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Anthracite-based activated carbons for the efficient solution of important environmental problems

Victor M. Mukhin⊠

JSC "Elektrostal Scientific and Production Association "Neorganika", 4, K. Marx St., Elektrostal, 144001, Russian Federation

🖂 VictorMukhin@yandex.ru

Abstract: This article examines the issues of environmental pollution as a result of man-made activities and determines the most effective ways to protect the biosphere with the help of carbon-adsorption technologies. Due to their physical and chemical properties, activated carbons are an ideal adsorbent and allow solving a wide range of environmental safety issues.

Based on the theoretical assumptions expressed by Academician M. M. Dubinin, it is shown that anthracite is an excellent raw material for producing activated coal. A technology for obtaining CAS (Crushed Anthracite Sorbent) grade activated carbons from anthracite has been developed and its adsorption properties have been studied. Tests of CAS activated carbon in the purification of drinking water and wastewater, protection of the atmosphere from harmful gases and vapors, and detoxification of soils from herbicide residues were carried out. The necessity and requirements for the creation of new production facilities for active coals based on anthracite in Russian coal basins are substantiated.

Keywords: anthracite; activated carbon; adsorption properties; environment; drinking water purification; atmosphere protection; soil detoxification.

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Активные угли на основе антрацита для эффективного решения важных экологических проблем

В. М. Мухин

АО «Электростальское научно-производственное объединение «Неорганика», ул. К. Маркса, д. 4, Электросталь 144001, Российская Федерация

⊠ VictorMukhin@yandex.ru

Аннотация: Данная статья рассматривает вопросы загрязнения окружающей среды в результате техногенной деятельности и определяет наиболее эффективные пути защиты биосферы с помощью углеадсорбционных технологий. В силу своих физико-химический свойств активные угли являются идеальными сорбционными материалами, которые позволяют решать большой круг вопросов экологической безопасности.

На основании теоретических предпосылок, высказанных академиком М. М. Дубининым, показано, что антрацит является отличным сырьем для получения активных углей. Разработана технология получения активных углей марки ДАС (дробленый антрацитовый сорбент) из антрацита и исследованы его адсорбционные свойства. Проведены испытания активного угля ДАС в очистке питьевой и сточных вод, защиты атмосферы от вредных газов и паров и детоксикации почв от остатков пестицидов. Обоснована необходимость и потребность в создании новых производств активных углей на основе антрацита российских угольных бассейнов.

Ключевые слова: антрацит; активный уголь; адсорбционные свойства; экология; очистка питьевой воды; защита атмосферы; детоксикация почв.

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1. Introduction

The progressive pollution of the environment has made environmental safety an important component of national security in general. Today, almost the entire planet and, especially, areas of mass population of people are subject to serious environmental threats, the main of which are radiation contamination of territories, soil oppression by acid rain, soil pollution with chemicals and pesticides, oil spills on land and sea and the destruction of the atmosphere. Biosphere pollution dramatically reduces the quality of life of people. According to the WHO (2002), factors affecting human health depend on diet and lifestyle (51 %), environment (39 %), medicine (10 %) [1].

The problems of global pollution of the environment were raised even earlier by N.V. Keltsev, the Russian scientist, Professor at Mendeleev Moscow Institute of Chemical Technology, who proposed the main way to resolve the situation. As he wrote, since not only the army was faced with the question of life and death, but all the humanity was concerned about the pollution of the biosphere, it was time to turn again for help to adsorption - one of the most effective methods of protecting the environment from pollution. [2].

Due to their physicochemical properties, carbon adsorbents (activated carbons) are unique and ideal sorption materials that allow solving a wide range of issues related to ensuring the ecological safety of humans, the environment and infrastructure.

Activated carbons (ACs) are highly porous materials obtained in the form of grains or powder based on various carbon-containing raw materials, which have a developed inner surface (up to $2500 \text{ m}^2\text{g}^{-1}$) and have high absorption characteristics for impurities in the purified media (air, gases, water and other liquids, soil) [3, 4].

Various carbon-containing materials, such as coal, peat, wood, nut shells and seeds of fruits, various crop wastes (straw of various crops, etc.), can be used as a raw material for obtaining such ACs [5]. In the porous structure of activated carbon (micropores 1.2–3.0 nm and mesopores 3.1–100 nm), any types of organic microimpurities are absorbed due to adsorption forces (surface interaction forces).

Activated carbon is the second most widely used material on earth (not by tonnage, but by fields of application). The first is iron and the second is active carbon. But according to the size of its surface, activated carbon is the first material on Earth. If you roll 1 ton of iron into a sheet, then its surface area will be about 100 m^2 , and in 1 ton of active

carbon the interface is about $1,000 \text{ km}^2$. In a tablespoon of active carbon, the interface is equal to the area of a football field.

ACs is widely used in many areas of the economy, ecology and defense of the country. In the economy, this is oil and gas production and gas processing, mining (flotation of non-ferrous metal ores), metallurgical industry (including gold hydrometallurgy). chemical. chemical and pharmaceutical industries (suffice it to say that ACs is used in the production of millions of medicines), food industry (including vodka production) and many other branches of the Russian Federation.

The role of ACs is also irreplaceable in the country's defense: from gas-mask equipment to life support systems for spaceships, orbital and (in the future) interplanetary stations.

But the most outstanding role of ACs is in ensuring environmental safety and protecting the environment from man-made pollution. The meaning of the word "ecology" is incomplete without the word "activated carbon".

Table 1 shows the main environmental technologies for ACs application in the protection of all parts of the biosphere: the atmosphere, hydrosphere, lithosphere and man himself as the main object of the biosphere [6].

The description of all environmental technologies necessary for the ACs application, it might need to publish a monograph, equivalent in size to an encyclopedia. Partially ecological technologies for using ACs are described in our monographs [5, 7].

To assess the significance of ACs in environment protection, it is worth highlighting the most vital area that ensures the environmental safety of the population – the purification of drinking water and wastewater.

Despite the huge reserves of fresh water on our planet, the shortage of drinking water on Earth is constantly growing. Currently, out of 6 billion people of the world's population, 1.5 billion (i.e., one quarter) lack drinking water (there is evidence that by 2,025 this number will reach 2.5 billion). Even if water purification is carried out, yet, due to the lack of quality water, 36 million people will die, which is comparable to the number of people dying from AIDS [8].

According to the most recent information, 40 % of the Russian population drink water that is undesirable for consumption, leading to chronic diseases and poisoning. The reason is the pollution of water supply sources with industrial wastewater and agricultural wastewater (Radio Echo of Moscow, February 9, 2021).

Component of the biosphere	Carbon-adsorption technology
Atmosphere	Recovery of solvents, sanitary cleaning of waste gases, incl. desulfurization, gas cleaning system of nuclear power plants (NPP), capture of gasoline vapors emitted by vehicles, destruction of chemical weapons and solid household waste, purification of air in living and working premises (air conditioning)
Hydrosphere	Drinking water treatment, wastewater disposal, liquid radioactive waste processing, gold and non-ferrous metal mining
Lithosphere	Soil protection from xenobiotics, incl. pesticides, soil remediation, zones of sanitary protection of water sources
Person	Means of individual and collective protection of the filtering type, production of chemical and pharmaceutical preparations, vitamins, antibiotics, entero- and hemosorption, obtaining environmentally friendly food

Table 1. Environmental technologies for the use of active coals

Russia's water resources account for 20 % of all world fresh water reserves, including the cleanest water on the planet of Lake Baikal (depth 1,600 m, length about 800 km, width 80 km). Forecasts of futurists say that the third world war may start not because of energy resources (oil and gas), but because of fresh water. The total intake of fresh water from natural sources in Russia per year is 80–85 km³, or 2% of the total reserves. In Moscow, the consumption is ~ 1 million m³ per day of water, that is, 400 liters per person, while in the countries of Europe, the USA and Canada, this consumption is much more economical 120–150 liters per day [9, 10].

To provide cities and large settlements with drinking-quality water, surface water supply sources must be purified, and active coal cannot be dispensed with. Most often, such waters are polluted with oil products, pesticides and other very stable (including volatile) substances, as a rule, of organic origin. They are mainly represented by humic acids with a molecular weight of 1,300-1,500, petroleum products, organochlorine substances, dioxins and some other carcinogens (compounds with a molecular weight of 200-300), phenols, ammonia and residual chlorine (substances with a molecular weight of 70-80). In some cases, this pollution causes not only an unpleasant odor and taste of water (dung, earthy, chemical, etc.), but also the danger (and even impossibility) of its direct (without treatment) use for drinking.

In order to remove the bulk of pollutants from natural waters, a wide range of technological methods are used, including carbonation (for deodorization), flotation, coagulation, oxidation, sedimentation, filtration, and final sorption on granular active carbon [11].

However, final sorption on AC, which ensures 100 % safety of drinking water, is implemented in Russia at only a few waterworks.

The Decree of the President of Russia V.V. Putin No. 204 of 05 July 2018 (p. 7) of May 2018 focuses on the need to improve the quality of drinking water by modernizing water supply systems using promising water treatment technologies, including those developed by the organizations of the military-industrial complex. It stresses the need to improve the quality of drinking water for the population, including that for settlements not equipped with modern centralized water supply systems [12].

As mentioned above, it is impossible to create an effective water treatment system without ACs. Currently, only six sources are used as raw materials for ACs production: bituminous coal, brown coal, coconut shells, oil residues, waste from pulp mills, and charcoal [13, 14]. However, the search for new sources of raw materials reasonably led to the choice of anthracite. It can be assumed that ACs from anthracite will have properties that are not found in other types of activated carbons [13].

2. Materials and methods

Anthracite is widely represented in various regions of Russia as a fossil coal raw material. Table 2 shows the potential reserves and volumes of this type of coal raw materials. Of greatest interest are the anthracites of the Donetsk Basin, Kuznetsk Basin and Magadan Region, that is, to organize new production of active coals on their basis, no more than $2 \cdot 10^{-3}$ of their reserves per year will be consumed [15]. Table 3 shows the characteristics of the original anthracite of the Gorlovskove deposit in Kuzbass. As follows from Table 3, the initial anthracite is characterized by a low ash content (3 %) and high strength (over 85 %), which makes it, of course, a promising raw material production of carbon for the adsorbents. It is especially important to note the low content of volatile substances (less than 5 %), which allows such material to be directly activated without carrying out the operation of carbonization and de-volatilization.

In 1976, Academician M.M. Dubinin [16] said that in order to ensure a high adsorption capacity of the ACs in a cubic capacity (filters, adsorbers, etc.), the development of the volume of micropores per unit volume (cm³·cm⁻³) is important, rather than that per unit of weight (cm³·g⁻¹). It follows from this that in order to ensure a high adsorption capacity, and, consequently, a high service life (filters, adsorbers, etc.), it is necessary to prepare ACs with a high bulk density. Then, even with a low development of the volume of micropores in $\text{cm}^3 \cdot \text{g}^{-1}$, there will be a high development of the volume of micropores in $\text{cm}^3 \cdot \text{cm}^{-3}$. The conversion of the volume of micropores from $\text{cm}^3 \cdot \text{g}^{-1}$ to $\text{cm}^3 \cdot \text{cm}^{-3}$ is carried out by multiplying the first value ($\text{cm}^3 \cdot \text{g}^{-1}$) by the bulk density of ACs in g·cm⁻³.

The original samples of anthracite in the form of pieces of 90 mm in size were crushed in a jaw crusher with the inoculation of the target fraction of 0.5–2.0 mm. To improve the quality of the prepared ACs, anthracites were de-volatilized in a laboratory rotating electric furnace in an inert atmosphere of carbon dioxide (flow rate 5–7 L·min⁻¹ at a temperature of 750 °C). The carbonized sample was characterized by the following parameters: bulk density 830-900 g·cm⁻³, total pore volume 0.11–0.18 cm³·g⁻¹, strength 85–87 %. The activation of anthracites was carried out in a laboratory rotating electric furnace at a temperature of 850 °C in an environment of carbon dioxide and water vapor in a ratio of 1 : 3; the activating agent was supplied at a flow rate of 5–7 L·min⁻¹ [17].

	Total	Reserves accounted for by the State Balance Sheet of the RF			Forecast resources	
Coal basin	inventory	$A + B + C_1$	C ₂	$\begin{array}{c} \text{Total} \\ (A+B+C_1+C_2) \end{array}$	Total	Including P ₁
Donetsk, RF	15,942	5,716	1,604	7,320	8,358	1,093
Gorlovsky	6,453	323	425	748	5,243	858
Kuznetsky	11,384	553	275	828	10,247	5,448
Pechorsky	479	_	_	_	479	_
Eastern Urals	88	_	_	_	88	55
Magadan region	50	28	22	50	_	_
Total	34,553	6,620	2,326	8,946	24,415	7,454

Table 2. Reserves and resources of anthracite (million tons) of the main coal basinsand deposits of the Russian Federation (RF) as of 01 January 1997

Table 3. Characteristics of the initial anthracite of the Gorlovsky deposit of Kuzbass

The sample	Dulle donaites a dus ⁻³	Strongth 0/	Cont	ent, %	Total many values $am^3 a^{-1}$
No. Buik	Burk density, g-din	Strength, 70	ash	bats	Total pore volume, cm ·g
1	1,020	88.6	3.05	4.5	0.10
2	1,100	87.5	3.26	4.8	0.10

The adsorption isotherms of the prepared AC CAS (Crushed Anthracite Sorbent) measured on an ASAP 2020 specific surface area and porosity analyzer (Micromeritics, USA) with the development of a micropore volume of 0.21-0.23 cm³·g⁻¹ made it possible to calculate the micropore width, which was 1.58 nm. This micropore width is most favorable for the absorption of a wide class of organic pollutants from both liquid and gaseous media.

Table 4 shows the quality indicators of the AC CAS from anthracites of various pools.

As follows from the data given in Table 4, the quality indicators of AC obtained from anthracites of various coal basins of Russia are quite close and are characterized by high adsorption properties per unit volume.

Table 5 shows the technical characteristics of the AC CAS prepared from the anthracite from the Gorlovskoye deposit of Kuzbass in comparison with the activated carbon prepared from AG-3 coal (SS grade) for water treatment purposes (JSC "Sorbent", Perm) in RF and the AC prepared from GCN 830 coconut shells ("Norit" company, Netherlands), which is widely used in the world.

Table 4. Qualitative characteristics of CAS based on anthracite from various de	leposits
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Quality indicators	CAS Omsuk-chansky	CAS Donbass	CAS Kuzbass
Bulk density, $g \cdot dm^{-3}$	720	780	798
Abrasion resistance, %	80.0	75.2	75.8
Ash content, % by weight	3.1	2.2	3.8
The micropore volume:			
$- \text{ cm}^3 \cdot \text{g}^{-1}$	0.23	0.22	0.21
$- \text{ cm}^3 \cdot \text{cm}^{-3}$	0.16	0.17	0.17
Dynamic activity for benzene, min	54	53	51
Iodine adsorption activity:			
$- \text{mg} \cdot \text{g}^{-1}$	600	600	570
$- \text{mg}\cdot\text{cm}^{-3}$	432	468	455

Table 5. Technical characteristics of active coals

Quality indicators	AG-3	Anthracite-based CAS	GCN 830 Norit
Bulk density, g·dm ⁻³	400–500	780	450
Abrasion resistance, %	70–75	85	92
Ash content, % by weight	12–15	4.5	2.4
The micropore volume:			
$- \mathrm{cm}^3 \cdot \mathrm{g}^{-1}$	0.20	0.18	0.50
$- \text{ cm}^3 \cdot \text{cm}^{-3}$	0.09	0.14	0.22
Dynamic activity for benzene, min	40-42	53	62
Iodine adsorption activity:			
$- \text{mg} \cdot \text{g}^{-1}$	650	600	1,000
- mg·cm ⁻³	297	468	450
methylene blue:			
- mg·g ⁻¹	120	89	110
- mg·cm ⁻³	56	69	60

As follows from the data in Table 5, CAS activated carbon in terms of the development of a microporous structure and adsorption properties for iodine and methylene blue is 1.5 times higher than that of domestic AG-3. But it is not inferior to the imported GCN 830, while maintaining a sufficiently high abrasion strength according to Russian Standard 16188-70. The purity of the obtained DAS activated carbon (which is especially important for water purification) is indicated by the low ash content (4.5 %), which is at the level of activated carbon from coconut shells and 3 times less than in AG-3. The patent for active carbon made of anthracite grade DAS belongs to JSC ENPO Inorganica (RF) [18].

3. Results and Discussion

It was expedient to consider the possibility of using this type of active carbons for water purification from organic substances dissolved in water.

3.1. Extraction of organic pollutants from water

Table 6 shows the test results of activated anthracite brand DAS, domestic AG-3 (JSC "Sorbent", Perm, RF) and Belgian TL-830 ("Filtrosorb", Belgium) on the efficiency of formaldehyde removal. Studies have shown that activated anthracite can compete with AG-3 and TL-830 for the extraction of formaldehyde from water. Moreover, testing was carried out by the carbonization method, when activated carbon was introduced into a flask with water at a contact time of 0.5 hours.

Studies have also been conducted on the effectiveness of removing phenol from water. The results given in Table 7 showed that DAS is not inferior to industrial active coals of domestic and foreign production.

Similar studies on the efficiency of extraction of difficultly sorbed phenol as the most common anthropogenic pollutant in both waste and natural waters were carried out for the DAS sorbent and industrial active carbon KAD-I (Sorbent JSC, Perm). The results of these tests are shown in Table 8.

Table 6. The coals efficiency to formaldehyde

The coals	Initial formaldel	nyde concentra	tion, mg·L ⁻¹
	0.110	0.100	0.060
AG-3	0.032	0.040	0.016
TL-830	0.042	0.040	0.022
CAS	0.033	0.038	0.019

Table 7. The coals efficiency to phenol, $mg \cdot L^{-1}$

Indicatora	The coals				
indicators	AG-3	TL-830	DAS		
Phenol initial concentration	0.0100	0.0100	0.0100		
Equilibrium concentration	0.0083	0.0077	0.0091		
Phenol initial concentration	0.0200	0.0200	0.0200		
Equilibrium concentration	0.0170	0.0140	0.0182		
Phenol initial concentration	0.0600	0.0600	0.0600		
Equilibrium concentration	0.0510	0.0430	0.0530		
Note : Test conditions: 1 g of coal per 1 liter of water, contact time 0.5 h.					

Table 8.	Efficiency	of drinking	water purification	from phenol	by active	carbons
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Indicators	The	Europa timos			
Indicators	CAS	KAD-I	Excess, times		
Sorption capacity to slip, $mL \cdot g^{-1}$:					
- at a layer height of 120 mm	9.40	2.15	3.8		
 at a layer height of 520 mm 	3.98	8.84	-		
Sorption capacity to saturation, $mL \cdot g^{-1}$					
 at a layer height of 120 mm 	72.20	29.85	2.5		
 at a layer height of 520 mm 	94.00	38.16	_		
Note : Test conditions: sorbate concentration 50 mg·dm ⁻³ , filtration rate 4 m·h ⁻¹ .					

In this experiment, drinking water was filtered through columns with active carbon and the CAS advantage in terms of a high volume of micropores per unit volume ($V_{\rm mi}$, cm³·cm⁻³) was fully manifested.

Thus, it can be stated that the sorption capacity for phenol of the CAS sorbent exceeds the sorption capacity of the industrially manufactured semicokebased KAD-I sorbent by $\sim 2.5-3.5$ times. CAS sorbent can be effectively used for the purification of phenol-containing wastewater as a load into sorption filters.

Studies on the effectiveness of reducing highly toxic contaminants such as acid fluorides by the CAS sorbent have shown that its dispersed composition is of significant importance when used in filters with a load not exceeding 1.0 m. The research results are presented in Table 9.

The studies were carried out under the same dynamic conditions for three fractions of the CAS sorbent:

- layer height 180 mm;

- filtration rate of sorbate solutions 10 m per h;

- sorbate concentration in working solutions $\sim 1.0 \text{ mg} \cdot \text{dm}^{-3}$.

Based on the results of the studies carried out, the following conclusions can be drawn:

- the dispersed composition of the sorbent for water purification is of great importance in filters of

water purification means with a charge layer height of no more than a meter;

- the dispersion of the CAS sorbent for filters of water treatment means should not exceed 0.3 mm.

3.2. CAS application in mobile water treatment facilities

AC CAS was used in mobile water treatment facilities to compare it with the BAU-MF sorbent widely used for these purposes (UralKhimSorb, Perm, RF). It should be noted that the bulk density of these sorbents is significantly different; therefore, the studies were carried out by comparing them both in terms of the height of the filtering layer and in terms of the sorbent mass. The research results are presented in Table 10.

The analysis of the research results showed that the dynamic capacity of the CAS sorbent was approximately at the same level as BAU-MF. At the same time, the application of the CAS sorbent in filters of mobile water treatment facilities will increase their resource by two times while maintaining the hydrodynamic parameters of the filter. It should be noted that the mass of the filter will increase the resource for the water treatment agent, the application of the CAS sorbent will reduce the dimensions of the filter.

Table 9. The decrease in the concentration fluoro-anhydrides in the purified water

 by passing it through the filter elements with CAS

The CAS dispersion, mm	The fluoro-anhydrides concentration, $mg \cdot L^{-1}$, after min				
	30	60	90		
1.0	0.09	0.12	0.60		
0.6	0.006	0.02	0.08		
0.3	< 0.0001	< 0.0001	0.0001		

Table 10. Efficiency of BAU-MF and CAS sorbents for water purification from fluoro-anhydrides

The sorbent	The sorbent layer height,	The fluoro-anhydrides concentration, $mg \cdot L^{-1}$, after min				
type	cm (weight, g)	20	60	180		
BAU-MF	18 (13.5)	0.0005	0.0008	0.0300		
CAS	18 (35.3)	0.0001	0.0001	0.0001		
CAS	6 (13.5)	0.0002	0.0060	0.0800		

3.3. CAS application in household filters

Household filters for the purification of drinking water are an important tool for preserving health due to the lack in most settlements of the final purification of drinking water at waterworks with the help of granulated active carbon. Therefore, the CAS in efficiency for household filters was measured using the water filter "Mechta" produced by JSC "ENPO" Inorganic" (Elektrostal, RF), which has an adsorption system in the form of a porous block.

Table 11 shows the comparative characteristics of the sorption blocks of the "Mechta" filter made from the CAS prepared from anthracite activated carbon and also industrial AC prepared from AG-3 coal, previously used in these blocks.

As follows from the data given in Table 11, the use of active carbon DAS in the sorption units of filters for additional purification of drinking water provides a higher purification efficiency from both organic and inorganic pollutants.

The tests of another filter for the additional purification of drinking water "Barrier", operated with grained AC, were carried out in the company JSC "BVT Barrier RUS" (Moscow, RF). It was shown that CAS coal with a grain size of 1–3 mm fully meets the technical requirements that apply to AC based on coconut shells used in these filters.

The efficiency of wastewater purification from heavy metals was measured at the wastewater treatment facility of the gold recovery plant of "Polymetal" company in the Magadan region (RF) through a layer of coal of class (-3.0 + 0.2) mm at a filtration rate of 0.5 m per h. The findings of the filtration efficiency evaluation through the CAS sorbent layer with a height of 150 mm at a filtration rate are shown in Table 12.

As can be seen from the data presented in Table 12, the CAS sorbent has a very high efficiency in the extraction of heavy metals from water. Moreover, for all metals, except for iron, it was lower than the MPC, and for such metals as manganese, zinc, copper, cadmium, nickel, the concentration in the treated waste water decreased tens and even hundreds of times.

Based on the above studies, it can be concluded that a simple replacement of the sorption load in the existing water supply systems for the CAS sorbent at water treatment plants will increase their resource at least twice. In addition, the bulk density of the CAS sorbent is comparable to the bulk density of quartz sand, so it will not be washed out during

Block Type	The water purification efficiency		
	From organic pollutants, %	The content of Fe^{3+} in the filtered water, $\mathrm{mg} \cdot \mathrm{dm}^{-3}$	
Based on the AG-3	85	0.5	
Pagad on CAS	04	0.4	

 Table 11. Comparative characteristics of sorption blocks

	The water purmeation enterency		
Вюск Туре	From organic pollutants, %	The content of Fe ³⁺ in the filtered water, $mg \cdot dm^{-3}$	
Based on the AG-3	85	0.5	
Based on CAS	94	0.4	

Recoverable metal	Unit of measurement	MPC	Source water	Purified water
General iron	mg∙dm ⁻³	0.10	5.6	4.8
Common manganese		0.01	2.3	< 0.1
Common zinc		0.01	51	< 0.04
Common lead		0.01	< 0.2	< 0.2
Common copper		0.00	48	< 0.1
Common cadmium		0.01	0.12	< 0.05
Common magnesium		40.0	51	40
Common nickel		0.01	0.32	< 0.2

backwashing of the filtration unit. Consequently, it can be assumed that a simple replacement of quartz sand at the final filtration stage with CAS will allow simultaneous filtration of mechanical impurities and sorption of molecular toxicants. This will provide high quality, clean and healthy water to the population without significant capital expenditures, without building an additional coal cleaning section. Calculations show that for an average city with a population of 100 thousand people, this will save 100 million rubles.

Thus, the high adsorption activity of CAS activated carbon with respect to both organic and inorganic pollutants during water treatment makes it possible to predict its effectiveness in both mobile and stationary water supply systems. CAS activated carbon has a certificate for its use for the purification of drinking water and circulating and waste water [19].

3.4. Ambient air quality monitoring

In the Presidential Decree (May 2018), great importance is attached to a radical reduction in the level of air pollution in large industrial centers, including a reduction by at least 20 % of the total volume of emissions of pollutants into the air in the most polluted cities [12].

Benzene is a test substance for assessing the quality of AC when extracting organic vapors from air. Therefore, in accordance with Russian Standard 17218-71 [20], an assessment of CAS activated carbon for the time of protective effect (TPE) was carried out for benzene vapors with a vapor concentration in the air of 5 mg·L⁻¹ in comparison with industrial activated carbon AG-3 (Sorbent JSC, RF). The test results showed that the TPE for benzene vapors for CAS activated carbon was 51–54 minutes, and for AG-3 – 40–42 min, i.e. the TPE for benzene vapors for CAS is 20–35 % higher than for industrial activated coal AG-3.

Purification of gas emissions from nuclear power plants is perhaps the most important aspect of using AC to protect the atmosphere, because the half-life of some isotopes of radioactive iodine is 1.5 million years.

In the laboratory of activated coals of ENPO Inorganika JSC in February 2021 on the basis of CAS activated carbon prepared from anthracite from the Gorlovskoye deposit of Kuzbass, in accordance with the technological regulations VTR 2568-379-04838763-2010 (however, the amount of impregnants was halved: potassium iodide was reduced to 0.75 % from 1.5 %, and triethienediamine was reduced to 1 from 2 %), a sample of the CAS-IK sorbent

Table 13. The sorption properties
of sorbents for radionuclides

Sample	Cleaning efficiency (sorption activity), %		
1	I ¹³¹	CH ₃ I ¹³¹	
VSK-5IK	99.992	99.91	
TC for VSK-5IK	99.900	99.00	
CAS-IK	99.998	99.97	

(VSK-5IK type) was prepared to absorb gaseous iodine radionuclides: I^{131} and CH_3I^{131} (methyl iodide).

Table 13 shows the results of the study of the adsorption activity for iodine radionuclides of the obtained prototype and the commercial VSK-5IK sorbent, as well as the requirements of TC 2568-372-04838763-2010 for the VSK-5IK sorbent currently produced by ENPO Inorganic.

As follows from the data given in Table 13, the sorbent CAS-IK in sorption of iodine radionuclides is not inferior to the industrial sorbent VSK-5IK, obtained on the basis of AC from coconut shells and exceeds the requirements of the technical conditions for the industrial sorbent VSK-5IK by two orders of magnitude. Thus, the developed new sorbent CAS-IK can be successfully used in gas cleaning systems at Russian NPPs and NPPs built abroad using Russian technologies.

The high volume of micropores and high adsorption properties of CAS per unit volume can significantly increase the resource of sorption air purification systems at nuclear power plants or dramatically reduce the size of treatment plants, which is important from an economic point of view.

3.5. Monitoring of the lithosphere quality

A particularly significant threat to the biosphere is the decline in soil fertility and even the complete depletion of farmland as a result of man-made activities. But the soils of farmland on the planet are only 6% of the total land area, and almost 30 % of the most fertile soils – chernozems – belong to Russia. Considering that by the end of the 21st century more than 10 billion people will be living on the planet, the protection and rehabilitation of soils should be given top priority. In the Russian Federation alone, there are almost 50 million hectares of soils contaminated with pesticides in excess of the established standards [21]. That is why the Federal Law of 03.08.2018 No. 280-FZ "On organic products and on amendments to certain legislative acts of the Russian Federation" was adopted, which explicitly states that when implementing organic farming, methods, methods and technologies are used to ensure favorable the state of the environment, strengthening of human health, preservation and restoration of soil fertility.

The essence of carbon-adsorptive detoxification of soils contaminated with pesticides consists in introducing AC into the contaminated soil in the form of grains or powder with a micropore volume of 0.20–0.30 cm³·g⁻¹ and then embedding it to a depth of 10–15 cm; then a given crop is sown into the charcoal-treated soil.

When solving environmental problems of the agro-industrial complex (AIC), ACs are characterized by such advantages as selectivity of sorption of organic toxicants, universality of sorption properties, high absorption capacity, hydrophobicity, convenient preparative form (grain, powder) and low cost.

It has been established that agrosorbents should have a micropore volume of at least $0.2-0.3 \text{ cm}^3 \cdot \text{g}^{-1}$ with a significant development of thin pores (0.8-1.2 nm), which allows to firmly retain both the molecules of the pesticides themselves and the products of their destruction, while the transport porosity (volume of macro- and mesopores) must also be well developed to ensure good kinetics of absorption of these substances. On the basis of numerous theoretical and experimental studies, we proposed DAS active carbon for detoxification of farmland soils from herbicide residues using the Agrosorb technology.

Table 14. Results of soil detoxificationfrom phytotoxicants using active carbons

The activated carbon trade mark	The level of soils detoxification from phytotoxicants, % decrease from the initial concentration*	Protected yield, % to control
CAS	89–90	15–16
SKT-3	75–76	6–8
AG-3	73–74	5–6

* Residual amounts of phytotoxicants in the soil were determined by the HPLC method.

In 2001, the Herbology Department of All-Russian Research Institute of Phytopatology carried out research on the restoration of soil fertility of agricultural lands using the method of carbon adsorption detoxification (Agrosorb technology) of residual amounts of pesticides and endogenous phytotoxins accumulated in soils during natural soil fatigue. As adsorbents-detoxifying agents, we used new anthracite-based AC CAS, as well as industrial active carbons SKT-3 (JSC EKhMZ, Elektrostal) from peat and AG-3 coal at doses of 100 kg per ha. Cucumbers, tomatoes, beets, and radishes were chosen as the main test plants, which exhibit the most pronounced sensitivity to various phytotoxicants (sulfonylureas, imidazolinones) present in soils. The findings of the small-plot experiments are summarized in Table 14, where, for comparison, similar dependences are shown for standard industrial adsorbents such as SKT-3 and AG-3.

As follows from the data in Table 14, the application of the new ACs CAS gives an 89–92 % decrease in the concentration of phytotoxicants in the soil and an increase in the yield of test plants in contaminated areas up to 15–19 % versus, respectively, 73–76 % and 5–8 % for well-known coals SKT-Z and AG-3. Similar patterns were established for other crops (corn, rapeseed).

The performed studies allowed us to make the following conclusion that the new ACs trade mark DAS based on anthracite provides a higher level of detoxification of phytotoxicants in the soil compared to the previously known brands of AC. Thus, AC DAS is an effective adsorbent, promising for use in crop production in order to improve the ecological state of agricultural land.

The expected economic effect from the restoration of soil fertility using the CAS carbon adsorbent will be up to \$ 500 per hectare.

3.6. ACs production volumes and production organization prospects

To implement the above-described most important coal adsorption technologies that ensure the environmental safety of Russia, attention should be paid to the development of the production of active coal in our country.

The total volume of ACs production in the world today is 1 million 250 thousand tons per year and is characterized by a steady growth of 5 % per annum. The maximum productivity for active coals of the 4 main enterprises of the USSR reached 40 thousand tons per year (1989). Currently, the Russian Federation produces only 3 thousand tons per year at the only remaining plant. About 25-30 thousand tons per year are purchased imported ACs (USA, Holland, France, China, etc.) [22].

Speaking about the environment and economy of the country, one should pay attention to the specific production of ACs, which in the USA, Japan, and Western Europe is at the level of 0.5 kg per capita annually, in Russia, this figure is currently 0.02 kg per capita a year. Thus our ecology, especially drinking water supply, is 25 times lower than that of the world level. Based on the foregoing, our country needs to produce at least 70 thousand tons of AC per year for sustainable economic development and creating a high quality of life for the population. The same approach will make it possible to implement the set by the President of Russia V.V. Putin on October 30, 2015 the task of improving individual and collective protective equipment [23].

Thus, the earliest possible organization of new ACs production in the Russian Federation on the basis of domestic (primarily Kuzbass) coal raw materials will certainly give a powerful impetus to the development of productive forces and ensure high quality environmental protection, which fully fits into the concept of sustainable development and creation high quality life of people.

4. Conclusions

Based on the results of this study, it was found that due to its physicochemical properties, ACs can solve a wide range of issues of biosphere protection. In terms of adsorption properties per unit volume, anthracite-based activated carbon corresponds to the world level and significantly exceeds domestically produced ACs.

The study confirmed the high adsorption properties of CAS activated carbon for drinking water purification, wastewater treatment, protection of the atmosphere and detoxification of farmland soils. The necessity of building new active coal plants has been substantiated.

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6. Conflict of interests

The authors declare no conflict of interest.

References

1. Mukhin VM, Korolev NV. Adsorption is returning (the role and place of active carbons in ensuring environmental safety. *Al'manakh «Bezopasnaya Rossiya»*. 2019:46-49. (In Russ.) 2. Keltsev NV. *Basics of adsorption technology*. Moscow: Chemistry; 1976. 511 p. (In Russ.)

3. Fenelopov VB. *Porous carbon*. Novosibirsk: Boreskov Institute of catalysis Publ.; 1995. 517 p. (In Russ.)

4. Barinov SV, Gerunova LK, Tirskaya JI, Pyanova LG, Baklanova ON, Liholobov VA. Development of carbon sorbents and prospects of their use in obstetric practice. Omsk: Maksheyeva YeA publ.; 2015. 130 p. (In Russ.)

5. Mukhin VM, Klushin VN. *Production and use of carbon adsorbents*. LAR LAMBERT Academia Publ.; 2018. 352 p. (In Russ.)

6. Mukhin VM, Kurilkin AA, Voropaeva NL, Leksyukova KV, Uchanov PV. A position of active carbons in the ecology and economy, new technologies of their production. *Sorbtsionnyye i khromatograficheskiye protsessy = Sorption and chromatography processes*. 2016;16(3):346-353. (In Russ.)

7. Mukhin VM, Tarasov AV, Klushin VN. *Active coals of Russia*. Moscow: Metallurgiya; 2000. 352 p. (In Russ.)

8. World health organization. *Water safety and quality*. Available from: https://www.who.int/water_sanitation_health/water-quality/ru/ [Accessed 11 April 2019] (In Russ.)

9. Popular science encyclopedia Water of Russia: State report "About the condition and use of the Russian Federation water resources in 2018". Available from: https://water-rf.ru/water/gosdoc/612.html [Accessed 20 September 2019]. (In Russ.)

10. *Worldwide water consumption*. Available from: https://www.yestravel.ru/world/geography/freshwater_ withdrawal/ [Accessed 30 July 2019]. (In Russ.)

11. Smirnov AD. Sorption water treatment. Leningrad: Khimiya; 1982. 168 p. (In Russ.)

12. Decree of the President of the Russian Federation of 05/07/2018, No. 294 "On national goals and strategic objectives for the development of the Russian Federation until 2024". (In Russ.)

13. Schauz JJ, Parry RH. Industrial production of activated carbons. *Industrial and Engineering Chemistry*. 1962;54(12):24-28.

14. Olontsev VF, Mokrova NV, Sazonova EA. Modeling the processes of intentional production of activated carbons from fossil coal. Yekaterinburg: USURT Publ.; 2012. 104 p. (In Russ.)

15. Kizilstein LA, Spitsgluz AL. Atlas of microcomponents and petrogenetic types of anthracites. Rostov-na-Donu: SFedU Publ.; 1998. 254 p. (In Russ.)

16. Dubinin MM. Scientific basis for the development of active carbon production. Moscow: IPCE RAS Publ.; 1976. 45 p. (In Russ.)

17. Mukhin VM, Uchanov PV, Sotnikova NI. Development of technology for active carbon-based coal and study of its properties. *Sorbtsionnyye i* *khromatograficheskiye* protsessy = Sorption and *chromatography processes*. 2013;13(1):83-90. (In Russ.)

18. Mukhin VM, Soloviev SN, Dubovik BA, Pupyrev EI, Limonov NV, Sotnikova NI, Uchanov PV. *A method for producing active carbon based on anthracite*. Russian Federation Patent No. 2518964. 10 June 2014. (In Russ.)

19. Expert opinion No. 1210 FBUZ "Center for Hygiene and Epidemiology of the Vladimir Region". 04 September 2014. (In Russ.)

20. Russian Standard 17218-71. Active carbons. Method for determination of protective action time by benzene. 15 July 1986. (In Russ.) 21. Mukhin VM, Spiridonov YuY. Improvement of soil contaminated with pesticides using carbon adsorption technologies. *Agrarnaya nauka*. 2019;(2):156-159. DOI:10.32634/0869-8155-2019-326-2-156-159 (In Russ.)

22. Mukhin VM, Korolev NV. Ecological aspects in using active charcoal in oil and gas industry. *Neft. Gas. Novacii.* 2019;(4):60-62. (In Russ.)

23. Mukhin VM, Korolev NV. Synthesis of active coal on the basis of the coal tar pitch composition. *Khimiya v interesakh ustoychivogo razvitiya* = *Chemistry for Sustainable Development*. 2018;(26):577-582. DOI:10.15372/KhUR20180602 (In Russ.)

Информация об авторах / Information about the authors

Мухин Виктор Михайлович, доктор технических наук, профессор, начальник лаборатории активных углей, эластичных сорбентов и катализаторов, АО «ЭНПО «Неорганика», Электросталь, Московская область, Российская Федерация; Author ID (Scopus) 7103124020; e-mail: victormukhin@yandex.ru Victor M. Mukhin, D. Sc. (Engineering), Professor, Head of the Laboratory of Active Carbons, Elastic Sorbents and Catalysts of the JSC "Elektrostal Scientific and Production Association "Neorganika", Elektrostal, Moscow region, Russian Federation, AuthorID (Scopus) 7103124020; e-mail: victormukhin@yandex.ru

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