Carbon Adsorbents and Catalysts Produced from Worked out Gas Mask Cartridges

N.T. Kartel*, S.S. Stavitskaya, S.V. Zhuravsky and V.V. Strelko

Institute for Sorption and Problems of Endoecology, National Academy of Sciences of Ukraine,
General Naumov Street 13, 03164, Kiev, Ukraine

Abstract

It is offered here the procedure of utilization of gas mask or respirator charge when operation term is expired. This technique enables to get not only high quality active carbon but also its oxidized variety that has properties of polyfunctional carboxylic cationite and catalyst decomposition of hydrogen peroxide (catalysis activity). Structure-sorption properties of the obtained adsorbents are listed below.

Introduction

Respirator protection is one of the oldest areas of application of active carbons [1]. They are widely used in collective and individual means of protection of breathing organs (respirators and gas masks) at the industrial plants, agro-industrial branches and armed forces of all countries to protect military contingent against chemical agents. To increase operation effect of respirator carbons they are modified with different agents, such as oxides, hydroxides, carbonates, etc., including complex compounds of transition and noble metals (copper, zinc, chromium, silver and others). Such modification of active carbons increases their capacity for refining of the inspired air not only due to physical adsorption of hazardous and poisonous substances but also owing to their chemical adsorption and catalytic decomposition up to innocuous compounds.

It is necessary to note, that according to quite understandable reasons some information about the grade of used carbon as well as formula of modifiers and technique of their application on carbon is kind of information which publication is limited. At the same time typical composition of modifier is well known. According to data [2] for impregnation of 100 kg of active carbon three solutions are used:

- 6 kg of primary copper carbonate, 5 kg of ammonium carbonate, 10 L of 25% ammonia water solution and 10 L of water;
- 6 kg of potassium dichromate and 34 L of water;
- 170 g of silver nitrate and 0.5 L of water.

As appears from the above that carbonic adsorption-catalyst has inorganic admixtures in its structure from 12% to 15%.

In view of stockpiling of used respirators and gas masks, as well as obsolescence of their strategic stocks, the problem of their complete utilization has emerged. It looks attractive to use adsorption-catalytic charge (batch powder) of respirators as adsorbent in solving many practical problems of refinement, isolation and separation of substances. However, high content of modifier practically excludes the usage of batch powder as active carbon in traditional scope of activity. Hence, it is necessary to work out the procedures of regenerative conversion of gas mask batch powder into active carbon.

The goal of the given information is as follows – to evaluate the effectiveness of liquid-phase process of regeneration (demineralization with acids or alkali) and quality analysis of the obtained adsorbents.

Experimental

We offer liquid-phase method of oxidation-destructive processing batch powder with 25% of HNO_3 solution, i.e. demineralization together with simultaneous partial oxidation of carbon matrix surface as well as organic substance that are in pores of initial material.

Proportion S:L made up 1:(1-5) and processing time took 2-6 hrs at a temperature 95-100°C. Then

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*corresponding authors. E-mail: kartel@mail.kar.net

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batch powder was separated from liquid phase, washed out with distilled water up to pH 7 and then, step-by-step, with 5% NH$_4$OH solution, 3% HCl solution and again with water till neutral washing water. In the course of regeneration, partial loss of carbon matrix mass (burning, corrosion, solution) is possible as well oxidation of carbon surface and creating of proton-genetic functional groups that are able to ion exchange. Indicated processes are accelerated (catalyzed) by transition metal, the content of which is quite high in the original charge (batch powder).

Obtained oxidized carbon was subjected to extra processing in argon atmosphere during 1 h (at 850°C) for decomposition of surface oxides and transition of oxidized carbon into the form of active carbon.

Besides we used the traditional method of liquid-phase demineralization of carbon surface with 1% KOH solution, 3% HCl solution and also method of combined (in turn) processing batch powder by these reagents, taking into account that alkaline solution removes chromates from carbon surface and acid liquor – from salt-containing copper.

Spent acid and alkaline solutions were saved for subsequent quantitative determination (atomic absorptive spectroscopy) of copper and chromium desorbed from the charge surface.

Properties of the received samples of oxidized and active carbons were studied concurrently according to standard procedures [3] (Table 1); in particular we determined bulk density, ash content, adsorption pores volume (desiccative method according to benzene), specific surface area (according to thermal desorption of argon), static cation-exchange capacity (for oxidized carbon). We also evaluated final product outcome regarding original charge material (batch powder).

We also have studied catalytic reactivity of the obtained samples in the test reaction of decomposition of 1% H$_2$O$_2$ solution.

Results and Discussion

It was ascertained (Table 2, Figs. 1 and 2) that as the result of oxidative regeneration ash content of charge specimens came down from 24% to 9.5% (Figs. 1b, 2b). Apparently, due to removing saline impregnation (in volume of 14.5%) the capacity of adsorptive pores has slightly expanded from 0.25 to 0.36 cm^3/g (Fig. 1a, 2a) as well as specific surface area of pores – from 750 to 1180 m^2/g (Figs. 1c, 2c). At the same time specimens (test 1-8, Table 2) gained

Table 1

The main characteristics of gas mask batch powder before and after processing

No	Parameter	Before processing	After processing
1	Granule size, %:		
	d < 1 mm	66	56
	d < 0.5	34	44
2	Mass content, %:		
	wet	< 14.1	< 13.0
	ash	< 24.0	< 9.4
3	Mechanical strength by friction, %	> 75	> 75
4	Bulk density, g/cm^3	0.55	0.56
5	Total volume of pore, cm^3/g	0.75	0.60
6	Dynamic activity on benzene, min	> 130	> 150
7	Static capacity on benzene, mg/g	> 158	> 180
8	Specific surface area, m^2/g	750	1180
9	pH of water extract	7.75	7.0
10	Limited volume of adsorption space, cm^3/g	0.25	0.37

cationite properties with static exchange capacity (SEC according to Na$^+$) 1.0-1.4 meq/g; when proportion S:L increases, SEC also goes up (Figs. 1d, 2d) even to a greater extent than having the same mentioned above ratio (1:3) but increasing oxidation time (compare Figs. 1d and 2d).

However, it is necessary to notice that even after two-staged oxidation, when at the second stage new portion of nitric acid was used, we cannot reach SEC value higher than 1.4 meq/g.

Analyses of elements (copper and chromium) that were washed out during this procedure showed that increase of nitric acid quantity during oxidation and especially the duration of the oxidation process makes positive impact on the stage of demineralization, *i.e.* this is true that in the proposed plan of gas mask charge regeneration in addition to the process of partial oxidation of carbonic surface different modifiers, which block sorption pores, are also removed; at that together with reduction of ash content of the analyzed samples their specific surface area is increasing (Figs. 1c, 2c).

Table 2

Results of oxidative-destructive regeneration of gas mask batch powder

| No	Features of processing and amounts of chemicals	W_s, cm³/g	S_{sp}, m²/g	Ash, %	Mass yield, %
	Initial gas mask batch powder	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 No 6 treated in argon; t = 1 h, T = 850℃	0.48	1065	12.5	-
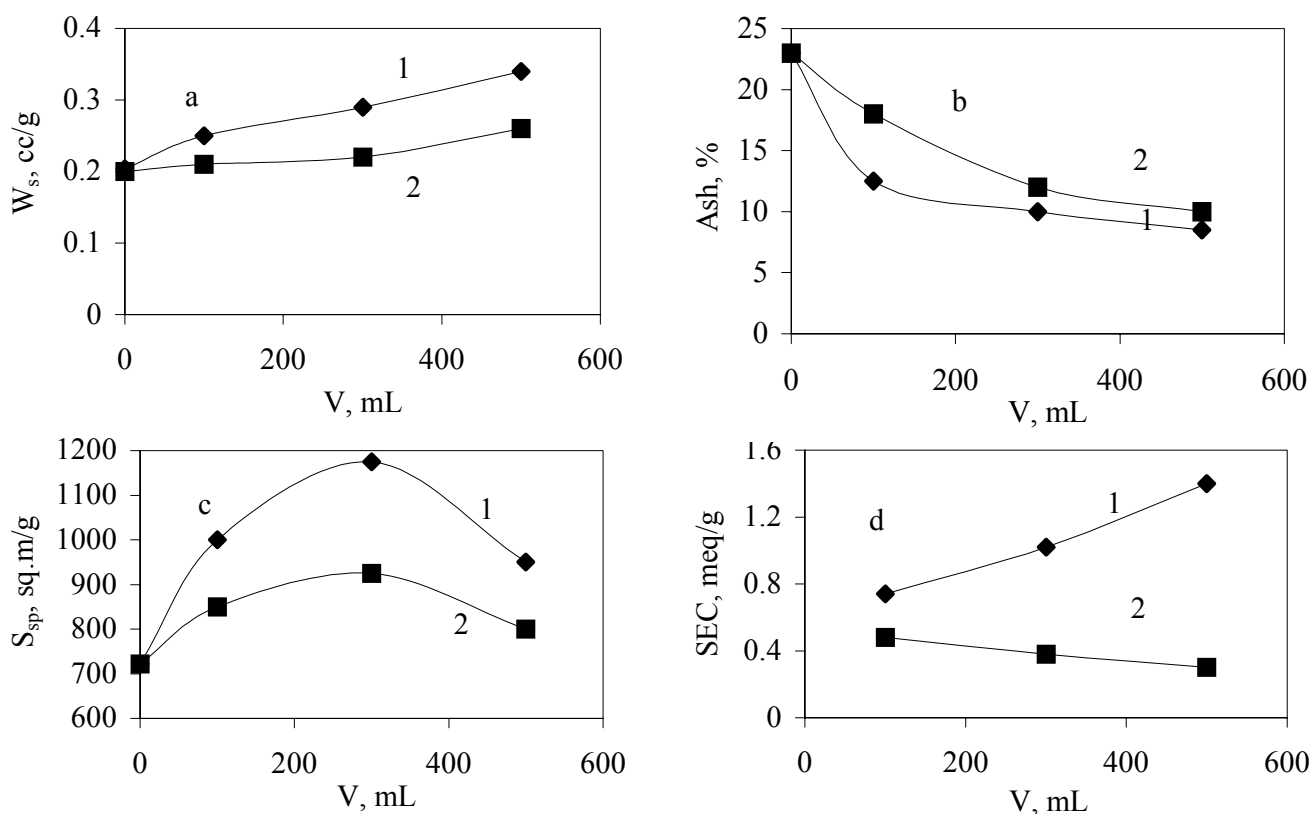
Fig. 1. Change a) volume of adsorption pore on benzene (W_s, cm³/g), b) ash content (%), c) specific surface area (S_{sp}, m²/g), and d) static exchange capacity (SEC, meq/g) on 0.1 N NaOH after oxidative-destructive (1) and alkaline-acid (2) processing's during 4 hrs; V - volume of added reagent to 100 mL of initial batch powder.

Moreover, during oxidative treatment carbon, practically, does not lose its hardness and carbon-composite loss was not indicated; despite process duration and multiple treatment of carbon by different
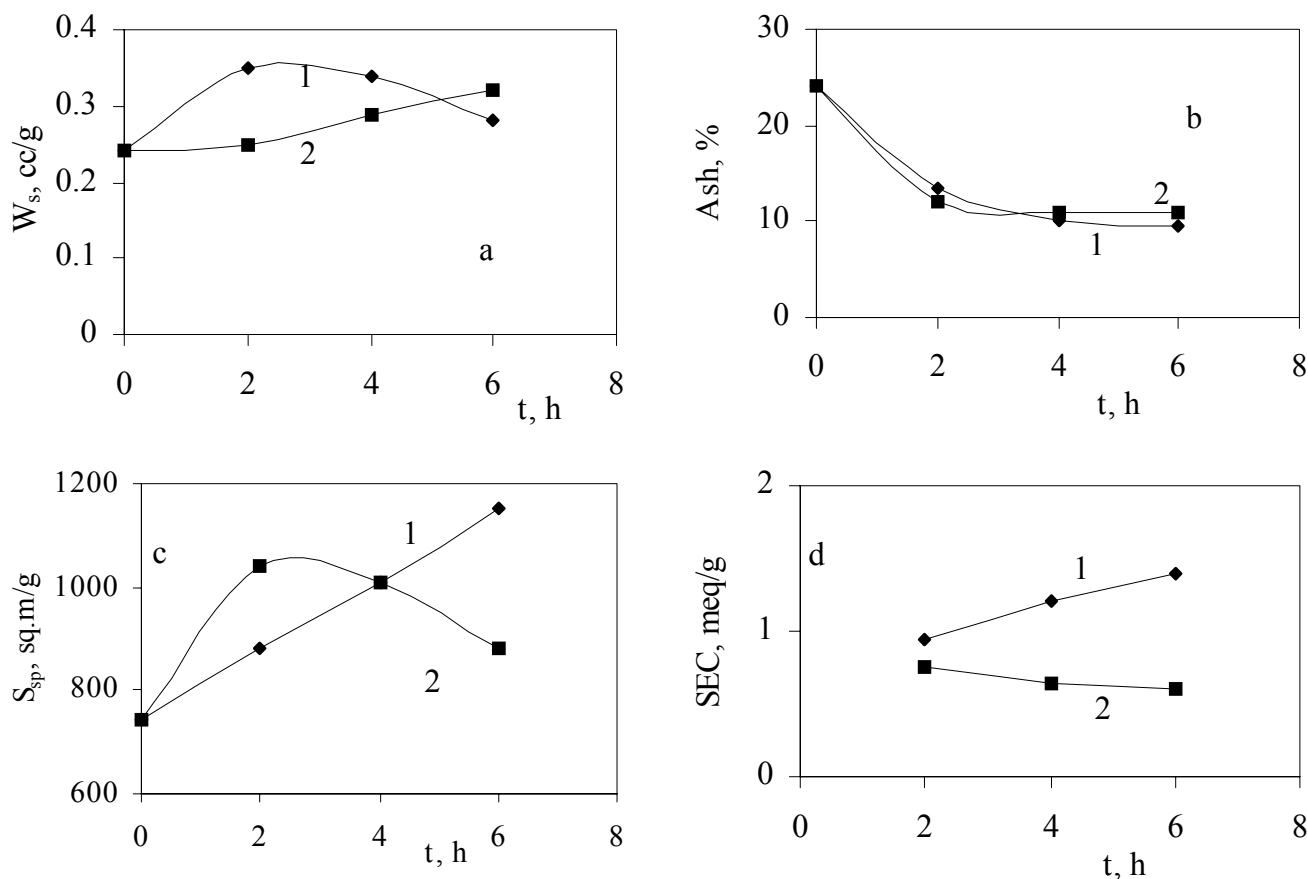
Fig. 2. Change a) volume of adsorption pore on benzene (W_s, cm³/g), b) ash content (%), c) specific surface area (S_{sp}, m²/g), and d) static exchange capacity (SEC, meq/g) on 0.1 N NaOH after oxidative-destructive (1) and alkaline-acid (2) processing's of initial batch powder at ratio S:L = 1:3; t – time of processing.

reagents and water, outcome of the target product made on average 85-86%.

Similar analysis of getting active carbon was made during chemical demineralization of gas mask batch powder by 1% KOH solution and then 3% HCl solution.

As a consequence of such treatment active carbon with high value of specific surface area – 900-1040 m²/g (Table 3) is received as compared with original material (750 m²/g).

It is necessary to notice that after special treatment of oxidized charge (test 7, Table 2) during 1 h in argon current at 850°C high quality samples of activated carbon was received, that has high volume of sorption pores 0.48 cm³/g (original batch powder – 0.25 cm³/g), high specific surface of pores – 1060 m²/g and ash content two times less.

Pilot analysis of data given in the Tables 2 and 3 and Figs. 1, 2 showed that the most optimal conditions of oxidation – destructive as well as alkali – acid treatment to obtain adsorbent with acceptable char-

acteristics are as follows – ratio of solid phase: reagent = 1:3 and treatment time – 2 hrs. To reach better characteristics of regenerated carbon of special purpose, it is necessary to increase time of treatment and quantity of reagents.

Thus, as a result of respirator charge regeneration and using oxidation–destructive procedure as well as hydrochloride acid treatment in liquid phase two ranks of carbon adsorbent were obtained – active carbon with high adsorption characteristic and also its oxidized modification allowing considering this substance as cation-exchanger. In this connection we have studied ion-exchange sorption of oxidized samples concerning copper, chromium and iron ions out of their relevant individual solutions (Figs. 3, 4).

It turned out that such carbonic cationite consolidate quite well ions Fe^{3+} and Cu^{2+} but ion Cr^{3+} – worse, which is typical for most oxidized carbons under similar conditions [4].

Active carbon obtained as a result of regeneration (conversion) of gas mask charge most likely can
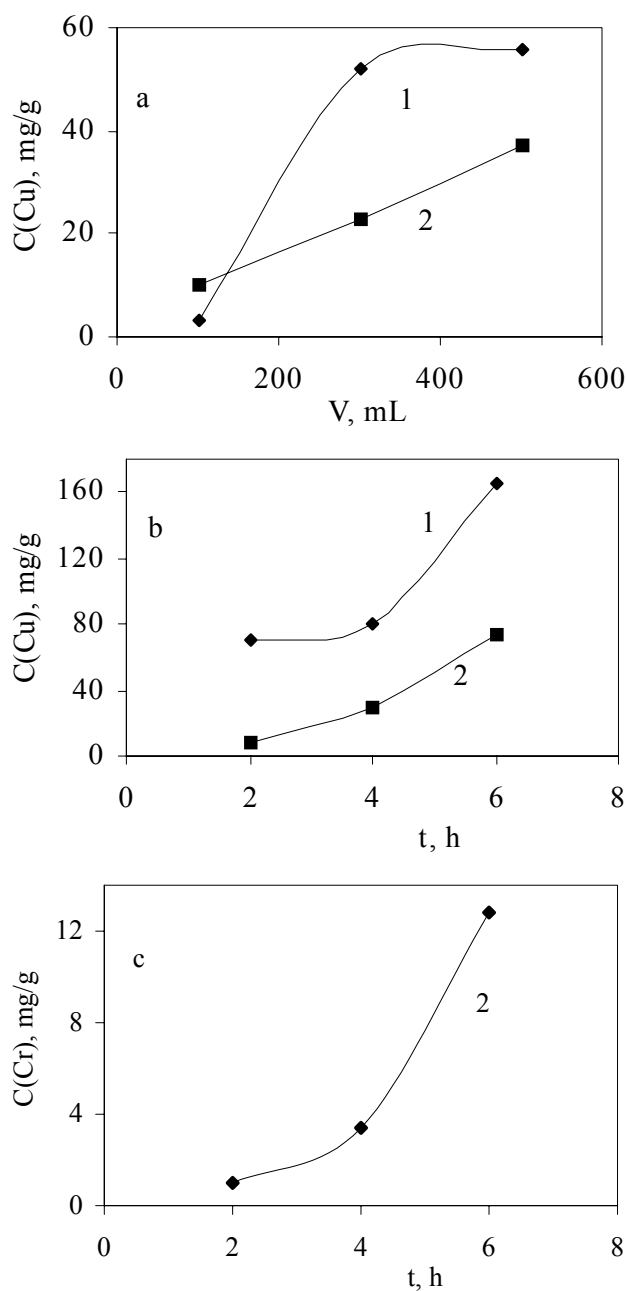
Table 3

Results of alkaline-acid regeneration of gas mask batch powder

No	Features of processing and amounts of chemicals	W_s, cm³/g	S_{sp}, m²/g	Ash, %	Mass yield, %
	Initial gas mask batch powder	0.25	745	23.6	-
1	M = 50 g, S:L = 1:3, t = 2 h; 1% KOH - 0.3 L, H₂O - 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, H₂O - 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, H₂O - 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, H₂O - 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, H₂O - 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, H₂O - 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, H₂O - 5 L	0.26	920	10.8	79.8

Fig. 3. Desorption (C, mg/g) of copper (a, b) and chromium (c) at oxidative-destructive (1) and alkaline-acid (2) processing's of initial batch powder during 4 hrs 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 initial material; t – time of processing.
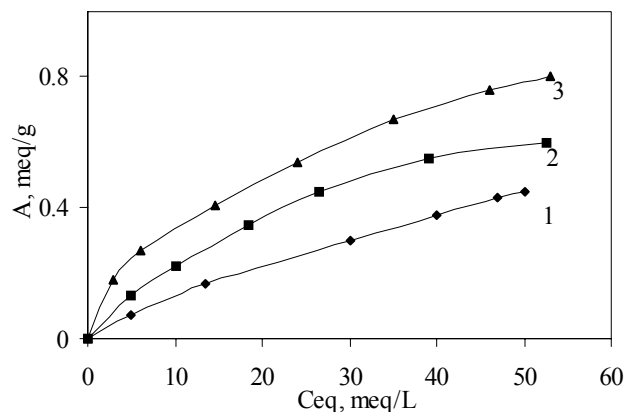

Fig. 4. Isotherms of adsorption (A, meq/g) of Cr^{3+} (1), Cu^{2+} (2), and Fe^{3+} (3) by oxidized carbon from aqueous solutions of nitrates. C_{eq} – equilibrium concentration of metal ions.

be used for treating gas effusion of organic substances of different type (VOC, dyes, petrol, diesel oil, *etc.*) and as catalyst carrier for decontamination of gas effusion, having organic admixtures, carbon oxide and others.

Moreover, we have studied catalytic reactivity of batch powder from worked out gas mask in 1% H_2O_2

solution decomposition reaction. To carry out researches we took the original respirator carbon charge, activated and oxidized carbon and two adsorbents modified by special procedure with different nitrogen content.

It is known [4] that nitrogen-containing carbon has the best catalytic reactivity. Activated carbon

substances decompose hydrogen peroxide quite well, while oxidized modifications inhibit this process. In our case there is similar series of carbon activity rating. Obtained results are given in the Table 4, where comparative activity of different samples during H_2O_2 decomposition is presented. It is necessary to note that the original batch powder also manifested catalytic reactivity because of the presence of catalyst-active saline treatment (copper and chromium) in it.

Table 4
Decomposition of 1% H_2O_2 solution on various carbon adsorbents from gas mask batch powder.
Conditions of experiment: m = 0.5 g, V = 25 mL,
T = 20ºC, t = 20 min

Sample	Decomposition, %
initial gas mask batch powder	30
oxidized carbon	10
activated carbon	53
nitrogen-containing carbon (3.5% N)	96
nitrogen-containing carbon (4.5% N)	100

Conclusions

It is worked out the liquid-phase process of oxidized-destructive utilization of used gas mask batch powder without considerable loss of carbon substance and its solidity. Proposed carbon treatment causes its demineralization and simultaneous partial surface oxidation, given cation-exchange properties to carbon. Additional heat treatment of oxidized substance in the inert atmosphere makes it possible to receive activated form of regenerated carbon adsorbent. Activated form of the analyzed gas mask charge is possible to get during its either hydrochloric acid or alkali-hydrochloric acid treatment.

According to standard procedures it is studied and determined some physical-chemical as well as structure-sorption characteristics of the original gas mask batch powder and regenerated substance, obtained as a result of directed modification. It is shown that oxidized and regenerated forms are noted for improved characteristics as to porous structure, impurity mixture, and ion-exchange and catalyst properties. Especially, it is worthy of notice high catalyst activity of nitrogen-containing modifications of the obtained carbon and consolidation selectivity of copper, iron and chromium by oxidized samples.

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