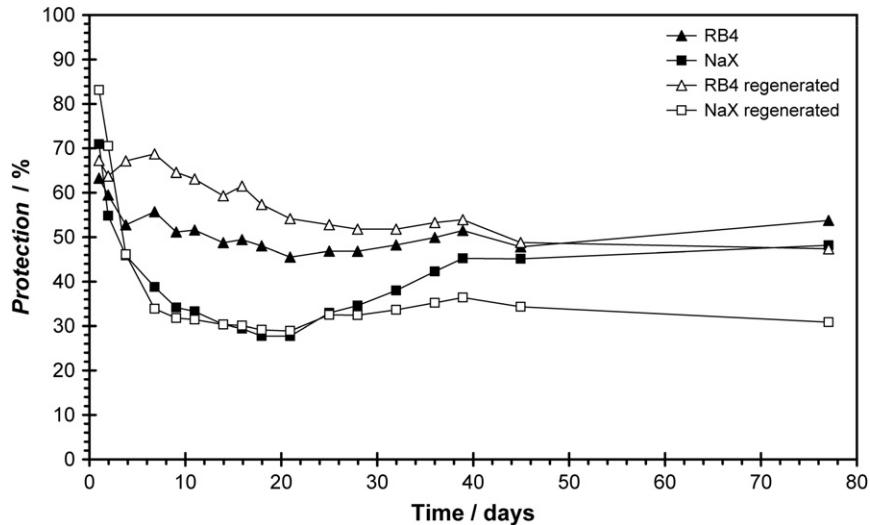


Fig. 5. Protection provided to the lead sensors by the adsorbents in experiment set 2, which intended to compare the efficiency of the adsorbents before and after regeneration. Some of the results allow the comparison of the efficiency of the two adsorbents, as the results obtained in the set 1.

adsorption obtained here is 31% while a value of, at least, 77% was previously obtained with an atmosphere of pure acetic acid. It should be recognized, however, that this value of 77% also takes into account, in addition to the adsorbed materials, the products resulting from the chemical reaction between the acetic acid vapor and the zeolite, that were not detected here. If, for that reason, we take into account instead the microporous volume (23%), determined by nitrogen adsorption, we must conclude that, in the case of the zeolite, the adsorbent is actually exhausted. Eventually, this situation can be in the origin of the greatest efficiency of the RB4 activated carbon after the first days founded in some of the experiments (Figs. 4 and 5).

We must point out that a solution of acetic acid 0.08%, instead of 2%, as source of the acetic acid vapor inside the flasks, did not lead to a significant difference on the value of the mass increase of the adsorbents corresponding to the

plateau. In fact, with the more diluted solution, the values obtained were 39% ($s = 2\%$; $n = 4$) and 14% ($s = 0.6\%$; $n = 4$) for the RB4 and NaX, respectively. Therefore, if the concentration of acetic acid in atmosphere, in general, influences the value of maximum adsorption, as mentioned above, that does not seem to happen in this range of concentrations (from about 5 to about 200 mg m^{-3}).

An important observation that results from the comparison of the plots in Figs. 4 and 6 is that the protection provided by the adsorbents has a scope that significantly goes beyond the saturation time. Although the mass increase of the adsorbents was higher than the mass of acetic acid initially present in each flask, due to the presence of water in much higher concentration and, consequently, to its preferential adsorption, at the end of the tests significant concentration of acetic acid still existed in the atmosphere, as was verified through the odor of acetic acid detected when the flasks were open.

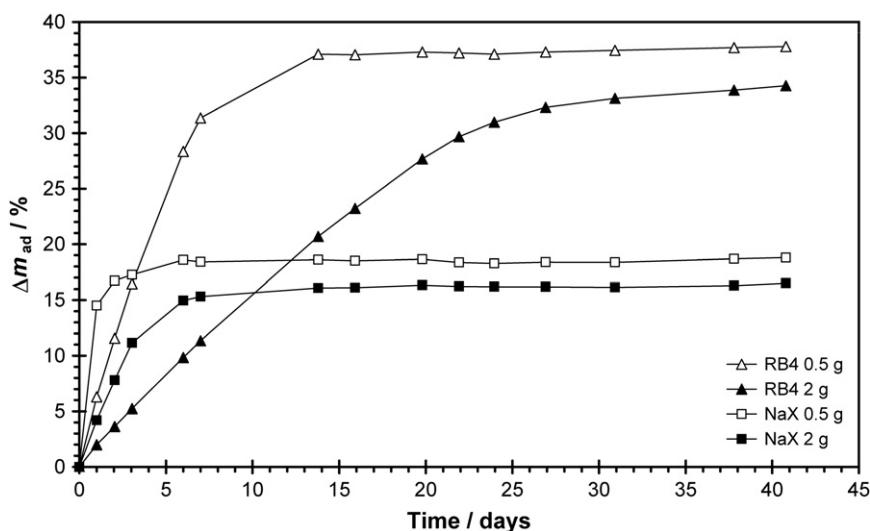


Fig. 6. Increase of the mass of the adsorbent in the experiment set 1.

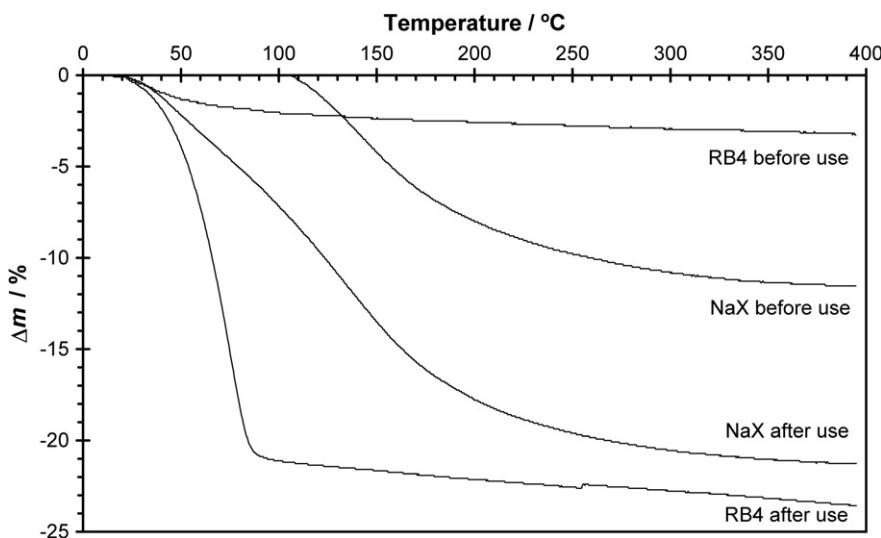


Fig. 7. Thermogram (mass loss) of the adsorbents before and after use.

Therefore, the protection provided by the adsorbents after its saturation time, although it can also be related with the decrease of the concentration of acetic acid in the atmosphere, probably, and above all, should be related with the formation of corrosion products with passive properties at the lead surface which are more easily formed in the presence of the adsorbents.

3.3. Reuse of the adsorbents

The regeneration of the adsorbents studied in this work took into account the conditions that, in principle, are easily available in any museum. Therefore, the adsorbents were heated up to the temperature of 120 °C. According to the results obtained by thermal analysis, at that temperature the release of compounds adsorbed during the tests originates a mass decrease of 9 and 19% for the NaX zeolite and the RB4 activated carbon, respectively (Fig. 7). During the regeneration, the effective mass decrease was 11 and 25% for the NaX and the RB4 adsorbents, respectively. Although these values are higher than those obtained by thermal analysis, the differences are in agreement with the long heating time used in the regeneration process. After the necessary calculations, we can estimate that, after 24 h at 120 °C, 78% of the adsorbed compounds were removed from the zeolite and 96% from the activated carbon. Therefore, for the activated carbon, the regeneration is more efficient and it is almost complete.

The main results obtained in the experiment set 2 are summarized in Fig. 5. In the case of RB4, the protection provided by the recycled adsorbent after 77 days is 47%, against 54% of the material used for the first time. After 45 days the difference is not significant: 49 against 48%. Furthermore, it happens that in all but the last weigh the protection for the recycled adsorbent is the highest, although the difference, usually, is inferior to 10%. Hence, no significant loss in the efficacy of the adsorbents was detected upon recycling. In the case of NaX, there are also no significant differences during the first month, but after that the performance of the recycled adsorbent begins to decrease

systematically. Probably, this situation should be related with the poor yield of the recycling for the zeolite. Having in account these data, it is probable that the efficacy of the zeolite will decrease more rapidly in subsequent cycles than the efficacy of the activated carbon. Consequently, it seems to be more advantageous the use of RB4 adsorbent.

3.4. Effect of the quantity of the adsorbents

The effect of the quantity of the RB4 adsorbent in the protection of lead was investigated in one set of the experiments in which different amounts of the RB4 carbon were used. The results obtained (Fig. 8) are partially in agreement with the expected: in general, a large amount of the adsorbent provides a large protection. However, this is not always the case. In the first days, the protection of the lead in the experiments done with the largest amount of adsorbent (3 g) was smaller than the protection obtained with 2 g or, in some cases, with 1 g. Only after 11 days the expected trend was observed. For longer times (40 days), however, the alteration of the sensors in the systems with 0.2 g of adsorbent is smaller than in the systems with 1 g. In another perspective, it can be noticed that the protection provided by 1 g of RB4 for relatively short times is comparable to that obtained with large amounts of adsorbent, while in the final part of the experience the protection achieved with 1 g is similar to that provided by a small amount (0.2 g). In spite of these observations, the increase in the mass of the adsorbents occurred as expected.

Although it can seem unexpected the inversion of the protection in the first days of the experiments, such a fact probably can be related with the formation of different alteration products to which correspond different mass increments. It should be noticed that it was already shown the important effect of the conditions, namely the concentration of the acetic acid in the atmosphere, in the alteration of lead, particularly in what concerns the nature of the alteration compounds formed [18].

In this set of experiments, 2 g of RB4 carbon originates a protection of 70% at the end of 55 days. Nevertheless, after

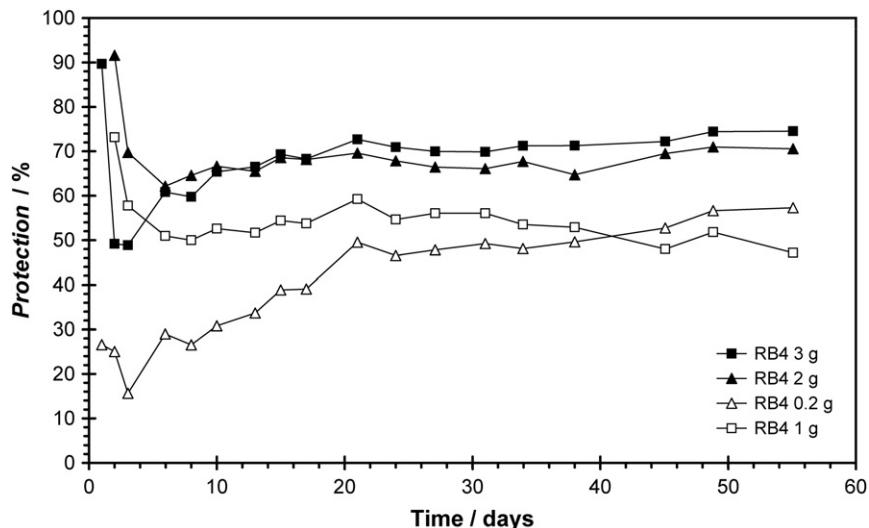


Fig. 8. Protection provided to the lead sensors by the adsorbents in experiment set 3, which intended to compare the effect of the amount of the adsorbents.

the first 15 days the protection already had a value close to that. In sets 1 and 2, however, the same amount of the adsorbent provided a protection of about 50%, therefore quite inferior. Although we expected differences among the sets, because the laboratory conditions were not exactly the same, this difference is superior to the expected.

Fig. 8 does not show significant differences resulting from the use of 2 or 3 g of adsorbent, except in the beginning, when the more favorable results were obtained with 2 g of the RB4 activated carbon. Adding to these reasons the costs related with the use of large quantities, we suggested that, in the conditions employed, 2 g of the RB4 activated carbon should be selected. Generalizing, this means that 3.3 kg of the adsorbent should be used per m^3 of the showcase volume.

4. Conclusion

In the conditions employed, which simulated a museum showcase with a concentration of acetic acid of about 160 mg m^{-3} in its atmosphere, appropriate amounts of activated carbon RB4 and zeolite NaX significantly reduced the alteration of the lead sensors exposed to the acetic acid vapors, even in the presence of water and other compounds. Although in some tests the effectiveness has been more or less similar, the activated carbon RB4, however, seems to present some advantages: is more efficiently recycled and much more inexpensive. An amount of RB4 corresponding to 3.3 kg m^{-3} provided a protection for several months of, at least, 50% but that can reach 70%. Considering a wholesale price of 5 euros per kg of the adsorbent, the cost of the protection of the lead objects against the deterioration by the acetic acid vapor can be estimated in 16.5 euros per m^3 of the volume showcase. If the adsorbent is used for 2 months and is recycled five times, that cost corresponds to the annual cost.

It is very probable that the protection can be extended to materials other than lead when also exposed to the released acetic acid vapors. However, in those cases the regeneration

of the adsorbent should be most probably more frequent because there is no guarantee that the alteration products formed at the surface of other materials also have passive properties that allow the effect of the adsorbents to continue even after its maximum adsorption was reached.

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