ADSORPTION PURIFICATION OF INDOOR AIR, MAINLY FROM FORMALDEHYDE

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ABSTRACT

Formaldehyde (FA) adsorption, including that in the presence of water vapours, has been evaluated on sorbents of various nature and porous structure. The efficiency of porous adsorbents (active carbons, silica-gels) with a pore size of 2-200 nm, providing rapid adsorption of low FA concentrations from dry air and a high sorption from the FA-water mixture, has been demonstrated. Recommendations on the practical use of adsorbents for indoor purification have been given.

INTRODUCTION

Due to wide application of polymer materials and composites in building (wood-particle and wood-fibre boards - WPB and WFB, linoleum, lacquers, paints, etc.) and in living accommodations (furniture, synthetic carpets, synthetic detergents means, etc.) considerable concentrations of organic toxic substances, sufficiently exceeding the permissible concentration (PC), are accumulated [1-3]. As the complete substitution of the synthetic materials for the natural ones is unreal, then the problem of indoor air purification has become actual.

Formaldehyde stands apart in this group of substances due to its 'universality' from the viewpoint of emission from quite different materials, due to its high toxicity and reactivity and, often, due to its considerable concentration excess in indoor air if compared with PC. The PC values are defined by Health Departments and are equal to, e.g., 0.3 ppm in the USA, 0.1 ppm in Germany, and 0.0125 ppm in Latvia.

WPB and WFB having ureaformaldehyde resins as one of the basic components, used in building (floors, walls) and furniture production appear to be the main source of formaldehyde emission. The reasons for FA emission are as follows: excess of FA in adhesives, incomplete condensation in the production of boards, hydrolysis of adhesives (the primary bonding agents) when exposing WPB and WFB under humid conditions.

Some technological methods must be undertaken to decrease FA emission, i.e. the application of FA-low or FA-free adhesives (which are very expensive if compared with the ureaformaldehyde one), improvement of the condensation technology in the production of WPB and WFB, use of protective films (particularly, laminates for furniture), as well as painters and wall-paper glue containing FA acceptors. Electrondonating compounds (ammonia, ammonium salts, mono- and polyglycols, ureas, etc.) usually act as acceptors [1].

There is some evidence in the literature concerning the effective use of physical adsorbents for this purpose [4], although, these investigations are erratic.

The aim of the current study is the search for an effective FA adsorbents for indoor air purification in living accommodations equipped with WPB and WFB. We have studied the FA sorption by various groups of sorbents under static conditions and also in the presence of water vapours.

EXPERIMENTAL

Materials: Some substances have been tried as FA adsorbents: non-porous fillers and pigments – chalk (chemically precipitated, the average size of particles **D** = 1-3 μm), talc, zinc oxide (**D** = 5 μm), titanium dioxide (**D** = 1-5 μm), non-porous calcium metasilicate (wollastonite); porous adsorbents – mineral: silica-gels having narrow pores size distribution-KCM (the average pore size **d** = 2.2nm), KSS (**d** = 5.0nm) and KSK (**d** = 10.5nm), the natural ceolites (type of klinoptillolite), calcium metasilicate; carbon – active carbons of various porous structures (industrial and laboratory samples produced in Russia).

Methods: FA sorption was defined at 298K using vacuum spring scales with quartz spiral at the vacuum residual pressure 1 Pa, the length of spirals was measured by a horizontal microscope having a 0.005 mm accuracy. Paraformaldehyde (PF), decomposed by heating up to 100-120 °C, served as the FA source [5]. The pressure of vapours was measured by a deformation gas-discharged manometer with a 0.02 mm Hg scale graduating mark within the 0.2-5÷6 mm Hg range, that corresponds to the area of the relative pressures of a sorbate 0.00002 – 0.0001 (pressure of the FA-saturated vapour at 298K is 11700 mm Hg - calculated according to R. Spence [5]).

The adsorption of the water vapours-FA mixture was defined on some active coal samples (Table 1) in desiccators over the formalin solution (FA content 37% mass, partial FA pressure 2.78 mm Hg [5]). For comparison, the adsorption of dry FA in desiccators over PF (pressure of FA vapours at 298K 1.45 mm Hg) and water at the relative pressure of water vapours 0.95 was defined.

RESULTS

FA adsorbtion isotherms are of arching mode with saturation (I type according to the BET classification [6] (Fig. 1). In some cases, the adsorption efficiency of low-FA concentrations appears to be so high (some coals and silica-gels) that we cannot manage to measure the pressure in the initial part.

By the values of adsorption close to saturation **a**, the sorbents may be related to 3 groups: **a** < 0.01-0.02 g/g – roughly-dispersed non-porous sorbents (talc, wollastonite); **a** ≅ 0.1 g/g – finely-dispersed non-porous (zinc oxide, titanium dioxide) and micro-porous (KSM, ceolites) sorbents; **a** ~ 0.3-0.4 g/g – porous metasilicate, micro- and macro-porous carbons (AUL BAU); **a** ~ 0.6-0.8 g/g – meso- and macro-porous silica-gels (KSS, KSK) and carbons (AG-3, SKT-0).

Obviously, the porous sorbents are more effective due to their developed surface. However, the micro-porous sorbents, the absorption on which is rather low in spite of a high specific surface, are exceptions. To our mind, this may be explained by FA polymerization and difficulties of the diffusion into narrows pores (or entrances into pores as in ceolites) for the oligomer FA structures.

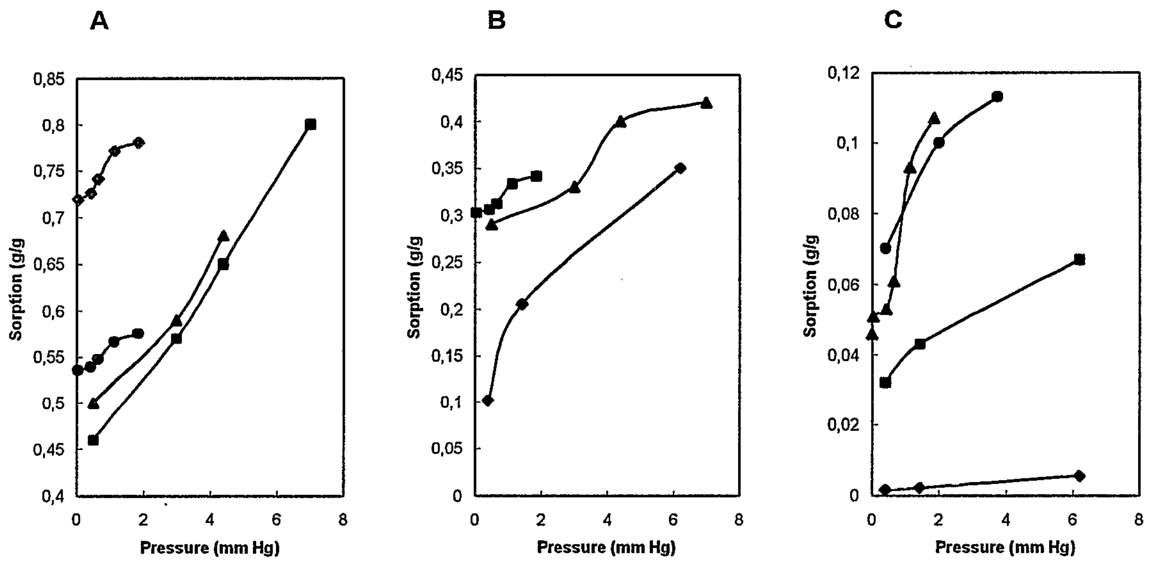

Fig.1. The adsorption isotherms of FA. A: ■ - on SKT; ▲ - on KCK; ● - on AG-3; ◆ - KSS; B: ◆ - on AUL; ▲ - on UAF; ■ - on BAU; C: ◆ - on talc; ■ - on ceolite; ▲ - on titanium dioxide; ● - on KSM.

Table 1. Characteristics of porous sorbents

Sorbent	Specific surface area, m^2/g	Volume of pores, cm^3/g			Irreversible FA adsorption, %
		Total	Size less 200 nm	Size less 20 nm	
Carbons:					
ACB	1000-1200	0.80	0.60	0.45	-
AG-PR	-	0.90	0.45	0.35	34.6
SKT-0	1200-1500	0.60	0.55	0.40	13.0
AG-3	800-1000	0.95	0.38	0.32	
FAS-3	1200-1400	0.96	0.94	0.45	98.8
BAU	400-500	1.70	0.35	0.22	47.5
UAF	-	-	0.44	0.25	-
AUL	1200	0.65	0.60	0.25	96.9
Silica-gels					
KSM	530	-	0.30	-	98.2
KSS	525	-	0.66	-	13.6
KSK	350	-	0.92	-	68.7

It has been found that FA sorption is irreversible on all the sorbents under study, while the share of the FA retained from the vacuum treatment depends on the sorbent structure (some examples are shown in the Table 1). It can be seen, the micro-porous adsorbents do not practically desorb FA. However when heated to 100°C, FA in all cases is desorbed practically completely.

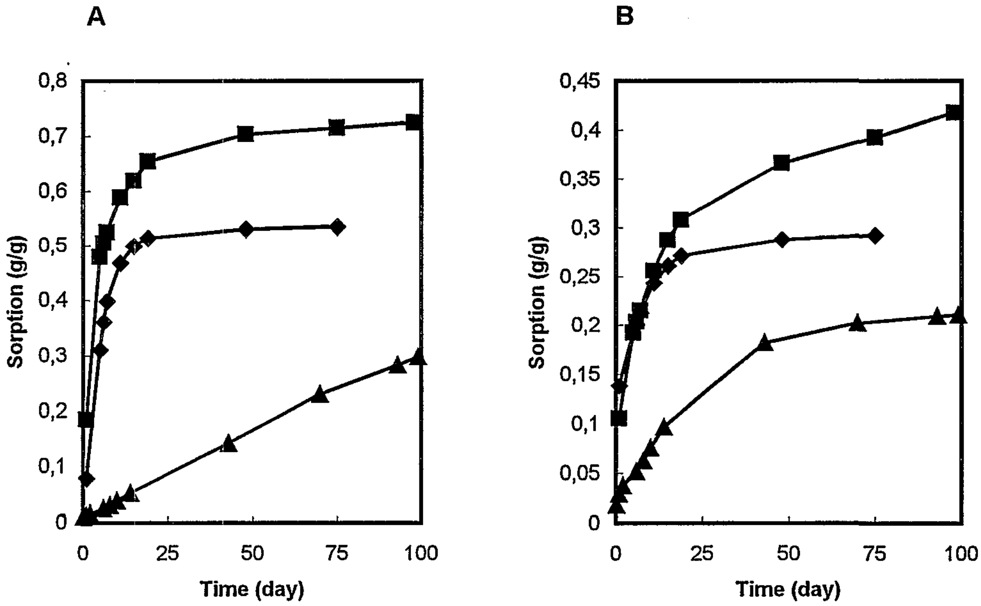

Fig. 2. Adsorption kinetics: ▲ - FA; ◆ - water; ■ - FA-water mixture (**A** – ACB, **B** – BAU).

Due to a large variety of sorbents, it is rather difficult to find common features for the evaluation of their efficiency. According to the data shown on Fig. 1, silica-gels and active carbons can be recommended for practical application. We have chosen the latter due to their availability and a sufficiently wide enough assortment.

Kinetics and equilibrium sorption of the water vapours, FA and FA-water mixture have been performed for some samples of active carbons using the desiccator method (Fig. 2).

The kinetic curves of FA sorption by the micro-porous - carbons (FAS, AUL) testify a lower rate of FA diffusion in comparison with macro- and meso-porous sorbents (BAU, UAF), although the maximal sorption in the first case can be higher. Hence, for quick FA adsorption, more widely-porous carbons are preferable.

At the same time, the diffusion of water vapours into micro-porous carbons occurs rapidly. It also indicated kinetic difficulties connected, apparently, with the FA polymerization near the surface.

The character of the kinetic curves of the water - FA mixture (over formalin) is similar, in most cases, to that of water. However, as a rule, the mixture sorption exceeds the water one, and, consequently, the FA part is adsorbed by a sorbent due to dissolving in the adsorbed water.

A linear correlation between FA adsorption and the pore volume, including micro- and mesopores, the width of which does not exceed 200 nm, has been determined for all the groups of active carbons under study (Fig. 3).

The relationships between the water and the water-FA mixture adsorption and the volume of pores (Fig. 3) can be presented by a curve with a maximum, thus indicating that the decisive factor in sorption is not the volume of pores but the accesible specific surface area which decreases with the increase of the pores volume (caused by the increase of their sizes).

A distinct character of this dependence in the case of FA on the one hand, and water and the FA-water mixture on the other hand indicates the possibility of the polymerization of dry FA in the pores of sorbents.

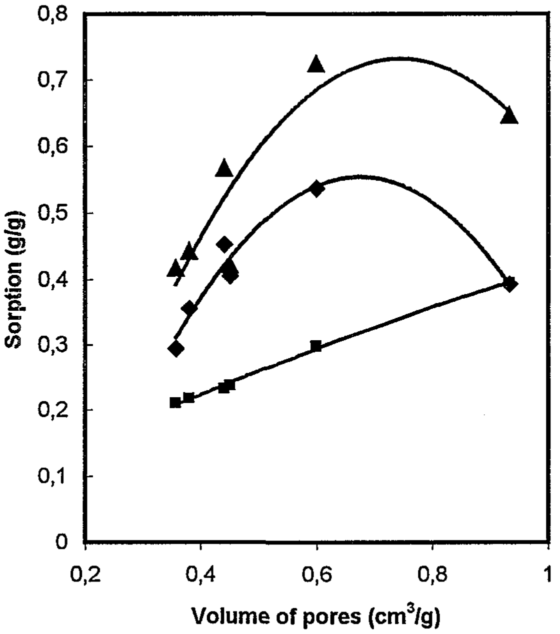

Fig. 3. Adsorption of FA (■), water (◆) and FA-water mixture(▲) against volume of pores (micro- and mesopores).

Based on the experimental data, some variants have been suggested and tested for the indoor air purification from FA by adsorbent using: a domestic air cleaner equipped with a holder with adsorbent and with a ventilator; developed and approved formulations for pigments composition, containing adsorbents capable to accept FA; developed compositions of heat-insulation compounds having FA adsorbents.

CONCLUSION

The adsorption of FA on sorbents is determined, first of all, by the porous structure of the sorbent - pores volume and size, and not the chemical nature of the surface. The adsorption of FA on porous sorbents exceeds that on non-porous powders hundred times. The adsorption of FA from dry air is directly proportional to the sorbents pores volume and, in the presence of water vapours, it is maximum at a pore volume of 05-0.6 cm^3/g, characteristic for mesoporous sorbents.

The polymerization of FA at the surface is the reason for its slow diffusion in narrow porous (**d** < 2 nm) sorbents. In these sorbents, the sorption of FA at normal temperatures is practically irreversible. For rapid purification of indoor air from FA, supra- mesoporous sorbents (**d** ≅ 10-200 nm) - active carbons and silica-gels - are most effective.

It should be mentioned that these sorbents, mainly active carbons, also readily adsorb other organic toxic substances.

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