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Adsorbent media for the sustainable removal of organic air pollutants from museum display cases

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Abstract

The application of adsorbents in museum display cases appears auspicious, as the selection of low-emitting building and decoration materials does not necessarily ensure low pollution levels. Furthermore, historical furnishings may form an integral part of a museum and consequently cannot be substituted. Therefore, comprehensive experiments regarding the filtration efficiency of 37 different adsorbent media, both under active and passive conditions, have been conducted in order to simulate conditions in display cases with/without forced air exchange. The adsorbent media comprised pure and impregnated activated charcoal, charcoal foams and cloths, zeolites, molecular sieves and materials specially designed for museum purposes, such as archival cardboard, textiles and silica gels. Formaldehyde, formic acid, acetic acid, toluene and alpha-pinene were chosen as ubiquitous airborne pollutants in the museum environment. Tests were performed in environmental test chambers. The air exchange rate during active-mode tests was 0.5 h^{-1}. The concentrations of single substances in the chamber air ranged between 0.3 mg m^{-3} and 6 mg m^{-3}. For the passive-mode experiments, the chamber air was doped with 432 µg m^{-3} to 1371 µg m^{-3} of the target compounds. Under active conditions, most of the pure and impregnated charcoals were able to reduce pollutant levels quickly. The lowest adsorption efficiency was found for charcoal foam and cloths, zeolites, molecular sieves and special products designed for museum purposes. However, these materials also removed pollutants very efficiently within a short time under passive conditions with no forced air circulation. As pure activated charcoals performed best in both experiments, there is no need to use impregnated or cost-intensive sorbents in museum display cases. However, regular monitoring during application is recommended, as it was found that some adsorbent media might act as emission sources themselves by releasing volatile organics both before and after exposure to pollutants. It was also shown that emissions might be generated due to fragmentation reactions or pollutant-adsorber interactions; the selection and application of sorbents should therefore be performed with caution.

Keywords: Adsorbers, Activated charcoal, Zeolites, Molecular sieve, Formaldehyde, Acetic acid, Museum, Display cases, VOCs, Emissions

Introduction

Global climate change and, along with this, new energy saving concepts and ventilation technologies affect indoor microclimates in museum facilities. The term microclimate covers not only climatic parameters but also indoor air quality aspects. Against the background of low energy consumption, enclosing artefacts in airtight cases as a kind of protective shell seems to be the best solution to minimize the infiltration of external air pollutants, the entry of dust and pests as well as the influence of climatic fluctuations. Hence, showcases are today an integral part of museums' furniture in order to realize a so-called "box in a box" model [1] as an underlying strategy to preserve artefacts in an optimum way. The majority of museum

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enclosures are constructed as airtight as possible at the request of conservators and exhibition technicians. The microclimate inside seems to be more controllable and easier to tailor to object-specific demands than within non-airtight shells. Security reasons are also an important topic. Air exchange rates in passive-type display cases can vary and have been reported to be lower than 0.3 h^{-1} or even 0.05 h^{-1} [2–4]. The airtightness results in almost static conditions favouring the accumulation of volatile organics which are released by construction and decoration materials within the case [3]. Some display cases might be equipped with technical devices, e.g. for active air circulation to regulate relative humidity levels or for flushing with inert gas. However, most enclosures are passive systems due to financial reasons.

Previous studies have shown that heightened concentrations cannot be detected solely in showcases of traditional types, which were predominantly made of high-emissive materials such as wood-based products and fabrics, but also in modern and new enclosures, which are mainly built from low-emitting materials such as metal and glass in accordance with actual aesthetic requirements and preventive conservation recommendations [3, 5]. Table 1 summarizes published levels of organic pollutants. López-Aparicio et al. [5] reported concentrations of volatile organic compounds (sumVOC) inside of microclimate (MC) frames between 107 µg m^{-3} and 5274 µg m^{-3}. Also, levels of formic and acetic acid were elevated with 510 µg m^{-3} and up to > 2000 µg m^{-3}, respectively. Modern constructed frames showed higher concentrations than traditional ones, perhaps due to lower air exchange rates (AER) and a decrease of material emissions with time within older enclosures. These findings were supported by an extensive study on indoor air quality in passive-type museum display cases [3]. Whereas enclosures of traditional construction types were characterized by a rather low range of VOCs and heightened levels of formaldehyde, formic acid and acetic acid, a broad variety of VOCs and further increased levels of acetic acid were detected in modern cases. This fact was explained by the use of solvent-borne lacquers as coatings for constructional elements, whose main primary emissions are (di)carboxylic esters and glycol esters. Due to hydrolytic cleavage of these acetyl esters, acetic acid is generated as a secondary emission product [3]. In particular modern enclosures, directly after production, showed high pollution levels, as can be seen in Table 1. It was also shown that even though a careful selection of building materials and construction products is of high importance, low-emissive structures will not inevitably give low pollutant levels within museum enclosures, which is mainly due to the static conditions under which saturation vapour pressure might be reached. Moreover, a fast ventilation of airborne pollutants is also only possible if these emissions are primary and evaporation controlled. Pollutants which are formed and released due to secondary reactions cannot be successfully reduced by ventilation over a short time span [6]. The same applies for diffusion-controlled emissions [7]. These facts confirm that even though extensive knowledge exists concerning the impact of airborne pollutants on cultural assets [8–13], pollutant levels within showcases have been difficult to reduce efficiently so far. The installation of adsorbent media therefore appears to be a promising further approach in order to prevent degradation of enclosed assets.

Currently, a broad range of different adsorbent media is commercially available, ranging from activated charcoals and zeolites to molecular sieves. Some of them have already been investigated concerning the application in museum environments [14–16]. These early studies focused on inorganic outdoor pollutants such as ozone

Table 1 Concentrations of sumVOC, formaldehyde, formic acid and acetic acid in museum enclosures as published in the literature

Measurement location	AER	sumVOC	Formaldehyde	Formic acid	Acetic acid	References
	n [h^{-1}/d^{-1}]	Concentrations [µg m^{-3}]				
Traditional wooden cabinets		–	16–470	< 1–116	85–1836	[12]
Modern metal cabinets		–	24–26	< 1	49–51	
Traditional wooden display cases		–	15–71	13–48	84–337	
Wooden cases with metal barrier foil		–	51–136	< 1	62–175	
Modern wooden cabinets		–	74	2	131	
Showcases, not specified		–	–	16–438	113–3215	[35]
Microclimate (MC) frames	0.15–15 d^{-1}	107–5274	–	< 10–510	100– > 2000	[5]
Modern showcases directly after production	0.02–0.05 h^{-1}	3819–25,213	27–68	30–80	397–2352	[3]
Modern showcases in museum use	0.01–0.04 h^{-1}	102–26,516	< 2–158	< 12–350	< 42–5698	
Traditional showcases		87–2800	69–57	106–782	452–3282	

(O_3), nitrogen dioxide (NO_2), sulphur dioxide (SO_2), hydrogen sulphide (H_2S), peroxyacetyl nitrate (PAN), some chlorinated hydrocarbons and formaldehyde (HCHO). The most recent publication regarding laboratory studies of adsorbent materials for use in display cases [14] included acetic acid by exposing lead coupons to quite high concentrations (about 6.4 mg m^{-3}) within small glass flasks. Realistic indoor-related conditions have not been considered so far in laboratory experiments. The same applies for low atmospheric concentrations of target substances that may also cause damage in the long term or concerning mixtures of different airborne pollutants. Furthermore, most experiments are based on a theoretical calculation of doped target substances without analytical verification [14]. Moreover, mainly inorganic compounds with a known impact on cultural object materials have been studied in depth. In addition, removal and deposition rates of formic and acetic acid in passive-type display cases on activated carbon adsorbents seem to differ depending on the type of sorbent, as shown in a comprehensive field study [17]. As explained above, volatile organic compounds (VOCs) are the largest group of pollutants indoors today and are therefore of increasing importance. However, this pollutant group has not been considered so far when testing adsorbent media for preventive conservation purposes. According to specifications for the purchase of new showcases, the sum concentration of volatile organic compounds (TVOC, total volatile organic compounds) must fall under specific threshold values which are defined individually by the contractor. In addition, Gunschera and co-workers [18] have shown that a sole evaluation of the decay rate of pollutant concentrations is not sufficient in order to assess adsorbent media, as reaction products may occur which can significantly affect indoor air quality.

Thus, targeted systematic and comprehensive experiments have been conducted in order to evaluate the adsorbing properties of different media for use in museum display cases. Most of them are constructed as passive types with no technical units for active air ventilation and filtration. In contrast, active-type display cases are equipped with technical compartments which are usually located in the base area as an enclosed space that is separated from the exhibition space above. The filtration efficiency of a sorbent bed depends on a sufficient contact between the polluted air and the sorbent surface. Therefore, an active air flow is needed in order to ensure an adequate flow of the polluted air through the sorbent bed. For this reason, the filtration unit in a technical compartment sucks a given volume of air out of the display case, presses the air through the sorbent bed for filtration, then releases it back into the exhibition space of the display case after humidifying the air if needed. Whereas in this active mode the polluted air is drawn through a sorbent bed, the air has to penetrate the sorbent bed solely through gradient-driven diffusion in the passive mode. Therefore, experiments were performed in such a way as to simulate active and passive conditions (with/without forced air flow). Furthermore, the question as to whether undesired fragmentation products might be generated by sorbate-sorbent interactions was investigated. Also, desorption effects were studied, as adsorbents might act as a kind of secondary emission source under changed environmental conditions by releasing gaseous volatiles that have previously been adsorbed.

Materials and methods

Target substances

Due to their ubiquitous occurrence in museum environments, formaldehyde, formic acid, acetic acid, toluene and alpha-pinene were selected as target substances. Formic and acetic acid have been broadly discussed regarding their corrosive impact on sensitive surfaces of museum artefacts [8, 13, 19–21]. Even though the hazardous potential of formaldehyde has not been clarified so far, it is assumed to affect museum collections [22]. The aromatic hydrocarbon toluene and the monoterpene alpha-pinene were chosen as representatives for the wide variety of VOCs which can be detected in museum interiors and also within museum enclosures. Table 2 summarizes the main characteristics and typical emission sources of the target substances.

Table 2 Target substances selected for laboratory experiments. Kinetic diameters are taken from [36]

Substance	MW [g l^{-1}]	BP [°C]	KD [Å]	Main emission sources
Formaldehyde	30.03	− 19	4.0	Wood, wood-based products, adhesives
Formic acid	46.03	100.8	4.0	Wood, wood-based products
Acetic acid	60.05	118–119	4.4	Wood, wood-based products, paints, cleaning products
Toluene	92.14	110.6	5.85	Solvent-containing products
Alpha-pinene	136.23	155	144.8	Wood, wood-based products, coatings, oils, fragrances, cleaning products

MW molecular weight, *BP* boiling point, *KD* kinetic diameter

Adsorbent media

In total, 37 different adsorbent materials were included in the experiments. All adsorbent materials tested, their physical properties and application recommendations as given by the manufacturers are provided in Table 3.

The selection comprised pure activated charcoal (PC), activated charcoal with alkaline impregnation (IC), activated charcoal cloth (CC), natural and synthetic zeolites (NZ and Z) and molecular sieves (MS). Also, a polymer foam with embedded copper particles (CF), a cotton fabric with embedded fine particles (PS) and an archival cardboard with embedded synthetic zeolites (AC) were included. In addition, two forms of silica gel (SG) were considered, as these are commonly used for buffering relative humidity in museum showcases. All chosen materials are commercially available; some are specifically designed for museum purposes, such as some activated charcoal cloth adsorbers (CC) and the materials equipped with adsorbers (CF, PS, AC).

Activated charcoals are produced from carbonaceous materials, such as wood, nutshells, peat, hard coal or lignite. They have a fine-porous structure and a high inner surface (300–2000 $m^2\ g^{-1}$). The iodine number characterizes the activity level of the activated carbon. It usually ranges from 500 to 1200 mg g^{-1}. The higher the number, the higher the degree of activation. It is usually equivalent with the surface area [23, 24]. The density varies between 200 kg m^{-3} and 600 kg m^{-3}. Activated charcoal is available as powder or granulate and reduces contaminant gases by physical adsorption at the inner surface. This mechanism is generally based on relatively weak intermolecular forces, namely van der Waals interactions; both the sorbate and the sorbent remain unchanged. Organic compounds with a molecular weight greater than 45 are considered to be good adsorbates on activated carbon [25]. In order to improve the adsorptive capacity and the performance efficiency especially for gases which might be difficult to trap using standard non-treated carbon media, activated carbon can be chemically impregnated. The charcoal is modified through a fine distribution of chemicals and/or metal particles on the internal surface of the pores. Gaseous pollutants are neutralized at the surface by oxidation of the impregnation agent in mineral compounds. Target substances are irreversibly captured by chemisorption. The chemisorption process is instantaneous; a desorption of gaseous substances is not possible [25]. The adsorption capacity of activated charcoals is determined by the pore size according to their diameter: micro pores < 1 nm, meso pores 1–25 nm and macro pores > 25 nm.

Zeolites are crystalline aluminosilicate minerals which might occur naturally, or which might be synthesised. Due to their property to adsorb water and other low-molecular substances and to desorb them under heating, they are well suited for application as adsorbent media. Zeolites have a microporous structure which allows them to filter molecules according to their size. Therefore, zeolites belong to the group of molecular sieves. An appropriate selection of the molecular sieve enables a dedicated separation of different-sized molecules. Molecular sieves are available as powder, sticks or granulates and can be regenerated, e.g. by controlled heating which will not influence the molecule structure.

Materials and methods

Sorbent test modes

Active-mode test (with forced air exchange)

The experimental set-up of the active-mode test simulated how polluted air is directed through a sorbent bed by a forced air flow. A gaseous mixture of the selected target substances (see Table 2) was created in a 1 m^3—glass emission test chamber. Concerning the construction and functioning of emission test chambers, the reader is referred to the literature [2, 26]. 10 ml each of formic acid, acetic acid, toluene and alpha-pinene as well as 12 mg of paraformaldehyde were filled into separate glass vials (volume: 20 ml) which were subsequently closed with a lid. To allow evaporation, needles were stuck through the lid. The vial containing paraformaldehyde was left open. The chamber air was heated to 30 °C to obtain the following constant concentrations of single target substances in the gas phase over several days: formic and acetic acid (each 1–2 mg m^{-3}), toluene (6 mg m^{-3}), alpha-pinene (3 mg m^{-3}) and formaldehyde (300 µg m^{-3}). The chamber air was directed by a pump with a flow rate of 5 l min^{-1} through six glass tubes in parallel. The flow rate through each tube was regulated by needle valves (max. flow rate: 1 l min^{-1}). The glass tubes contained sorbent beds (ca. 3 g) between glass wool end-plugs. One glass tube remained empty as blank value in order to check (i) possible interactions with the glass walls of the test chamber, which is known as a sink effect [26], and (ii) a possible loss of pollutants in the air stream on its way through valves and tubes (which are needed to suck the polluted air through the experimental set-up) and, finally, through the glass tubes. The air exchange rate in the test chamber was set to 0.5 h^{-1} which corresponds to an air flow rate of 8.33 l min^{-1}. This setpoint was chosen to ensure a sufficient air flow through the sorbent beds (1 l min^{-1}) under consideration of the air flow rate needed for performing active air sampling at the outlet of the glass tubes in order to determine pollutant concentrations (see the analytical section below). The experimental set-up is visualized in Fig. 1.

Active air sampling of formic acid, acetic acid, formaldehyde and VOCs was performed in parallel at the

Table 3 Categorisation and physical properties of tested adsorbent media

Adsorbent category	Adsorbent media	Supplier/distributor	Composition[a]	Physical characteristics[a]	Manufacturer remarks/application recommendations
Pure charcoal	PC1	A	Pure activated carbon, non-impregnated coconut shells, extra-fine pores	Dimensions: chips: 2.4–4.8 mm Apparent density: 450 ± 25 g/l Internal surface area: ~ 1100 m^2/g Iodine number: > 1050 mg/g Moisture (as packed): max 10 w/w% Ash content: max 5%	Adsorption of non-polar organic compounds (e.g. biocides), small amounts of acidic gases and substances; good adsorption of small pollutant concentrations due to narrow pores
	PC2	B	Virgin grade, activated charcoal with high inner surface, non-impregnated	Relative moisture content: max 2% Surface area: 1100–1200 m^2/g Moisture content: max 5% Ash content: max 2.5–3%	Designed to remove high molecular weight pollutants by means of adsorption; gases shall adhere to the surface of the media pellet during the adsorptive process
	PC3	C	Granular activated carbon; coconut shell steam-activated carbon, non-impregnated	Granular size: > 3.35 mm (max 8%), < 1.7 mm (max 5%)	
Impregnated charcoal	IC1	A	Granulated peat-carbon, impregnated with NaOH, base material: mineral coal	Dimensions: extruded cylinders: diameter ~ 4 mm Apparent density: 500 ± 5 g/l Iodine number: 900 mg/g Moisture (as packed): max 10 w/w%	Adsorption of acidic gases due to alkaline impregnation; chemical application, pollutants are firmly bonded on the charcoal; gases will not be liberated again in long-term application; avoid direct contact with sensitive surfaces due to alkaline impregnation
	IC2	A	Granulated peat-carbon, impregnated with KOH	Dimensions: extruded cylinders: diameter ~ 3 mm, 5 mm length Apparent density: 500 g/l Moisture (as packed): max 18 w/w%	Avoid direct contact with sensitive surfaces due to alkaline impregnation
	IC3	B	Spherical, porous pellets; formed from a combination of activated alumina and other binders, impregnated with potassium permanganate ($KMnO_4$); impregnant is uniformly distributed throughout the pellet volume	Moisture content: max. 35% Density: 800 kg/m^3 Nominal diameter: 3.175 mm (1.8″) Content $KMnO_4$: min 4% Filter capacity: H_2S: min 8% (mass fraction) SO_2: min 4% (mass fraction) NO_x: min 2.8% (mass fraction)	Primary adsorption of hydrogen sulphide (H_2S) and sulphur dioxide (SO_2); optimum adsorption, absorption and oxidation of a wide variety of gaseous contaminants; desorption not possible; Recommended airflow: 42.5–169.920 m^3/h Recommended air velocity: 18–150 m/min
	IC4	B	Spherical, porous pellets, impregnated; impregnant is uniformly distributed throughout the pellet volume; impregnant not specified		Manufactured specifically for the control of ammonia and amines
	IC5	B	Equal mix (by volume) of impregnated (IC3) and pure charcoal (PC2, 50/50); spherical, porous pellets, impregnated with $KMnO_4$	Moisture content: max. 35% Density: 800 kg/m^3 Nominal diameter: 3.175 mm (1.8″) Content $KMnO_4$: min 4% Breaking strength: 35–70% Abrasion: max 4.5% Filter efficiency: 99.5%	Optimum adsorption, absorption and oxidation of a wide range of contaminants; for the control of hydrocarbons with a high surface area available for adsorption Recommended airflow: 42.5–169.920 m^3/h Recommended air velocity: 18–150 m/min Temperature range: − 20–51 °C Relative humidity: 10–95%

Table 3 (continued)

Adsorbent category	Adsorbent media	Supplier/distributor	Composition[a]	Physical characteristics[a]	Manufacturer remarks/application recommendations
	IC6	B	Generally spherical, porous pellets, formed from a combination of powdered activated alumina and other binders, impregnated with potassium permanganate ($KMnO_4$); the impregnant is uniformly distributed throughout the pellet volume	Moisture content: max. 35% Density: 800 ± 5 kg/m^3 Nominal diameter: 3.175 mm (1.8″) Content $KMnO_4$: min 8% Breaking strength: 35–70% Abrasion: max 4.5% Filter efficiency: 99.5%	Removes sulphur oxides and other odorous pollutants from makeup air, emissions from office furnishings and human bioeffluents; removes H_2S, NO_x, SO_2, HCHO, and low-molecular aldehydes/organic acids; optimum adsorption, absorption and oxidation of a wide variety of gaseous contaminants
	IC7	B	Generally spherical, porous pellets, formed from a combination of powdered activated alumina and other binders, impregnated with sodium permanganate ($NaMnO_4$); the impregnant is uniformly distributed throughout the pellet volume	Moisture content: max. 35% Density: 800 kg/m^3 Nominal diameter: 3.175 mm (1.8″) Content $KMnO_4$: min 12% Breaking strength: 35–70% Abrasion: max 4.5% Filter efficiency: 99.5% Filter capacity: H_2S: min 14% (mass fraction) SO_2: min 7% (mass fraction) NO_x: min 4.9% (mass fraction) HCHO: min 4% (mass fraction)	Filtration of H_2S, NO_x, SO_2, HCHO, high molecular aldehydes/organic acids; higher working capacity for broad-spectrum oxidation of contaminants; contains more permanganate as active ingredient for increased removal capacity; neutralization of target substances by chemisorption Recommended airflow: 42.5–169.920 m^3/h Recommended air velocity: 18–150 m/min Temperature range: − 20–51 °C Relative humidity: 10–95%
	IC8	C	Granular impregnated activated carbon; coconut shell, specially impregnated for chemisorption of formaldehyde	Surface area: 1150 m^2/g Apparent density: 620 kg/m^2 Moisture content: max 15%	
Charcoal cloth	CC1	C	Activated carbon adsorptive filter media; polyester non-woven on both sides	Basis weight: 310 g/m^2 Thickness AFM: 0.9 mm Thickness AFM: 2000 l/m^2s Content of activated carbon: 200 g/m^2	
	CC2	C	Synthetic composite carbon filter media	Basis weight: 119 g/m^2 Stiffness, MD: 1000 mgs	Patented gradient density, durable synthetic construction, pleatable, high efficiency, low resistance
	CC3	C	Non-woven carbon filter media	Nominal thickness: 6 mm Product weight: 290 gsm Carbon weight: 95 gsm Carbon content: 33%	
	CC4	C	Three-layer composite beaded carbon media, 2*100% PES with activated carbon layer	Weight: 295 (g/m^2) ± 15% Width: 152 ± 4 cm Thickness: 0.75 ± 0.15 mm Adsorption surface: 165.000 m^2/m^2 Iodine adsorption: 175,000 mg/m^2	

Table 3 (continued)

Adsorbent category	Adsorbent media	Supplier/distributor	Composition[a]	Physical characteristics[a]	Manufacturer remarks/application recommendations
	CC5	C	Activated carbon felt; fibre structure, low pressure drop, low ash content	Weight: 120 g/m^2 Butane uptake: 25% Length × width: 50 × 1.15 BET surface area: > 1200 m^2/g Thickness: 2–3 mm	
	CC6	C	Activated carbon-coated foam; reticulated polyurethane foam which is coated with activated granular carbon	Weight: 4300 g/m^2 Thickness: 30 mm Activated-carbon content: 2600 g/m^2	
	CC7	C	Open-cell polyurethane foam which is coated with activated granular carbon	Weight: ≥ 2000 g/m^2 Thickness: 11 ± 0.5 mm Activated-carbon content: ≥ 1300 g/m^2	
	CC8	C	Activated carbon cloth		Highly microporous, knitted structure, excellent kinetics, physically robust; maximum utilisation of available surface area; very good drape and good stretch; very fast adsorption of target contaminants; virtually zero shedding of carbon particulates
	CC9	A	Woven, bonded on one side to a white nonwoven	Activated carbon content: 120 g/m^2 Internal surface area: 900–1100 m^2/g Width: 108 cm Thickness: 0.5 mm	Can oxidize metal at direct contact; possible application for decontamination purposes; interleaf a neutral fabric between the carbon cloth and the object
	CC10	A	Woven, bonded on one side to a white nonwoven; alkaline impregnated	Internal surface area: 1000–1200 m^2/g Width: 100 cm Thickness: 0.5 mm	Alkaline impregnation for tenfold higher adsorption capacity for H_2S, NO_x and other acid gases; avoid contact with delicate surfaces
Zeolites	Z1	D	Synthetic ZSM (zeolite socony mobil) zeolite; pentasile structure; adsorption of molecules with a diameter of max. 5.6 Å		White, microporous, organophilic, inorganic zeolite powder, large adsorption capacity for odours and flavours and other organic compounds; high adsorption capacity is maintained even after incorporating into a polymer matrix; usually used for VOC adsorption of molecules to about 5.6 Å
	Z2	D	Synthetic US-Y zeolite (ultra-stable zeolite Y)		Generally used for VOC adsorption of molecules to about 7.6 Å
	Z3	D	Hydrophobic adsorption media; synthetic HPZ zeolite (high-performance zeolite); high silica/alumina-ratio zeolite product; cubic crystal structure with straight 10-membered ring channels of 5.3*5.6 Å; the channels are connected by sinusoidal channels of 5.1*5.5 Å		Removal of VOCs according to molecular size and polarity; catalytic reaction

Table 3 (continued)

Adsorbent category	Adsorbent media	Supplier/distributor	Composition[a]	Physical characteristics[a]	Manufacturer remarks/application recommendations
	Z4	D	Synthetic zeolite, pentasile structure without Al (pure silica); straight channels with a diameter of 5.1*5.6 Å, connected by 5.4*5.6 Å channels		
	Z5	D	Synthetic zeolite, tetragonal structure with 12-membered ring channels (7.6*6.4 Å), connected by 10-membered channels of 5.5*5.6 Å		Pores are composed of 12 tetrahedron; large pore zeolite
	Z6	D	Synthetic zeolite, sodium form of the type X crystal, large pore opening; adsorption of molecules with a kinetic diameter of < 9 Å (0.9 nm) and exclusion of those larger		Highest theoretical capacity of the common adsorbents, very good mass-transfer rates; removal of CO_2 and moisture from air, mercaptans, H_2S
	Z7	D	Natural zeolite, micro porous structure, silica/alumina tetrahedrons		
Molecular sieves	MS1	D	Molecular sieve, powder, pore opening 3 Å		
	MS2	D	Molecular sieve, powder, pore opening 4 Å		
	MS3	D	Molecular sieve, powder, pore opening 5 Å		
Silica gels	SG1	A	Silica gel, 97% SiO_2, 3% Al_2O_3, free of chlorides		
	SG2	A	Silica gel, 90% SiO_2, lithium chloride (LiCl)		No off-gassing; adsorption of small amount of VOCs; degradation by acid contaminants with time (not fixed, can be released again)
Miscellaneous	CF	A	Foam; copper particles embedded on polymeric matrix		Reduce contaminants attacking metals, such as SO_2, H_2S and others
	PS	A	100% cotton fabric embedded with fine silver particles (pure, colloidal silver)		Absorbs tarnish producing gases
	AC1	A	Cardboard embedded with synthetic zeolites; 100% cotton fibres, free of pulp wood and lignin, alkaline binder, alkaline lamination (water-based, solvent-free); colour: white		Acid-free, durable, absorbs and neutralizes pollutants
	AC2	A	Same as AC1; colour: black		

[a] According to the manufacturer/supplier

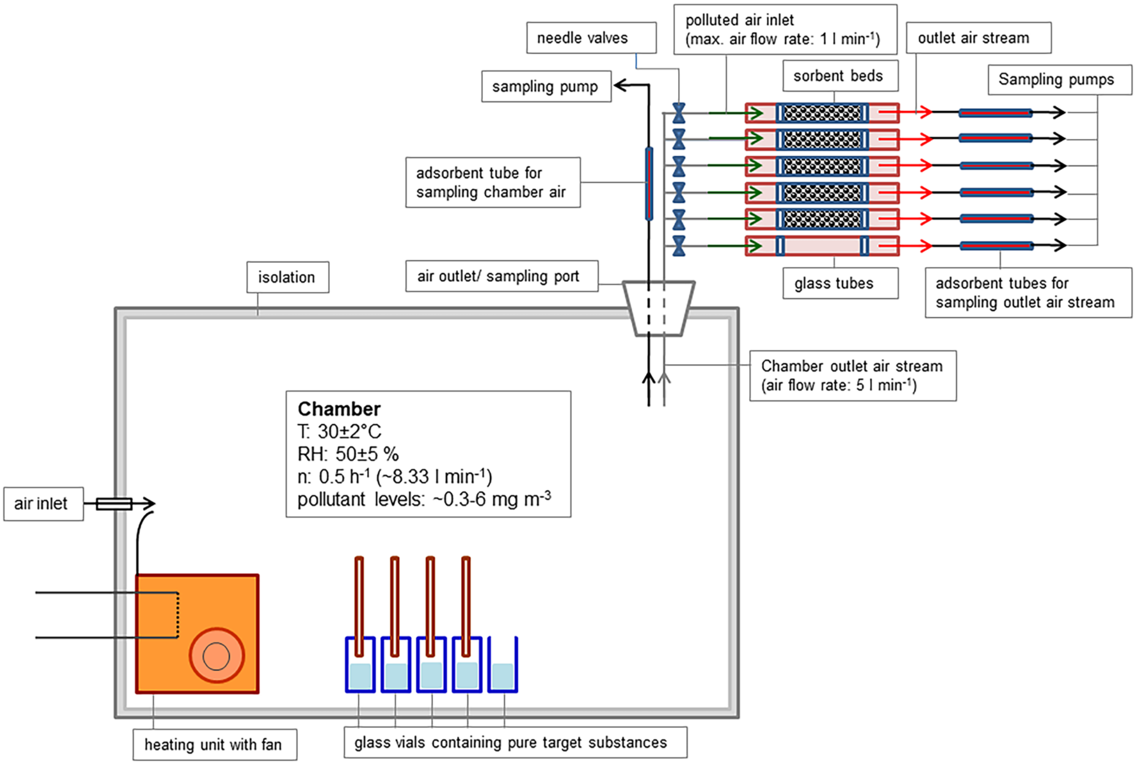

Fig. 1 Scheme of the experimental set-up of active-mode tests

chamber outlet 5 h and 24 h after placing the vials into the chamber to measure the start concentration of the gas mixture. Afterwards, the glass tubes were filled with the sorbent beds and the test started. Sampling was performed in parallel at the chamber outlet and at the outlets of the glass tubes after 5 h, 24 h, 30 h, 48 h and 72 h. Test conditions are summarized in Table 4.

Passive-mode test (without forced air exchange)

The passive-mode experiments were aimed at clarifying whether natural ventilation of polluted air to a sorbent bed is sufficient in order to remove airborne pollutants. Again, the tests were conducted in a 1 m^3-glass emission test chamber. The chamber air was doped with target substances by discontinuous injection of a pollutant

Table 4 Test conditions of active-mode tests (with forced air exchange)

Parameters	Adjustment/procedure
Chamber volume [m^3]	1
Adsorbent weight [g]	ca. 3
Temperature [°C]	30 ± 2
Relative humidity [%]	50 ± 5
Air exchange rate [h^{-1}]	0.5
Testing time [h]	72
Injected target substances [mg/ml]	Para-formaldehyde: 12 mg Acetic acid, formic acid, toluene, alpha-pinene: 10 ml
Sampling intervals [h]	5, 24, 30, 48, 72
Sampling VOCs	Adsorbent: Tenax TA®, sampling volume: 3 l, analysis: TD-GC/MS
Sampling formaldehyde	Adsorbent: distilled water, sampling volume: 30 l, analysis: acetylacetone-fluorescence
Sampling formic acid and acetic acid	Adsorbent: silica gel, sampling volume: 30 l, analysis: IC

mixture. 100 µl of toluene and alpha-pinene (mixture A) and of formic acid and acetic acid (mixture B) was weighed into a vial, of which an aliquot of 3 µl (mixture A) and 6 µl (mixture B), respectively, was injected into the chamber air as well as 100 µl formalin (1%). Injection of all three substances/substance mixtures was performed in parallel. To simulate the low air exchange rates in passive-type museum display cases, the air supply of the test chamber was switched off ($n = 0\ h^{-1}$). Chamber outlets and gaskets were securely closed, resulting in a minor natural air exchange rate. After injecting the pollutant mixtures into the chamber air, the decay of pollutant concentrations was measured after specific time intervals by active air sampling at the chamber outlet, as outlined in Table 5. During active sampling of chamber air, the air supply was switched on ($n = 0.5\ h^{-1}$). As there is always the possibility that the pollutants diffuse to the chamber walls due to a sink effect [26], a control experiment was conducted to determine the pollutant loss rate in an empty emission test chamber. Initial concentration levels 0.3 h after injection were between 770 µg m^{-3} (formaldehyde), 371 µg m^{-3} (formic acid), 1225 µg m^{-3} (acetic acid), 1185 µg m^{-3} (toluene) and 1371 µg m^{-3} (alpha-pinene). After 72 h, decreased concentrations ranged between 125 µg m^{-3} (formic acid) and 653 µg m^{-3} (alpha-pinene), respectively. Figure 2 shows the decrease of the pollutant concentrations over time in the empty chamber. Observed slight variations might be due to an unequal distribution of the pollutants in the chamber volume. In order to simulate the conditions in passive-type display cases with no active air circulation, the heating unit with fan (see Fig. 1) needed to be switched off.

Table 5 Test conditions of passive-mode tests (without forced air exchange)

Parameters	Adjustment/procedure
Chamber volume [m^3]	1
Adsorbent weight [g]	ca. 200
Temperature [°C]	23 ± 2
Relative humidity [%]	50 ± 5
Air exchange rate [h^{-1}]	0; during air sampling: 0.5
Testing time [h]	72
Injected target substances [µl]	Formalin (1%): 100 Acetic acid/formic acid: 6 Toluene/alpha-pinene: 3
Sampling intervals [h]	0.3, 2, 4, 6, 24, 28, 32, 48, 72
Sampling VOCs	Adsorbent: Tenax TA®, sampling volume: 3 l, analysis: TD-GC/MS
Sampling formaldehyde	Adsorbent: distilled water, sampling volume: 40 l, analysis: acetylacetone-fluorescence
Sampling formic acid and acetic acid	Adsorbent: silica gel, sampling volume: 40 l, analysis: IC

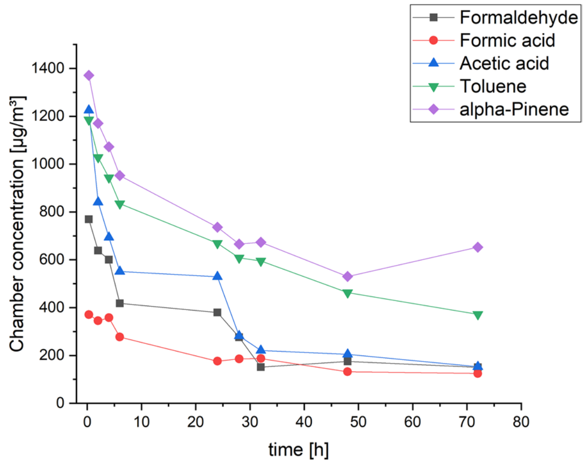

Fig. 2 Start concentrations and decay curves of target substances in a 1 m^3—environmental test chamber with no air supply to simulate conditions in passive-type display cases (control experiment)

The heating unit with fan is an integral part of an emission test chamber to ensure a specific air circulation and air flow rate as specified in DIN EN ISO 16000-9 [27].

For testing, ca. 200 g of a sorbent was placed at the bottom of the 1 m^3-glass test chamber on an area of 0.1 m^2 (loading factor of the chamber, $L = 0.1\ m^2\ m^{-3}$). After loading the chamber with the sample, the air supply of the chamber was switched off ($n = 0\ h^{-1}$). After 24 h, active air sampling was performed to detect potential emissions released by the sorbent bed itself. After sampling, the pollutant mixture was injected into chamber air and the test started. Test conditions are summarized in Table 5.

Active air sampling and analysis

Volatile organic compounds (VOCs)

Air sampling of volatile organic compounds (VOCs) was carried out with stainless steel desorption tubes (Perkin Elmer) filled with Tenax TA® (60/80 mesh, Chrompack). Sampling was performed actively by drawing the air through the sorbent by means of a pump with a flow rate of 150 ml min^{-1}. After sampling, the tubes were thermally desorbed (320 °C, 10 min; Perkin Elmer ATD 400) into a GC/MS system (Agilent 6890/5972). The compounds were separated on a HP-5 MS column (60 m × 0.25 mm, 0.25 µm). Qualifying was based on PBM library search [28]. Moreover, mass spectra and retention data were compared with those of reference compounds [29]. All identified substances were quantified using their own response factors. The areas of unidentified peaks were converted to concentrations using the toluene response factor. For calibration, the linear regression model was used [30]. The limit of quantitation

(LOQ) was approx. 1 µg m^{-3}. The TVOC is defined as the sum of all identified single VOCs eluting between hexane (C6) and hexadecane (C16) and quantified with their own response factor. The presented results were obtained from duplicate analysis.

Formaldehyde

The determination of formaldehyde was performed according to the acetylacetone method [31]. Air sampling was carried out by passing 30 l (active-mode tests) and 40 l (passive-mode tests), respectively, with a flow of 1 l min^{-1} through a liquid absorber (distilled water). For analysis, formaldehyde was derivatized to 3,5-diacetyl-1,4-dihydrolutidine (DDL) with 2,4-pentanedione and ammonium acetate. DDL was then measured photometrically at 412 nm. Limit of quantitation (LOQ) was 3 µg m^{-3}.

Formic acid and acetic acid

Sampling on formic acid and acetic acid was also performed actively by passing 30 l (active mode tests) and 40 l (passive mode tests), respectively, with a flow of 1 l min^{-1} through silica gel-filled cartridges according to VDI 4301-7 [32]. Subsequent analysis was carried out by IC (Methrom 881 Compact IC Pro). The compounds were separated on an anion separation column (Metrosep A Supp 7). For a sampling volume of 40 l, limits of quantitation (LOQ) for formic and acetic acid were 7 µg m^{-3} and 5 µg m^{-3}, respectively.

Headspace-GC/MS

Before and after performing the exposure tests under active and passive conditions, ~2 mg of each adsorbent material were weighed into vials in order to investigate emissions released by the adsorbent media itself. Analysis was performed at 60 °C via Headspace (Agilent 7697A) coupled with a GC/MS system (Agilent 7890A/5975C). The compounds were separated on a HP-5 MS column (60 m × 0.25 mm, 0.25 µm). Qualifying was based on PBM library search [28].

Results and discussion

Adsorption performances in the active-mode tests

The adsorption performance is given as the amount of target substance after passing the adsorbent (%) according to Eq. (1):

$$C_{at}/\left(C_{ct} * 0.01\right) = C[\%] \quad (1)$$

with C_{at} = concentration of target substance after passing sorbent bed at time t, C_{ct} = concentration in blank glass tube at time t, C = amount of remaining target substance. Standardization is related to the blank value (empty glass tube) to consider possible loss of target substances by pumping the air mixture out of the chamber through several tubes and finally through the glass tubes. Table 6 summarizes the adsorption performance of adsorbent materials under active conditions after 72 h of testing time. Unfortunately, formic acid could not be detected in the outlet stream of all glass tubes in more than half of the experiments. This demonstrates the difficulty in obtaining a constant concentration of formic acid in an emission test chamber under dynamic conditions. Even though formaldehyde is also a small molecule of high volatility, no problems occurred, which might be due to the use of paraformaldehyde as solid substance to dope the chamber air.

During some test series, not just a decrease of pollutant concentration due to successful filtration was observed but, in contrast, also an increase of the pollutant concentration after a specific time interval. The occurrence of target substances in the outlet stream in increasing concentrations after the polluted air has passed the sorbent bed is called breakthrough [25]. This may occur when the adsorption capacity of a sorbent bed has been exceeded (saturation within the bed) or due to the occurrence of displacement by other volatiles [16, 33].

The results showed clearly that activated carbons are the most efficient adsorbent media for removing airborne pollutants. These media are superior to zeolites and other products. Acetic acid could be removed efficiently by the majority of sorbents tested, whereas formaldehyde, toluene and alpha-pinene were filtered only moderately or badly, as shown in Figs. 3, 4, 5. Within the group of activated charcoals, pure charcoals and impregnated charcoals are more efficient than charcoal cloths. In particular, PC1 and PC3, both non-impregnated carbons from coconut shell, filtered all target substances very well. Also, IC8, a coconut-shell carbon specially impregnated for chemisorption of formaldehyde (impregnation not specified by the manufacturer) and CC6, an activated carbon coated foam, showed an efficient adsorption performance. In the group of zeolites, solely Z1, a synthetic ZSM (zeolite socony mobil) zeolite, adsorbed the carboxylic acids and toluene very well, but failed in adsorbing alpha-pinene. In contrast, Z2 was an ineffective sorbent, but with a very good reduction of alpha-pinene with a very slight breakthrough after 30 h (1.8%).

Filtration of formaldehyde was challenging for nearly all sorbents tested, as shown in Fig. 3. Just 5 out of 37 products showed a very good or good performance. The highest adsorption was achieved by IC7, a charcoal impregnated with sodium permanganate for an increased removal capacity. It is recommended for

Table 6 Removal efficiency of adsorbent materials under active conditions after 72 h

Adsorbent category	Supplier/adsorbent media	Removal efficiency [%]				
		HCHO	HCOOH	CH_3COOH	Toluene	Alpha-pinene
Pure carbons	A/PC1	−	n.d.	++[b]	++[b]	++[b]
	B/PC2	−[a]	n.d.	+[a]	○[a]	−[a]
	C/PC3	++[a]	++	++	++[a]	++[a]
Impregnated carbons	A/IC1	−	n.d.	++[a]	+[a]	○[a]
	A/IC2	−	n.d.	+	−	○
	B/IC3	+	n.d.	++	−	+
	B/IC4	−[b]	n.d.	++	+	++
	B/IC5	+	n.d.	++[d]	+[d]	++[d]
	B/IC6	+	n.d.	+[a]	−[b]	+[a]
	B/IC7	++[a]	n.d.	++[a]	−[a]	+[a]
	C/IC8	−[a]	++	++[b]	++[a]	+[a]
Charcoal cloth & foams	C/CC1	−	○	−[a]	−[a]	−[c]
	C/CC2	−	−	○	−	−
	C/CC3	−	n.d.	○[b]	++[b]	−[d]
	C/CC4	−	○[d]	−[a]	−[a]	−[b]
	C/CC5	−[b]	○/−[b]	−[a]	○/−[a]	−[d]
	C/CC6	−[b]	++	++[c]	++	++[a]
	C/CC7	−[b]	n.d.	−[a]	○[a]	○[a]
	C/CC8	−	n.d.	−[a]	−[a]	−[a]
	A/CC9	−	n.d.	○[d]	○[d]	○[d]
	A/CC10	−	n.d.	+[d]	○/−[a]	○/−[a]
Zeolites	D/Z1	−	n.d.	++	+[a]	−[a]
	D/Z2	−[b]	n.d.	−[a]	−[a]	++[b]
	D/Z3	−	-[b]	−[b]	−	−
	D/Z4	−[b]	○[c]	+[a]	−[a]	−
	D/Z5	−	○	○	−	−
	D/Z6	−	n.d.	++[a]	−[c]	−[c]
	D/Z7	−[a]	++/+	+[a]	−	−
	D/MS1	−	+[a]	−[a]	−	−
	D/MS2	−	○[a]	−[a]	−	−
	D/MS3	−	+[c]	−[a]	−	−
Others	A/SG1	−	−[a]	−[a]	○/−[c]	−[c]
	A/SG2	−	n.d.	−[a]	−	−
	A/CF	−	n.d.	−[a]	−[d]	−
	A/PS	−	○	−	−	−
	A/AC1	○/−	n.d.	○	−[a]	−
	A/AC2	○/−	n.d.	○[a]	−[a]	−

HCHO: formaldehyde; HCOOH: formic acid; CH_3COOH: acetic acid; n.d. not detected

++ very good (< 20%); + good (20–40%); ○ moderate (40–70%); − bad (> 70%)

[a] Breakthrough after 24 h; [b] Breakthrough after 30 h; [c] Breakthrough after 48 h; [d] Breakthrough after 72 h

chemisorption of formaldehyde and organic acids. This manufacturer information was confirmed by the test results; the relevant target substances were reduced to 18%, even though the concentration increased slightly after 24 h (reduction after 5 h: 10%).

For some of the adsorbent media tested, a breakthrough of pollutants was observed as concentrations increased again after a specific time interval which is also noted in Table 6. CC9, a woven charcoal cloth specially produced for museum purposes, showed 100% filtration of the target substances after 48 h. However,

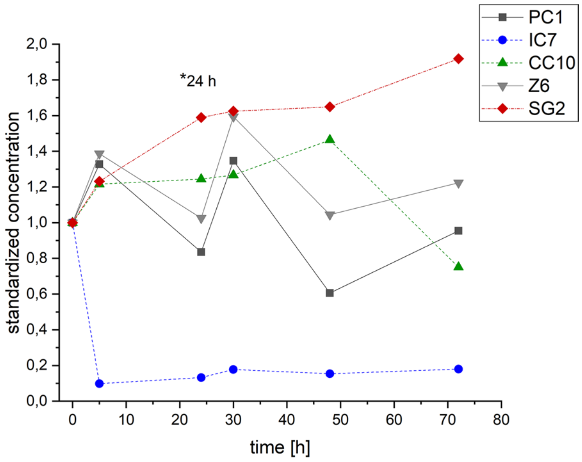

Fig. 3 Standardized decay curves of formaldehyde under active conditions after passing the adsorbent beds. Adsorbent media are representatively selected for each sorbent group. Occurred breakthrough after 24 h is marked with an asterisk. PC1: pure activated carbon (unimpregnated coconut shells), IC7: charcoal impregnated with $NaMnO_4$, CC10, alkaline impregnated charcoal cloth, Z6: synthetic zeolite (type X crystal), SG2: silica gel (90% SiO_2; lithium chloride). For further information, refer to Table 3

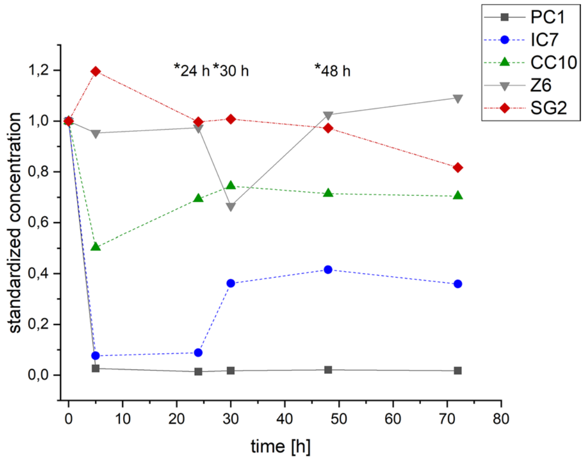

Fig. 5 Standardized decay curves of alpha-pinene under active conditions after passing the adsorbent beds. Adsorbent media are representatively selected for each sorbent group. Occurred breakthrough after 24 h, 30 h and 48 h is marked with an asterisk. PC1: pure activated carbon (unimpregnated coconut shells), IC7: charcoal impregnated with $NaMnO_4$, CC10, alkaline impregnated charcoal cloth, Z6: synthetic zeolite (type X crystal), SG2: silica gel (90% SiO_2; lithium chloride). For further information, refer to Table 3

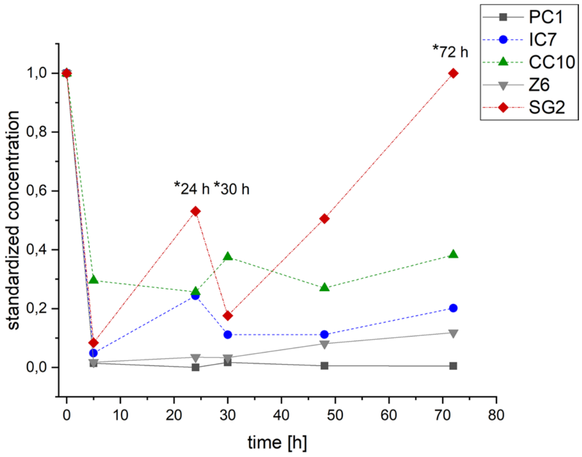

Fig. 4 Standardized decay curves of acetic acid under active conditions after passing the adsorbent beds. Adsorbent media are representatively selected for each sorbent group. Occurred breakthrough after 24 h, 30 h and 72 h is marked with an asterisk. PC1: pure activated carbon (unimpregnated coconut shells), IC7: charcoal impregnated with $NaMnO_4$, CC10, alkaline impregnated charcoal cloth, Z6: synthetic zeolite (type X crystal), SG2: silica gel (90% SiO_2; lithium chloride). For further information, refer to Table 3

after 72 h, between 50 and 57% of the injected pollutant concentrations (compared to the blank tube) were detected in the outlet stream after passing the adsorbent bed. Breakthrough also appeared as early as after 24 h testing time. IC1, a granulated peak-carbon impregnated with NaOH, lost 18% and 24%, respectively, of the filtration efficiency regarding toluene and alpha-pinene. For adsorbing acetic acid, a breakthrough was not detected before 48 h, even though the efficiency remained nearly constant after 24 h and 30 h testing time. Also, PC1 showed a loss of adsorption capacity after 30 h, but only to a minor extent (0.4–1.7% for acetic acid, toluene and alpha-pinene), meaning that the filtration capacity is not strongly influenced (see Figs. 4, 5). As regards PC3, IC1, IC8, CC6, Z2 and Z6, a slight breakthrough was also observed for these substances, which were well adsorbed according to Table 6.

Materials, which are specially designed for the efficient adsorption of specific target substances or particularly for museum purposes were not found to have a better reduction efficiency than conventional products. Filtration efficiency of charcoal cloth products (CC9, CC10) and a foam embedded with copper particles (CF) were low. All products are specially designed and distributed for museum display cases. Furthermore, the assumption that silica gels, which are installed in display cases to buffer relative humidity, might also act as pollutant adsorbers cannot be confirmed. The observed variations in target substance concentrations are more of an artefact than a real adsorption process (SG1, SG2). Archival cardboards, which are recommended for storing paper artefacts in boxes and which should act as an efficient barrier against pollutants from the indoor environment, had no significant effect on target

Table 7 Removal efficiency of adsorbent materials under passive conditions after 72 h

Adsorbent category	Supplier/adsorbent media	Removal efficiency [%]				
		HCHO	HCOOH	CH_3COOH	Toluene	alpha-pinene
Pure carbons	A/PC1	++	++	++	++	++
	B/PC2	++	++	++	++	++
	C/PC3	++	++	++	++	++
Impregnated carbons	B/IC3	++	++	++	○	++
	B/IC5	++	+	++	○	++
	B/IC6	++	++	++	○	++
	B/IC7	++	++	++	++	++
	C/IC8	++	++	++	++	++
Charcoal cloth & foams	C/CC1	+[d]	++	++[b]	++	++
	C/CC6	++	++	++	++	++
	C/CC7	++	++	++	++	++
	A/CC10	+[c]	++	++[c]	++	++
Zeolites	D/Z2	○	++	++	+[d]	++
	D/Z6	+[c]	++	++[c]	–[b]	–[b]
Others	A/SG2	○/–[a]	++	++[b]	○	○

HCHO: formaldehyde; HCOOH: formic acid; CH_3COOH: acetic acid

++ very good (< 20%); + good (20–40%); ○ moderate (40–70%); – bad (> 70%)

[a] Breakthrough after 6 h; [b] Breakthrough after 28 h; [c] Breakthrough after 48 h; [d] Breakthrough after 72 h

substance concentrations. Also, sample PS, which is designed for the protection of silver objects, showed no adsorption effect under active conditions. This might be due to the fact that it is produced to adsorb inorganic substances, such as sulphurous compounds, which are responsible for the tarnishing of silver.

In addition, the filtration efficiency of zeolites was disappointing. None of them was able to filter all target substances to a sufficient level. However, according to the adsorption properties outlined in Table 3, most zeolites (Z1, Z3, Z4, Z5) as well as the molecular sieves (MS2, MS3) should have been able to adsorb the C1-C2-carboxylic acids and toluene.

Testing adsorbent media without air exchange (passive-mode tests)

Based on the results from the active-mode tests, sorbents of each group were selected for passive-mode experiments. The selection comprised those materials with a very good adsorption performance for most target substances. Corresponding products with a weaker filtration efficiency were also included in order to check whether the results are confirmed under passive conditions. The following sorbents were selected: PC1, PC2 and PC3 (pure carbons), IC3, IC5, IC6, IC7 and IC8 (impregnated carbons), Z2 and Z6 (zeolites) and CC1, CC6, CC7 and CC10 (carbon cloths). Furthermore, a silica gel (sample SG2) was included in order to test the adsorption of formic acid which was observed under active conditions. Samples CC1 and CC10 were chosen to investigate whether charcoal cloth might perform better under passive conditions. The adsorption capacity of the tested media was evaluated according to Table 7. Figure 2 shows the initial concentrations and decay curves of the target substances over the testing time of 72 h.

According to Table 7, the filter performance of nearly all adsorbent media was evaluated as good or very good. Within 24 h, the formaldehyde concentration was efficiently reduced by nearly all adsorbent media, see Fig. 6. After 72 h, concentrations were near to the limit of detection (3 $\mu g\ m^{-3}$). Best-performing materials were again pure or impregnated activated charcoals, which lowered the formaldehyde concentration in the chamber air down to < 20% after only 2 h exposition time. A good adsorption rate was also achieved by zeolite Z6 and the activated carbon cloths CC1 and CC10. The worst performance was shown by zeolite Z2 and the silica gel SG2. After 72 h testing time, less than 30% of the injected formaldehyde concentration had been removed. The materials CC1, CC10 and Z6 showed first signs of saturation after 48 h and 72 h, respectively, as concentrations increased again.

A very fast decay was also observed for formic and acetic acid. Formic acid could not be detected in the chamber air directly after starting the test for nearly all adsorbent materials. Minor concentrations were detected for zeolite Z2, IC7 and SG2 after 24 h, but decreased to the limit of detection (5 $\mu g\ m^{-3}$) rapidly. As shown in Fig. 7, acetic acid was reduced by all tested sorbents

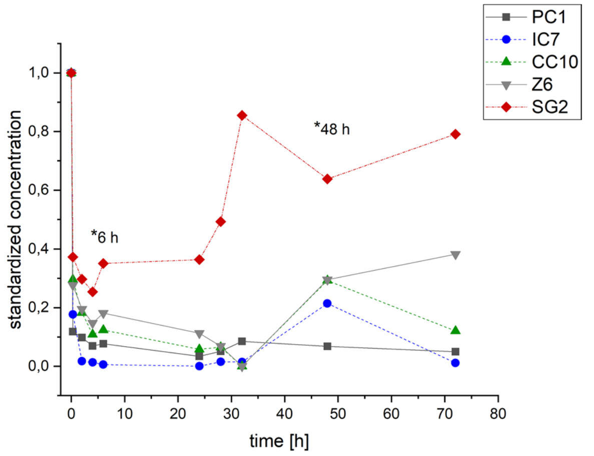

Fig. 6 Standardized decay curves of formaldehyde in a 1 m^3—environmental test chamber under passive conditions with no air supply. Adsorbent media are representatively selected for each sorbent group. Occurred breakthrough after 6 h and 48 h is marked with an asterisk. PC1: pure activated carbon (unimpregnated coconut shells), IC7: charcoal impregnated with $NaMnO_4$, CC10, alkaline impregnated charcoal cloth, Z6: synthetic zeolite (type X crystal), SG2: silica gel (90% SiO_2; lithium chloride). For further information, refer to Table 3

below the LOQ within two hours after doping the chamber air. Surprisingly, this also applied for those products with a bad adsorption rate during active-mode tests (CC1, CC7 and Z2). Again, pure and impregnated activated charcoals performed best (PC1, PC2, IC3, IC5 and IC7). The speed of adsorption was slower for the other media. Minor breakthrough was detected for CC1 and SG2 after 28 h and for CC10 and Z6 after 48 h testing time, as visualized in Fig. 7.

Even though most of the materials were not able to remove toluene quickly, most of them reduced it to an acceptable level after 72 h (< 20 µg m^{-3}). Products with a fast adsorption rate were again the activated charcoals (samples PC1, PC2 and PC3), the impregnated carbons and charcoal cloths and foams, namely samples IC7, IC8, CC1, CC6 and CC7. The adsorption process was slower regarding the impregnated charcoals IC3 and IC6 and the zeolite Z2, but with sufficient efficiency (< 10 µg m^{-3} after 28 h and 48 h, respectively). Worst-performing adsorbent media were IC5, SG2 and Z6. A minor breakthrough was observed after 72 h when testing Z2, but a high breakthrough after 28 h during testing Z6.

Alpha-pinene was adsorbed very well by all adsorbent media and, as for acetic acid, it was also removed quite quickly (see Fig. 8). Within 2 h, the chamber concentration was nearly reduced to the limit of detection (1 µg m^{-3}). Both zeolite Z6 and silica gel SG2 had only

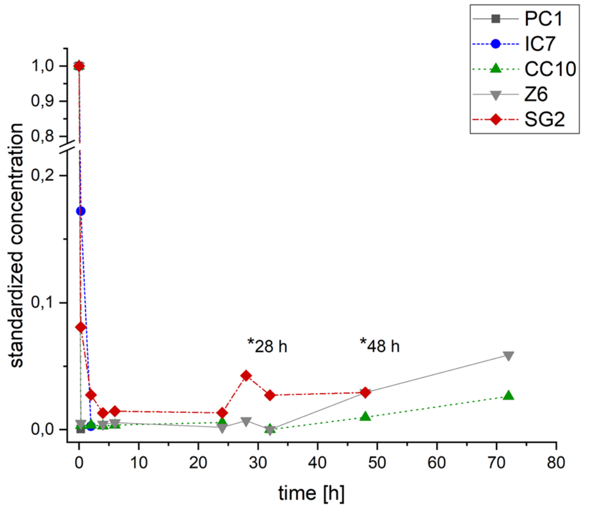

Fig. 7 Standardized decay curves of acetic acid in a 1 m^3—environmental test chamber under passive conditions with no air supply. Adsorbent media are representatively selected for each sorbent group. Occurred breakthrough after 28 h and 48 h is marked with an asterisk. PC1: pure activated carbon (unimpregnated coconut shells), IC7: charcoal impregnated with $NaMnO_4$, CC10, alkaline impregnated charcoal cloth, Z6: synthetic zeolite (type X crystal), SG2: silica gel (90% SiO_2; lithium chloride). For further information, refer to Table 3

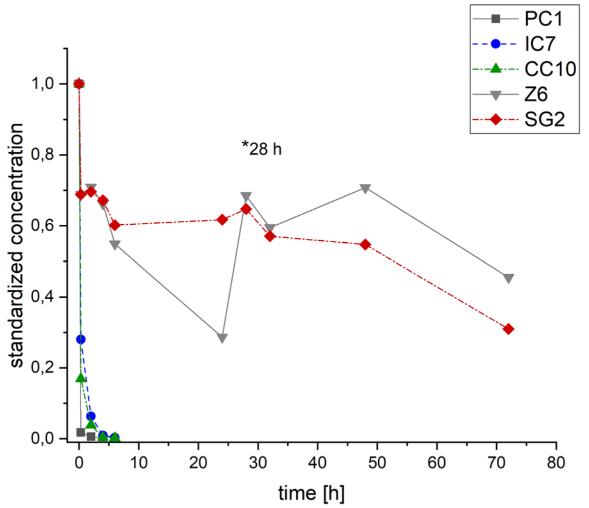

Fig. 8 Standardized decay curves of alpha-pinene in a 1 m^3—environmental test chamber under passive conditions with no air supply. Adsorbent media are representatively selected for each sorbent group. Occurred breakthrough after 28 h is marked with an asterisk. PC1: pure activated carbon (unimpregnated coconut shells), IC7: charcoal impregnated with $NaMnO_4$, CC10, alkaline impregnated charcoal cloth, Z6: synthetic zeolite (type X crystal), SG2: silica gel (90% SiO_2; lithium chloride). For further information, refer to Table 3

a slight adsorption effect by filtering ca. 70% of alpha-pinene after 72 h and are therefore not recommended for practical use. Moreover, Z6 lost adsorption capacity after 28 h resulting in increasing pollutant concentrations.

Emission behaviour of adsorbents before and after exposure tests

Before passing adsorbent tests, no emissions were detectable by Headspace-GC/MS for most materials. Just five sorbents emitted volatile organic compounds (VOCs), namely the natural zeolite Z7, the molecular sieve MS1, the adsorbent foam CF, the silica gel SG2 and the archival cardboard AC1. The detected substances are summarized in Table 8. The adsorbent foam released several substances, which are presumably used as solvents and film-formers within the material. The branched alcohol 2-ethyl-1-hexanol is probably emitted as solvent or decomposition product of the plasticizer diethylhexyl phthalate (DEHP). The archival cardboard AC1 emitted several siloxanes and plasticizers, of which dibutyl phthalate (DBP) could be identified and which is also known to act as plasticizer or additive in adhesives and printers' inks. Moreover, the isomers of the glycol ester 2,2,4-trimethyl-1,3-pentanediol-monoisobutyrate (TMPD-MIB) were identified. The compounds are often referred to as Texanol® and TXIB®, respectively, which are used as solvents, film-formers and plasticizers [2]. The silica gel (sample SG2), the natural zeolite (sample Z7) and the molecular sieve (sample MS1) only released some alkanes and aromatic hydrocarbons.

In contrast, more adsorbent media released volatile organics after exposure tests which are listed in Table 9. All compounds indicated in italics were not emitted by the sorbents before exposing them to organic volatiles. Moreover, the substances were not detected during chamber tests (active and passive mode). Zeolites and molecular sieves emitted the most VOCs. Most adsorbent media released the previously adsorbed substances alpha-pinene and toluene. Also, substances identified as terpenoic compound can be assumed to be alpha-pinene, but cannot be clearly identified. Some chemical substances had already been released before exposure tests, such as siloxanes from the adsorption foam (CF). There might also be a tendency for activated charcoal to only off-gas alpha-pinene and toluene, not organic acids and formaldehyde. This might be due to the quite good adsorption performance for these compounds.

It can be supposed that some of the identified substances are generated by the adsorption process due to secondary reactions by adsorber-pollutant interactions such as e.g. cyclohexane, dichloromethane, 2-butanone (MEK), acetaldehyde,

Table 8 Identified substances which were emitted by adsorption materials before exposure tests and their possible application in the product

Sample no./identified substance	Possible application in the product
Natural zeolite (sample Z7)	
Alkanes	?
Molecular sieve (sample MS1)	
Aromatic hydrocarbons, alkanes	?
Adsorption foam (sample CF)	
4,2-Methyl isobutyl ketone (MIBK)	Solvent
1,2-Propanediol	Solvent
Hexamethylcyclotrisiloxane	?
Octamethylcyclotetrasiloxane	?
2-Ethyl-1-hexanol	Solvent; decomposition product of diethylhexyl phthalate (DEHP)?
Silica gel (sample SG2)	
Toluene, benzene, alkanes, 2,2,4,6,6-pentane methylheptane	Solvents?
Archival cardboard (sample AC1)	
Siloxanes	?
Dibutyl phthalate (DBP)	Plasticizer
2,2,4-Trimethyl-1,3-pentanediol-monoisobutyrate (TMPD-MIB)	Solvent/film-former in paints, lacquers, adhesives; plasticizer

Table 9 Identified substances which were emitted by adsorption materials after exposure tests

Adsorbent material	Identified substances
Pure charcoal	
PC3	Alpha-pinene, toluene
Impregnated charcoal	
IC8	Alpha-pinene, toluene
Charcoal cloth	
CC5	Alpha-pinene, toluene, *cyclohexane*
CC6, CC8, CC10	Alpha-pinene, toluene
Zeolites	
Z2	Terpenoid compound
Z4, Z5	Toluene
Z1, Z8	Toluene, terpenoid compound
Z6	Toluene, *alkane*, alpha-pinene, *camphene, siloxanes*
MS1	*Acetone, dichloromethane*
MS2	*Acetone*, toluene, *2,2,4,6,6-pentamethyl heptane, 2,2,4,4-tetramethyl octane, alkanes*
MS3	Toluene, terpene, *2,2,4,6,6-pentamethyl heptane*
Others	
AC1	Toluene, pinene, unknown substances, siloxanes
SG1	Toluene, terpenes, *2,2,4,6,6-pentamethyl heptane*
CF	*Acetaldehyde, acetone*, toluene, siloxane, pinene
PS	Acetone, *siloxanes*

camphene and 2,2,4,6,6-pentamethyl heptane. The latter substance was detected as emission from molecular sieves and silica gel (MS2, MS3 and SG1). Camphene might be generated by Wagner-Meerwein rearrangement of alpha-pinene, which has been injected into an environment containing a synthetic zeolite [18].

Conclusions

The test results show that both under active and passive conditions (with/without forced air exchange), pure and impregnated activated carbons have the best adsorption efficiency for the target substances which were selected within this study as volatile organics which are often detected in museum environments as emissions from construction and furnishing materials. The substances which have been found to be of greatest concern for the preservation of heritage collections, namely formaldehyde, formic acid and acetic acid, were well adsorbed by the majority of activated charcoals tested. Under active conditions, charcoal cloths and foams, zeolites and other products, which are specially designed for museum purposes, showed a low adsorption efficiency. In addition, a breakthrough was observed after only a short time, meaning that a saturation of the adsorbents was achieved quickly. Surprisingly, even these materials were able to reduce the target pollutants under passive conditions. It can only be assumed that the residence time between sorbate and sorbent might play a role, as this is longer in the passive test mode than in the active mode. Grøntoft et al. [17] modelled the deposition velocity of organic pollutants to activated charcoal sorbents in museum display cases. The authors found differing reduction rates of initial pollutant concentrations but, unfortunately, did not explain these discrepancies. The results suggest that the reduction was lower at high air exchange rates in contrast to a higher removal rate at lower air exchange rates. However, it has to be considered that filtration devices installed in museum display cases will recirculate the display case air several times a day. In view of the results, the application of impregnated charcoal types, which are mostly more expensive than pure carbons, seems not to be urgently necessary for an effective removal of organic volatiles. Zeolites also have a higher cost and might be difficult to obtain. Due to their powdery nature, they are hard to use in display cases. They performed well in the passive-mode test, but no additional advantage was observed in comparison to activated charcoals. Products which are specially designed for museum purposes also had no additional advantages. On the contrary: The adsorption performance of most of them was evaluated as moderate or bad. Silica gels, which are often installed in museum display cases in order to buffer relative humidity, seem to have a slight filtration effect, but they cannot be recommended as effective adsorbent media.

In addition, the sorbents themselves might act as potential emission sources and release VOCs before and after exposure to a pollutant mixture. In particular a foam embedded with fine copper particles emitted a range of VOCs and had a strong smell. The analytical results also provided strong indications that most of the sorbents off-gas toluene and alpha-pinene in a changed atmosphere and might therefore act as secondary emission sources. Also, products formed by decomposition or secondary reaction processes might be released. Thus, the selection of adsorbent media for use in the environment of cultural assets has to be performed carefully. Regular monitoring to check the saturation of applied sorbents and the release of primary and secondary emissions is recommended. This can be carried out via discontinuous air sampling at specific time intervals in order to obtain information regarding the pollutant concentrations before installing sorbent media and the concentration gradient afterwards. When selecting monitoring devices, it should be taken into consideration that the chosen method must be able to detect the specific target substances even at low concentration levels [34].

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Authors' contributions
The author developed and performed the test series presented in this manuscript. The author read and approved the final manuscript.

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Availability of data and materials
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Competing interests
The author declares that she has no competing interests.

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References

1. Camuffo D, Sturano G, Valentino A. Showcases: a really effective mean for protecting artworks? Thermochim Acta. 2000;365:65–77.
2. Schieweck A, Salthammer T. Emissions from construction and decoration materials for museum showcases. Stud Conserv. 2009;54:218–35.
3. Schieweck A, Salthammer T. Indoor air quality in passive-type museum showcases. J Cult Herit. 2011;12:205–13.

4. Grøntoft T. Performance evaluation for museum enclosures. Measurement, modeling and mitigation of pollutant impact on objects in museum enclosures. e-Preservation Science. 2012;9:36–46.
5. López-Aparicio S, Grøntoft T, Odlyha M, Dahlin E, Mottner P, Thickett D, Ryhl-Svendsen M, Schmidbauer N, Scharff M. Measurement of organic and inorganic pollutants in microclimate frames for paintings. e-Preservation Science. 2010;7:59–70.
6. Schieweck A. Airborne pollutants in museum showcases—material emissions, influences, impact on artworks. Dresden: Hochschule für Bildende Künste; 2009.
7. Uhde E, Salthammer T. Impact of reaction products from building materials and furnishings on indoor air quality—a review of recent advances in indoor chemistry. Atmos Environ. 2007;41:3111–28.
8. Brokerhof AW, van Bommel M. Deterioration of calcareous materials by acetic acid vapour: a Model Study. In: Bridgland J, editor. Proceedings of the 11th triennial meeting of the ICOM committee for conservation. London: James & James; 1996. p. 769-75.
9. Niklasson A. Atmospheric corrosion of lead. The influence of organic acid vapours and inorganic air pollutants. A contribution towards understanding the environmental degradation of historic organic pipes. Department of Chemical and Biological Engineering. Göteborg/Sweden: Chalmers University of Technology; 2005.
10. Niklasson A, Johannson L-G, Svensson J-E. Atmospheric corrosion of lead: the influence of formic acid and acetic acid vapors. J Electrochem Soc. 2007;154:C618–25.
11. Niklasson A, Johansson L-G, Svensson J-E. Influence of acetic acid vapor on the atmospheric corrosion of lead. J Electroch Soc. 2005;152:B519–25.
12. Grzywacz CM, Tennent NH. Pollution monitoring in storage and display cabinets: carbonyl pollutant levels in relation to artifact deterioration. In: Roy A, Smith P, editors. IIC, Preprints of the contributions to the Ottawa Congress, preventive conservation—practice, theory and research. The International Institute for Conservation of Historic and Artistic Works. Ottawa; 1994, p. 164–70.
13. Menart E, De Bruin G, Strlič M. Dose-response functions for historic paper. Polym Degrad Stab. 2011;96:2029–39.
14. Cruz AJ, Pires J, Carvalho AP, de Brotas Carvalho M. Comparison of adsorbent materials for acetic acid removal in showcases. J Cult Herit. 2008;9:244–52.
15. Grosjean D, Parmar SS. Removal of air pollutant mixtures from museum display cases. Stud Conserv. 1991;36:129–41.
16. Parmar SS, Grosjean D. Sorbent removal of air pollutants from museum display cases. Environ Int. 1991;17:39–50.
17. Grøntoft T, Lankester P, Thickett D. Reduction of acidic pollutant gases inside showcases by the use of activated carbon adsorbers. e-PreservationScience. 2015;12:28–37.
18. Gunschera J, Andersen JR, Schulz N, Salthammer T. Surface-catalysed reactions on pollutant-removing building products for indoor use. Chemosphere. 2009;75:476–82.
19. Ligterink F, Di Pietro G. The limited impact of acetic acid in archives and libraries. Herit Sci. 2018;6:59.
20. Gibson LT, Watt CM. Acetic and formic acids emitted from wood samples and their effect on selected materials in museum environments. Corros Sci. 2010;52:172–8.
21. Ryhl-Svendsen M, Glastrup J. Acetic acid and formic acid concentrations in the museum environment measured by SPME-GC/MS. Atmos Environ. 2002;36:3909–16.
22. Raychaudhuri MR, Brimblecombe P. Formaldehyde oxidation and lead corrosion. Stud Conserv. 2000;45:226–32.
23. Itodo AU, Abdulrahman FW, Hassan LG, Maigandi SA, Itodo HU. Application of methylene blue and iodine adsorption in the measurement of specific surface area by four acid and salt treated activated carbons. NY Sci J. 2010;3:25–33.
24. ASTM D4607. Standard test method for the determination of iodine number of activated carbon. West Conshohocken: ASTM International; 2014.
25. Noll KE, Gounaris V, Hou W-S. Adsorption technology for air and water pollution control. Chelsea: Lewis Publishers, Inc.; 1992.
26. Salthammer T. Environmental test chambers and cells. In: Salthammer T, Uhde E, editors. Organic indoor air pollutants: occurrence, measurement, evaluation. Weinheim: Wiley-VCH; 2009. p. 101–15.
27. DIN EN ISO 16000-9. Indoor air—part 9: determination of the emission of volatile organic compounds from building products and furnishing—emission test chamber method. Berlin: Beuth Verlag; 2008.
28. McLafferty FW, Turecek F. Interpretation of mass spectra. Mill Valley: University Science Books; 1993.
29. Hübschmann H-J. Handbook of GC-MS. 3rd ed. Weinheim: Wiley-VCH; 2015.
30. Massold E, Bähr C, Salthammer T, Brown SK. Determination of VOC and TVOC in Air using thermal desorption GC–MS—practical implications for test chamber experiments. Chromatographia. 2005;62:75–85.
31. Belman S. The fluorimetric determination of formaldehyde. Anal Chim Acta. 1963;29:120–6.
32. VDI-Richtlinie 4301 Blatt 7. Messen von Innenraumluftverunreinigungen - Messen von Carbonsäuren. Berlin: Beuth Verlag; 2018.
33. Harper M. Sorbent trapping of volatile organic compounds from air. J Chromatogr A. 2000;885:129–51.
34. Schieweck A, Salthammer T. Schadstoffe in Museen, Bibliotheken und Archiven. Stuttgart: Fraunhofer IRB Verlag; 2014.
35. Kontozova V, Deutsch F, Godoi A, Joos P, Van Grieken R. Characterisation of air pollutants in museum showcases. Antwerpen: University of Antwerpen; 2002.
36. Jae J, Tompsett GA, Foster AJ, Hammond KD, Auerbach SM, Lobo RF, Huber GW. Investigation into the shape selectivity of zeolite catalysts for biomass conversion. J Catal. 2011;279:257–68.

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