

ADSORBENTS AND CATALYSTS ON THE BASE OF UTILIZED GAS MASK CARBONS

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Introduction

Now use of perspective raw sources for preparation of carbon sorbents and catalysts, and also regeneration of the fulfilled carbon materials, development and improvement of such methods [1-4] is actual. Use of new (cheap) kinds of raw material for manufacture of activated carbons is important both for a covering of deficiency, and for recycling waste products of some branches, in particular, catalysts of the fulfilled or out-of-date gas masks.

Gas mask protection is one of the oldest scopes of activated carbons [5]. By present time highly active gas mask carbons with a wide range of action are created. They are used not only in means for individual defense of bodies of breath, but also in the industry for clearing gas emissions, in ventilating installations of separate industrial boxes, vehicles, refuges, in electrochemistry, pharmacology, etc. For increasing efficiency of action gas mask sorbents, including carbons, are usually treated by various chemicals and impregnated by active components, therefore at clearing air as usual physical adsorption and chemisorptions, and catalytic reactions of decomposition of harmful substances occur. As impregnation chemicals are used oxides, hydroxides, carbonates and others (usual and the basic) salts of metals, more often copper, zinc, chromium, silver, etc. The obtained carbon adsorbent-catalyst contains till 15-20% of inorganic additives. Thus salts of copper, for example, bonds ammonia, amines and similar substances as complexes, promote hydrolysis of substances, in particular, chlorine cyan with transforming in harmless chloride of ammonium and carbonic acid; salts of silver promote catalytic oxidation of arsenic compounds and so on.

Gas mask carbon-catalysts are high-mineralized products; therefore their regeneration (conversion) should include also a stage of demineralization, for example, with diluted solutions of strong acids and alkalis.

An aim of this research – the development of a simple and effective way of conversion of gas mask carbon-catalyst into carbon adsorbent with the minimal loss of a carbonaceous component that would open an opportunity of its further use in standard technological processes involved activated carbons.

For this purpose a method of liquid phase oxidative-destructive regeneration of catalyst with nitric acid solutions was applied; it includes demineralization with simultaneous partial oxidation of a carbon matrix surface, as well as organic substances adsorbed in pores of initial material.

Besides the obtained oxidized carbon was subjected to additional processing in argon (at 850 °C, 1 h) to decompose superficial oxides and to transform the oxidized carbon into an ordinary form of active carbon. Active carbon was characterized in parallel with oxidized one [6, 7].

Except for mentioned method of liquid phase oxidative-destructive regeneration it was used more simple methods for chemical demineralization of carbon surface by solution of KOH, or solution of HCl, or alternate processing by these reactants of the same portions of carbon catalyst beginning with alkaline (removal of chromates), and then with acidic treatment (removal of copper salts).

During the offered regeneration it is possible partial mass loss of carbon matrix (corrosion, dissolving), as well as superficial oxidation of carbon with formation of protonogenic functional groups are capable to cation exchange. These processes are accelerated (promoted) in the presence of transitive metals; the contents of last are quite high in initial materials. It has caused search of optimum modes of regeneration for development of corresponding technologic schemes and producing schedules of appropriate process.

Experimental

The granulated carbon-catalyst from out-of-date gas mask was tested accordingly to standard specifications adopted in the former USSR. The following standards were used:

- GOST 16187-70 «The method of definition of fractional composition»;
- GOST 16188-70 «The method of definition of durability at friction»;
- GOST 16190-70 «The method of definition of bulk density»;
- GOST 12596-67 «The method of definition of a mass share of ashes»;
- GOST 12597-67 «The method of definition of a mass share of water in active carbons and catalysts on their basis»;
- GOST 17219-71 «The method of definition of total volume of pores on water»;
- GOST 17218-71 «The method of definition of protective action on benzene».

The main adsorption characteristics of obtained carbon adsorbents were determined by standard techniques [7]: specific surface area (S_{sp}) by gas chromatography method on thermal desorption of argon and volume of adsorption pores on benzene (W_s) by “executor” method”.

The initial gas mask catalyst had the following data:

- fractional composition - >1 mm (66%), 0.5-1 mm (34%);
- durability – 75%;
- bulk density – 550 g/dm³;

- mass share of ashes – 23,6%;
- mass share of water – 14%;
- total volume of pores – 0.75 cm³/g;
- protective action on benzene – 130 min (dynamics), 158 g/L (static capacity);
- pH of water extraction – 7.75;
- specific surface area on argon – 750 m²/g;
- volume of sorption pores on benzene – 0.25 cm³/g.

Oxidizing regeneration of gas mask catalyst were carried out in 25% solution of HNO₃ at boiling on a water bath with a variation of time of contact of material with acid at the same volume ratio solid: liquid (usually 1:3) from 2 till 6 h or with change of this ratio - 1:1, 1:3, 1:5 at identical time of processing - 4 h (Table 1, Figs. 1, 2).

The same conditions of experiences have been sustained also at processing by 1% KOH and 3% HCl solutions (see Table 2, Figs. 3, 4).

At oxidizing demineralization carbon catalyst loaded into the 2 L flat-bottomed flask supplied with a return refrigerator (usually took 50 g of material), added necessary volume of 25% nitric acids - 100 mL at ratio 1:1, 300 mL at ratio 1:3, and 500 mL at ratio 1:5, placed in a water bath; time of oxidation marked from the moment of boiling water in a bath.

After processing a material separated from a liquid phase, washed out by distilled water up to pH 7, and then alternately by 5% solution of the ammonia, distilled water, 3% hydrochloric acid (conversion into H-form [6]), and again by distilled water up to pH 7 in washing waters.

To increase cation exchange capacity of such processed gas mask catalyst an experience with replacement after 2.5 h of oxidation of the fulfilled acid by new portion with the subsequent boiling next 2.5 h have been carried out. The following processing by NH₄OH, H₂O, HCl was similar.

The fulfilled solutions of nitric acid, potassium hydroxide and hydrochloric acid after regeneration of material were collected, filtering through the paper filter from dust particles in separate utensils for the analytic definition of copper and chromium by atomic-absorption spectrophotometric method, and also for the further possible allocation of these elements by chemical or electrochemical methods.

Results and Discussion

It has been established (Table 1, Figs. 1, 2), that as a result of the offered oxidizing regeneration the content of ash has decreased from 24 till 9.5%. Apparently, due to removal of salts of impregnation (approximately 14.5%) a volume of adsorption pores has increased from 0.25 till 0.36 cm³/g, and a specific surface area - from 750 till 1180 m²/g. The samples NN1-8 (Table 1) have got property of cationite with static exchange capacity (SEC) 1-1.4 meq/g; an increasing in ratio of carbon: acid caused an increasing

in SEC, and it achieved greater degree, than at longer time of oxidation for parity of solid: liquid as 1:3.

Table 1. Results of oxidative-destructive regeneration of gas mask carbon catalyst.

N	Features of processing and amounts of chemicals	W_s , cm^3/g	S_{sp} , m^2/g	Ash, %	Mass yield, %
	Initial gas mask catalyst	0.25	745	23.6	-
1	M = 50 g, S:L = 1:3, t = 2 h; 25% HNO_3 – 0.3 L, 5% NH_4OH – 0.25 L, 3% HCl – 0.3 L, H_2O – 9.5 L	0.36	915	11.7	80.0
2	M = 50 g, S:L = 1:3, t = 4 h; 25% HNO_3 – 0.3 L, 5% NH_4OH – 0.25 L, 3% HCl – 0.4 mL, H_2O – 8 L	0.34	970	10.8	89.6
3	M = 50 g, S:L = 1:3, t = 6 h; 25% HNO_3 – 0.3 L, 5% NH_4OH – 0.25 L, 3% HCl – 0.3 L, H_2O – 10 L	0.29	1175	10.5	84.6
4	M = 50 g, S:L = 1:1, t = 4 h; 25% HNO_3 – 0.1 L, 5% NH_4OH – 0.25 L, 3% HCl – 0.4 L, H_2O – 8 L	0.17	850	9.4	88.0
5	M = 50 g, S:L = 1:5, t = 4 h; 25% HNO_3 – 0.5 L, 5% NH_4OH – 0.25 L, 3% HCl – 0.4 L, H_2O – 8 L	0.22	855	9.6	89.3
6	M = 50 g, S:L = 1:2.5, t = 2.5+2.5 h; 25% HNO_3 – 0.5 L, 1% KOH – 0.5 L, 3% HCl – 0.6 L, H_2O – 10 L	0.34	-	10,5	77.8
7	M = 70 g, S:L = 1:14, t = 5 h; 25% HNO_3 – 1.7 L, 1% KOH – 1 L, 3% HCl – 1 L, H_2O – 8 L	0.26	-	9.2	84.0
8	Sample N6 treated in argon; t = 1 h, T = 850 °C	0.48	1065	12.5	-

It is necessary to note, however, that we did not achieve the SEC value more than 1.4 meq/g neither at technologically unjustified big ratio carbon: acid 1:14, nor at two steps oxidation of catalyst with use of the fresh portion of nitric acid in the second stage.

The analysis of washed away elements - copper and chromium has shown that increase in amount of added acid at oxidation and especially duration of process of oxidation have rendered positive influence on a degree demineralization (Fig. 3). Thus, in the offered circuit of regeneration besides process of partial oxidation of a carbon surface there is also a removal of the various modifiers blocking adsorption pores, so reducing in ash of researched samples cause arising in their specific surface area (Figs. 1, 2).

Besides at oxidizing processing carbons practically do not lose the durability; it has not been marked appreciable losses of a carbon material: despite of duration of process,

repeated processing of carbon by various reactants and water the yield of a target product averaged 85-86%.

Table 2. Results of alkaline-acid regeneration of gas mask carbon catalyst.

N	Features of processing and amounts of chemicals	W_s , cm^3/g	S_{sp} , m^2/g	Ash, %	Mass yield, %
	Initial gas mask catalyst	0.25	745	23.6	-
1	M = 50 g, S:L = 1:3, t = 2 h; 1% KOH – 0.3 L, H ₂ O – 3.5 L	0.28	805	22.1	92.6
2	M = 50 g, S:L = 1:3, t = 2 h; 3% HCl – 0.3 L, H ₂ O – 2.5 L	0.38	1100	15.2	80.6
3	M = 50 g, S:L = 1:3, t = 2 h; 1% KOH – 0.3 L, 3% HCl – 0.3 L, H ₂ O – 4.5 L	0.23	1085	12.2	90.8
4	M = 50 g, S:L = 1:3, t = 4 h; 1% KOH – 0.3 L, 3% HCl – 0.3 L, H ₂ O – 5.5 L	0.24	1040	11.6	84.2
5	M = 50 g, S:L = 1:3, t = 6 h; 1% KOH – 0.3 L, 3% HCl – 0.3 L, H ₂ O – 7 L	0.34	895	15.3	81.0
6	M = 50 g, S:L = 1:1, t = 4 h; 1% KOH – 0.1 L, 3% HCl – 0.1 L, H ₂ O – 5 L	0.25	975	19.3	89.8
7	M = 50 g, S:L = 1:5, t = 4 h; 1% KOH – 0.5 L, 3% HCl – 0.5 L, H ₂ O – 5 L	0.26	920	10.8	79.8

Similar characteristics have been achieved after chemical demineralization of gas mask catalyst by 1% KOH, and then and 3% HCl solutions. As well as at oxidizing processing, in this case ash contents in material have reduced, values of W_s and S_{sp} have arisen, passing through a maximum (Figs. 1, 2); an amount of desorbed copper have increased at increasing time of contact of material with reagents and S:L ratio from 1:1 till 1:5, achieving practically the same significance of desorption, as in case of processing with nitric acid.

Alkaline-acidic regeneration was carried out also in static conditions at boiling certain amount of carbon (50 g) in a flat-bottomed 2 L flask with a return refrigerator on a water bath. After contact with solution of KOH carbon material was washed up to pH 7-8 by distilled water, then necessary amount of 3% HCl solution was added, and processing was continued at boiling during short time. After finishing an acid solution (also, as well as alkaline) was separated in utensils, filtering through the paper filter from dust particle, for the analysis of modifiers. Finally carbon was washed by distilled water at boiling.

It is necessary to note that as a result of such processing the activated carbon with anion exchange property ($SEC = 0.4-0.6 \text{ meq/g}$ on 0.1 N HCl) and increased value of specific surface area ($S_{sp} = 900-1040 \text{ m}^2/\text{g}$) was prepared.

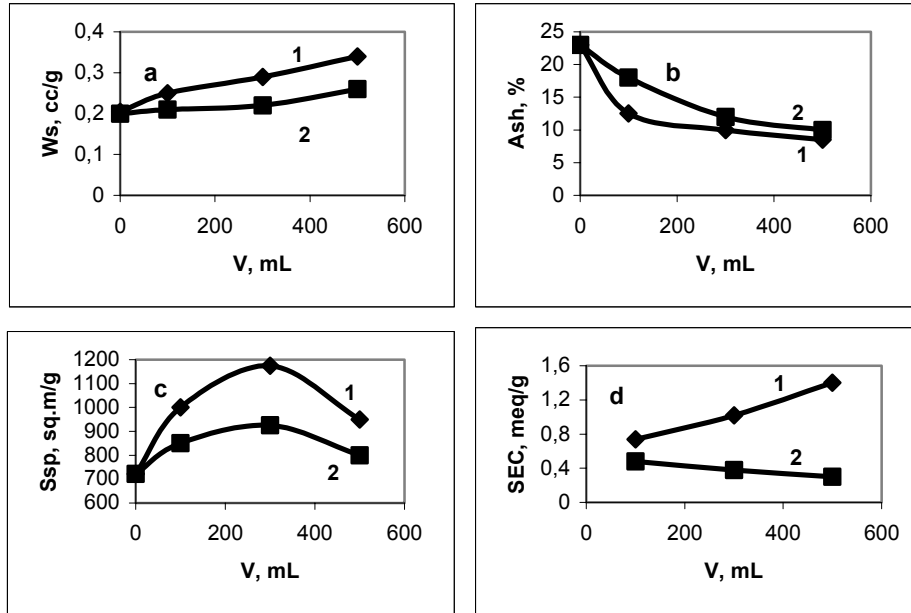


Figure 1. Change a) volume of adsorption pore on benzene (W_s , cm^3/g), b) ash content (%), c) specific surface area (S_{sp} , m^2/g), and d) static exchange capacity (SEC, meq/g) on 0.1 N NaOH after oxidative-destructive (1) and alkaline-acid (2) processing's during 4 h. V - volume of added reagent to 100 ml of carbon material.

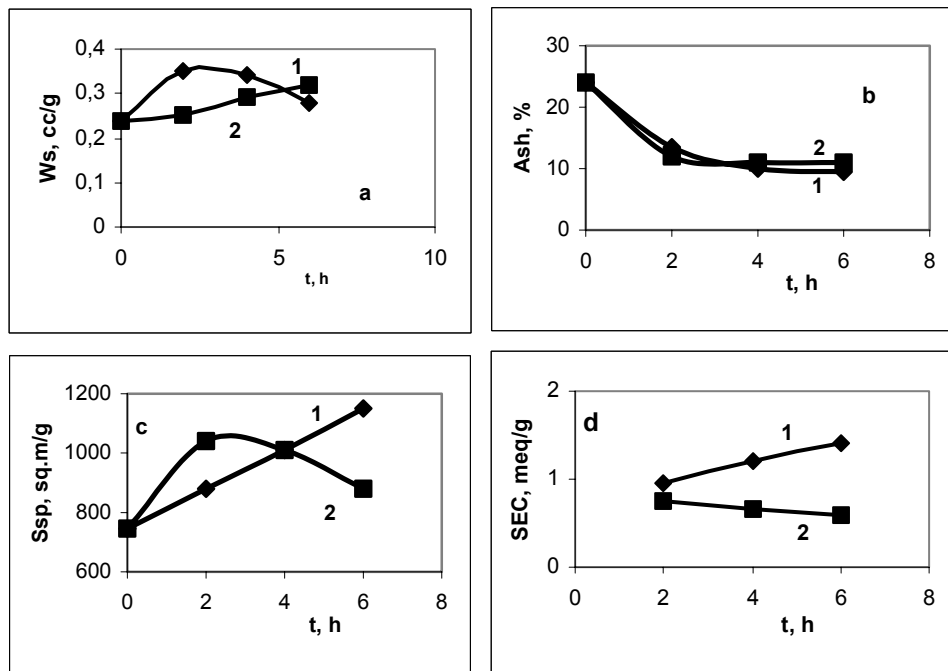


Figure 2. Change a) volume of adsorption pore on benzene (W_s , cm^3/g), b) ash content (%), c) specific surface area (S_{sp} , m^2/g), and d) static exchange capacity (SEC, meq/g) on 0.1 N NaOH after oxidative-destructive (1) and alkaline-acid (2) processing's at the S:L ratio = 1:3. t – time of processing.

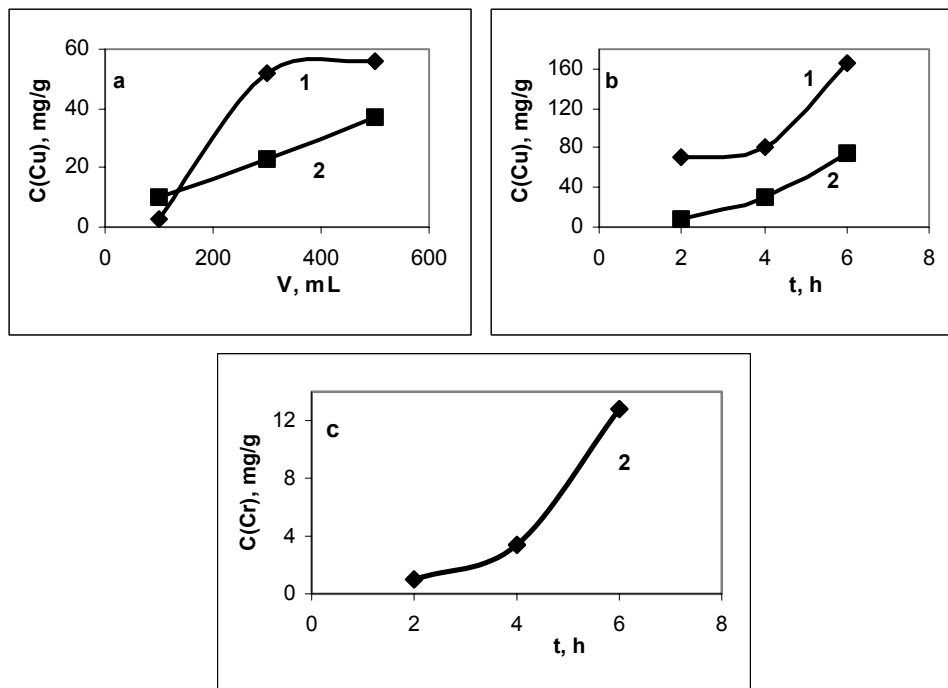


Figure 3. Desorption (C , mg/g) of copper (a, b) and chromium (c) at oxidative-destructive (1) and alkaline-acid (2) processing's during 4 h and various S:L ratio (a) and S:L ratio = 1:3 and various time of processing (b, c). V – volume of the reagent added to 100 mL of carbon; t – time of processing.

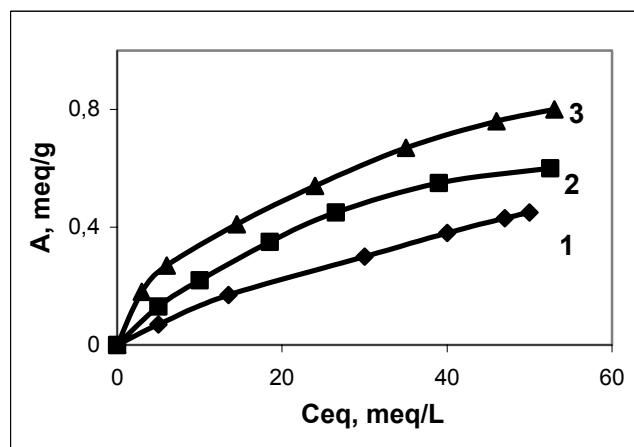


Figure 4. Isotherms of adsorption (A , meq/g) of Cr^{3+} (1), Cu^{2+} (2), and Fe^{3+} (3) from aqueous solutions of nitrates. C_{eq} - equilibrium concentration of metal ions.

Processing gas mask catalyst with only 1% KOH solution at two-hour boiling (Table 2) appeared insufficient for reception of carbon adsorbent of desirable quality; the sample was still high ash content with practically same value of S_{sp} , as initial carbon material. But boiling of catalyst with a solution of hydrochloric acid (experience 2, Table 2) during

the same 2 hours and the same ratio 1:3 (S:L) was more effective, than processing by alkali (see Table 2); thus quite high values of $W_s = 0.38 \text{ cm}^3/\text{g}$ and $S_{sp} = 1100 \text{ m}^2/\text{g}$, and desorbed copper (till 6%) have been achieved. At oxidation by nitric acid (see experience 1, Table 1) a sample with similar characteristics (some smaller $S_{sp} = 915 \text{ m}^2/\text{g}$, but some bigger desorbed copper – till 11 %) have been obtained.

After special processing oxidized carbon material (experience 7, Table 1) in atmosphere of argon at $850 \text{ }^\circ\text{C}$ during 1 h a high-quality sample of activated carbon with quite high volume of adsorption pores ($W_s = 0,48 \text{ cm}^3/\text{g}$) and specific surface area ($S_{sp} = 1060 \text{ m}^2/\text{g}$), and twice reduced ash content have been obtained.

The preliminary analysis of data resulted in Tables 1, 2 and on Figs 1, 2 has shown that optimum conditions both oxidative-destructive and alkaline-acidic processing's for reception of the carbon adsorbent with quite comprehensible characteristics were following: ratio S:L = 1:3 and time of processing - 2 h. For achievement of the best parameters for carbon adsorbents at carbon catalyst regeneration it is necessary to increase time of processing and amount of chemicals.

Thus, as a result of regeneration of gas mask catalyst by proposed two liquid phase methods it was obtained two types of carbonaceous adsorbents: activated carbon with high adsorption characteristics, and its oxidized modification possessed properties of cation exchanger. So, it was studied ion exchange ability of the oxidized sample in relation to ions of copper, chromium, and iron (Fig. 4). Appeared that such carbon cationites quite good bonded Fe^{3+} and Cu^{2+} ions, and less Cr^{3+} ions. This is typical for the majority of oxidized carbons in similar conditions [6].

An activated carbon obtained due to regeneration (conversion) of gas mask catalyst can be applied, most likely, to clearing gas emissions of various organic substances (VOC, dyes, gasoline, diesel fuel, etc.), as well as the carrier of the catalyst for partial and full oxidation of organic impurities in air and technological gases.

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