CARBON/POLYMER COMPOSITE ADSORPTION-FILTERING MATERIALS FOR INDIVIDUAL PROTECTIVE SYSTEMS

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Abstract. The aim of this work was the development of improved adsorption-filtering materials appropriate for individual or collective protection systems. The work focused on creating and studying novel composite adsorption-filtering materials (CAFM) based on 'Carbon Adsorbent [active component] - Polymer [matrix]' and optimizing the media characteristics. The following different methods for preparing optimized CAFMs were pursued: a) formation of block CAFM (hard structure); b) formation of an elastic CAFM based on polymer foams; c) and formation of an immobilized CAFM (adsorption-active components were immobilized on a polymeric filter material by the extrusion process). The optimized composites can be used as a means of protection for personnel, working in areas polluted by toxic (including radioactive) gases and dusts.

Keywords: composite; adsorption; filtering; protection

1. Introduction

A target of this work was to develop novel adsorption-filtering materials (CAFM) and to optimize their properties. Means of creating composite materials on the basis of carbon adsorbents and polymeric matrixes capable of carrying out simultaneous adsorption and filtering functions at the point of use in gas and

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M.D. Annable et al. (eds.), Methods and Techniques for Cleaning-up Contaminated Sites, 187–196.

liquid environments were developed (Marushko 1979). This research was conducted in this field developing appropriate technologies and preparation of new prospective adsorption-filtering materials in the framework of international cooperation (NATO grant SfP 977995).

An adsorption-active component the fruit-stones active carbon of KAU-type and its modifications were considered.

The polymeric systems include various commercial polymers – polyvinyl alcohol (PVA), polyvinyl chloride (PVC), linear polyurethane's (PU) and fiber polypropylene (PP), which formed the basis for composites of block, foamy and elastic characteristics. Appropriate modification of polymeric matrixes as carrier materials can also have additional functions, for example, bactericide or fungicide properties, complexion ability to metal ions, etc.

Physical and chemical properties of composites (adsorption activity, volume and distribution of pores volume, specific surface area) as well as their operational characteristics (gas and aerosol permeability, flow resistance, etc.) were investigated depending on ratio of carbon to polymer. The variants of use of such composites were considered as a basis to produce the improved filters and respirators.

2. Experimental

Three types of CAFMs have been generated - block and foamy types, and also immobilized particles of adsorbent on the non-cloth filtering material.

As a base carbon adsorbent, fruit-stone activated carbon KAU has been used. The generation techniques were developed at the Institute of Sorption and Problems of Endoecology, NAS of Ukraine (National Standard TU U 88.290.015-94). The fractions of carbon used were 0.5-1 mm (grains) and less than 0.1 mm (powder) in diameter. The main adsorption characteristics of the material: volume of adsorption pores of *benzene* (W_s) 0.6 cm^3/g; specific surface area on *argon* (S_{sp}) 1100 m^2/g.

As polymeric components for generation of composites of block type, polymers of industrial production PVA, PVC and PU were used. To prepare a CAFM of a foamy type, foamed polyurethane (FPU) was used. Immobilized composites were generated based on industrial non-cloth filtering material (NFM) from PP ultrafine fibers.

Method of generation of block CAFM. Active carbon KAU was initially processed using solvent (carbon tetrachloride, ethylbuthylacetate, methylene chloride, etc.), followed by drying at room temperature. After this, carbon was mixed with solutions of polymers of different concentration (5-30% wt.), placed in special "sieve" form and dried under loading (0.1-1 kg/cm^2) at temperature 50-60°C and the lowered pressure (2 mm Hg). The resulting ratio of carbon to polymer in the block CAFM was 85-99.8 : 0.2-15, % wt. (Patent 2002).

Method of generation of elastic (foamy) CAFM. Active carbon KAU was initially processed using solvent, dried at room temperature and mixed with the components necessary for producing a foamed PU. After this, formation and drying of the material was carried out. The resulting ratio of carbon to polymer in the elastic CAFM was 25-55 : 45-75, % wt. (Patent 2003a).

Method of generation of immobilized CAFM. The powder of high disperse active carbon KAU or its suspension in a polymer (PVA, PU) was delivered through a dosing device into a system of aerodynamic formation of ultrafine fibers from the melted PP simultaneously drawing components on a moving generation surface, where these were coupled. The resulting ratio of carbon to polymer in the immobilized CAFM was 15-85 : 85-15, % wt. (Patent 2003b).

Parameters related to the porous structure of initial carbon and the resulting CAFMs have been investigated including the parameters W_s, and S_{sp}. The distribution of volumes of macro- and mesopores on equivalent radii were determined with a mercury porosimeter (Model M9200, "Cultronics").

Research on kinetic and diffusion characteristics of carbon, KAU and CAFMs were carried out under static conditions and in a dynamic mode using a substance - marker (*methylene blue*) from corresponding water solutions. Also, the significance of the time to achieve adsorption for effective and true diffusion were determined and their comparative analysis was completed.

Operational properties of CAFM were estimated by the level of dust content (dust creation) for active carbon and composites, and on dynamic characteristics (time of protective action on *benzene* in accordance with GOST 12.4.158-75, resistance to a constant flow of *air* in accordance with GOST 10188-74, factors of penetration of *microgrinding powder M-5* and an *oil fog* in accordance with GOST 12.4.156-75).

3. Results and Discussion

By original technologies three principally different CAFMs derived from fruit stones carbon KAU (grains – KAU$^{(1)}$ and powder – KAU$^{(2)}$) and polymers of various structure (Table 1) were synthesized and investigated, namely: block (KAU-PVA, KAU-PVC, KAU-PU), elastic foamy (KAU-FPU) and immobilized (KAU-NFM) CAFMs.

A block CAFM was prepared from carbon grains suspended in solutions of polymers. On Figure 1 the relationship between polymer content in composite (C) versus initial concentration of polymer in solution (C*) and loading at formation of composite (P) are presented.

The synthesis of elastic foamy CAFM involved several chemical transformations in carbon grains or powder suspension with solution of urea, diisocyanate, chain longer and polyester:

- reaction of chain's growth
  2OCN-R-NCO + HO-R'-OH → OCN-R-NHCOO-R'-OOCNH-R-NCO
  2OCN-R-NCO + H-R'-H → OCN-R-NHCO-R'-OCNH-R-NCO
- reaction of gas-educing
  $R\text{-}NHCOOH \rightarrow R\text{-}NH_2 + CO_2$
- formation of the bonds with cross-links
  -HN-CO-NH- + OCN-R-NCO + -HN-CO-NH- →
  -HN-CON*-CONH-R-NHCO-N*CO-NH-

where: R – various radicals, N* - free valences were able to bond with carbon.

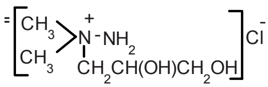
The immobilization of carbon particles on the non-fabric filtering material was produced during the formation of microfibers from melted PP using airflow technology. A principal scheme of producing CAFM of this type is presented in Figure 2.

By adsorption methods, weight analysis and *mercury* porosimetry, change in porous structure of CAFMs were investigated. It was determined that polymers acted basically as a blocking system to transport by pores in the carbon (macro- and partially mesopores). Intervals of insignificant influence of polymers on adsorption parameters of active carbon in CAFM can be determined from the data presented in Figures 3, 4 and Table 2.

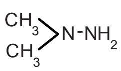
TABLE 1. Characterization of polymeric components to prepare CAFM with carbon KAU.

Polymer matrix	Elementary chain	Solvent
PVA	$(\text{-}CH_2\text{-}CHOH\text{-})_n$	H_2O
PVC	$(\text{-}CH_2\text{-}CHCl\text{-})_n$	DMFA
PU (PU-1, PU-2, PU-3)	$(R_1\text{-}CONH\text{-}R_2\text{-}NHCO\text{-}R_3\text{-}OCONH\text{-}R_2\text{-}NHCO\text{-}R_1\text{-})_n$, where $R_{1\text{-}3}$* – polyesters, diisocyanates, chain longer	DMFA, H_2O
PP	$(\text{-}CH_2\text{-}CHCH_3\text{-})_n$	-

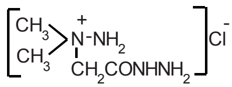
where R_1*: PU-1

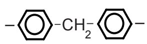


PU-2



PU-3



R_2*: 

R_3*: $\text{-}[\text{-}(CH_2)_4\text{-}O\text{-}]_n\text{-}$

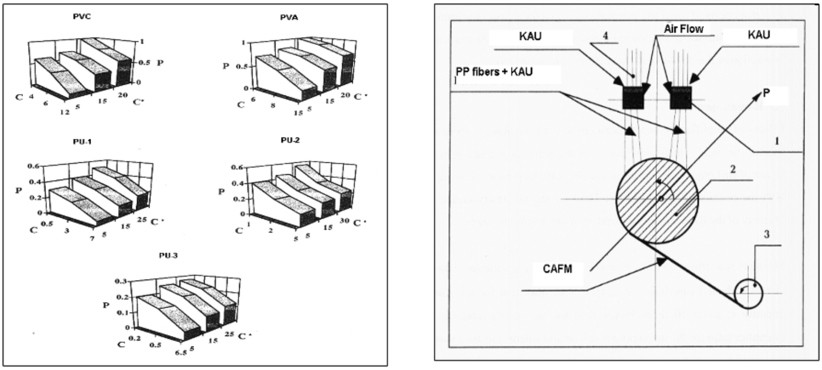


Figure 1. Diagrams of synthesis of block CAFM: C – content of polymer in composite, % wt.; C* - initial concentration of polymer in solution, % wt.; P – loading at formation of composite, kg/cm^2.

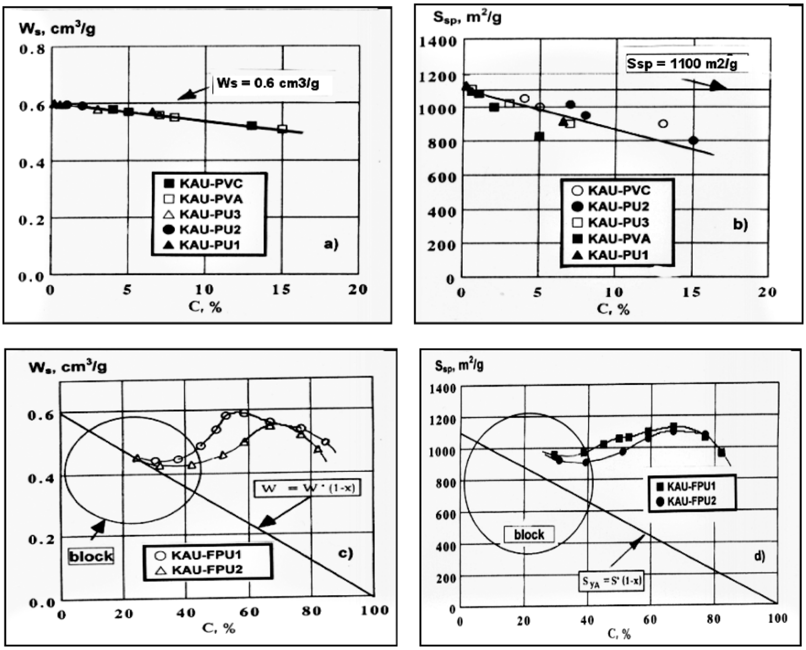


Figure 2. A principal scheme of producing CAFM of immobilized type on the base of carbon KAU (powder) and PP ultrafine fibers.

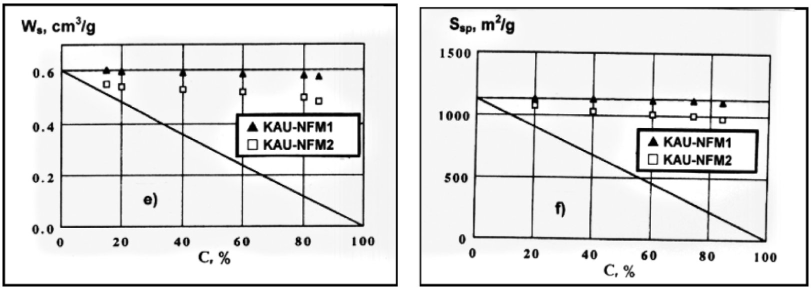


Figure 3. Significances of W_s (a, c, e) and S_{sp} (b, d, f) for carbon KAU in CAFM of various types: block (a, b), elastic foamy (c, d), and immobilized samples (e, f).

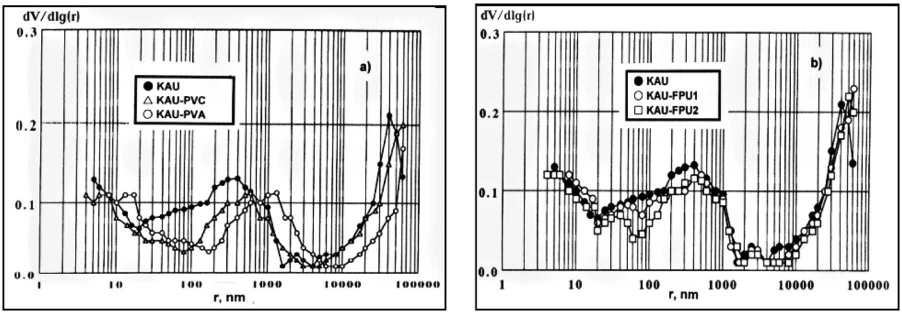


Figure 4. Distributions of pore volume on equivalent radii from mercury porosimeter study of carbon KAU and CAFM of block (a) and foamy (b) types.

TABLE 2. Changing parameters of porous structure of carbon KAU in block CAFM (1.5% wt. of polymer) and foamy CAFM (60% wt. of polymer).

Parameter	KAU(1)	Rigid blocks		Elastic foams	
		KAU(1)-PU-1	KAU(1)-PU-3	KAU(1)-FPU-1	KAU(2)-FPU-1
Volume of sorption pores (W_s), cm^3/g	0.60	0.59	0.58	0.59	0.58
Total volume of pores, cm^3/g	0.68	0.64	0.61	0.64	0.62
Volume of macropores, cm^3/g	0.22	0.19	0.18	0.19	0.17
Volume of mesopores, cm^3/g	0.24	0.23	0.21	0.23	0.23
Volume of micropores, cm^3/g	0.22	0.22	0.22	0.22	0.22
Predominant radius of pores, nm	0.72	0.88	0.91	0.88	0.90
Specific surface area (S_{sp}), m^2/g	1100	1050	1000	1080	1050
Surface area of transport pores, m^2/g	16.7	10.4	9.8	12.7	12.4

Based on the data obtained, the following conclusions result:

- In block composites, a polymer content up to 10% wt. linearly reduced W_s and S_{sp}, and reduced parameters proportionally to increased contents of the polymer in the CAFM;
- In foamy composites a polymer content within 50-70% wt. reduced parameters W_s and S_{sp} of the carbon in the composite near 3-5% wt.;
- Composites of immobilized type were characterized by almost full absence of influence of polymer content on adsorption characteristics of carbon in a composite (reduction of W_s and S_{sp} at any carbon to polymer ratio within the limits of 2-5% wt.).

The kinetics of adsorption was investigated using a model substance, *methylene blue,* from water solutions on CAFMs of block and foamy types and it was determined that the diffusion characteristics of these materials and found a delayed adsorption character on the composites comparable to the initial carbon. The corresponding decrease in diffusion coefficients were on average 5-20% wt. (Table 3).

TABLE 3. Effective and factual coefficients of diffusion at adsorption of *methylene blue* from aqueous solutions by carbon KAU and block and foamy CAFM on its base.

Sample	D_e*10^{-8}, cm^2/s (percentage from initial)	D_f*10^{-6}, cm^2/s (percentage from initial)
KAU$^{(1)}$	3.10 (100%)	5.80 (100%)
KAU$^{(1)}$-PVC	2.50 (81%)	5.20 (89%)
KAU$^{(1)}$-PVA	2.60 (84%)	5.22 (90%)
KAU$^{(1)}$-PU-1	2.70 (87%)	5.40 (93%)
KAU$^{(1)}$-PU-2	2.60 (84%)	5.30 (91%)
KAU$^{(1)}$-PU-3	2.70 (87%)	5.40 (93%)
KAU$^{(1)}$-FPU	2.64 (85%)	5.51 (95%)
KAU$^{(2)}$-FPU	2.48 (80%)	5.39 (93%)

Standard methods were used to estimate the operational characteristics of the resulting CAFMs. It was shown that these materials differed at high level of absorption of VOCs showing better physical mechanics characteristics than the initial carbon adsorbent, thus an increased durability, a low level of dust emission (in foamy - completely was absent) and insignificant resistance to a gas flow (Table 4).

The CAFM of the immobilized type was determined to be the simplest adsorption-filtering respirator for breathing protection of people simultaneously from VOC vapors, toxic or poisonous gases, dust particles and aerosols of various structure, including radioactive (see Table 5). Such a respirator can be considered an inexpensive mini-gas mask for short-term use designed for mass

TABLE 4. Exploitation characteristics of carbon KAU and block and foamy CAFM on its base.

Sample	Contents of polymer, %	Resistance to air flow, mm H_2O	Durability at pressing, kg/cm^2	Time of protective action on *benzene*, min	Dust particles emission, %
$KAU^{(1)}$	0	10.5	-	55	15
$KAU^{(1)}$-PVC	13	12	5	40	< 0.1
	5	11	5	45	0.1
	4	10.5	4.5	45	0.15
$KAU^{(1)}$-PVA	15	11	5	45	< 0.1
	7	10.5	5	45	0.1
	6	10	4.5	45	0.1
$KAU^{(1)}$-PU-1	7	10	4	45	0.1
	3	9	3.5	50	0.1
	0.5	9	3	50	0.1
$KAU^{(1)}$-FPU	50	0.65	-	30	Absence
$KAU^{(2)}$-FPU	50	0.55	-	25	Absence

TABLE 5. Comparison of exploitation characteristics of respirators prepared on the base of commercial (non-cloth PP fibers) filtering material NFM and developed immobilized CAFM (KAU-NFM).

Parameter	Commercial respirator on a base of NFM	Experimental respirator on a base of KAU-NFM
Coefficient of penetration of microgrinding powder, %		
D = 0.28-0.34 μ	1.4	1.4
D = 2 μ	0.8	0.8
Standard aerosol (M-5)	0.5	0.04
Resistance to air flow, mm H_2O		
at V = 30 L/min	< 2	< 2
at V = 3 L/min	0.60	0.48
Time of protective action on benzene		
at C = 50 mg/m^3, h	0	8 ± 1
at C = 10 g/m^3, min	0	5 ± 1
Protective action on radioactive ^{131}I -vapors, %	< 5	85 ± 5

use in extreme situations: collapses, fires, acts of terrorism, etc. (Figure 5). Further improvement of the characteristics of adsorption-filtering materials such as «active carbon - polymer» is possible by improving the carbon adsorbent (providing ion exchange, complexion, catalytic, antibacterial and other properties), and by improving a polymeric part (improving aero- and hydrodynamic characteristics, giving complexion, bactericidal or fungicidal properties, etc.).

Figure 5. Simplest respirators and filters produced on the base of CAFM of immobilized type (carbon KAU/PP ultrafine fibers non-cloth material).

4. Conclusions

1. The new techniques for preparation of carbon - polymeric adsorption-filtering materials of three types - block, foamy and immobilized ones have been developed and patented.

2. The character of porous structure changes for active carbon KAU in CAFMs of all types was investigated; the mixtures of carbon and polymer were determined that were expedient to use the resulting composites as adsorption-filtering materials.
3. The kinetic characteristics of adsorption on the resulting composites were investigated. It was shown that the coefficients of diffusion for carbon KAU were reduced in composites no more than 20%.
4. The estimation of the operational characteristics has shown that prepared samples of CAFM have a lot of the improved parameters, in comparison with used (commercial) analogues such as filtering materials.
5. The results for the CAFM of the immobilized type showed the simplest means of individual protection (filters and respirators), in particular adsorption-filtering respirators like the mini-gas masks as a quite inexpensive means for short-term protection of the population in variant of mass use at some extreme situations accompanied by pollution of air by toxic and radioactive gases and aerosols.

Acknowledgement

This work was supported by NATO - grant SfP 977995 “Novel Adsorption-Filtering Materials for Individual Protective Systems”.

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