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Original Research Article

Activated Carbons Importance in the Decision of Ecological Problems

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The questions of biosphere pollution are stated, carbon adsorption technology's role in solving ecological problems are underscored. The examples of new activated carbons (AC) development and their nature and application in protection technologies practice are showed. In particular, new AC using has the great efficiency in effluent air purification, water preparation, soil rehabilitation and other fields.

Keywords: Environmental pollution and safety, Adsorption, Adsorbents, Activated carbon.

INTRODUCTION

The progressive pollution of the environment made environmental safety an important constituent of national safety as a whole. Today, practically the whole planet, especially regions mass accumulation of people, are subjected to serious ecological threats, the main of which are: radioactive pollution of territories; soil oppression by acid rains; soil pollution with chemical agents and pesticides; oil spills on water and land; destruction of atmosphere [1]. Problems of global environmental pollution were earlier (1970th years) noted by Russian scientist, professor of D.I. Mendeleev, Moscow Chemical Technological Institute, N.V. Keltsev, who suggested one of the prospective methods of situation solving such as the application of adsorption means. [2].

The physical/chemical properties of carbonic adsorbents (AC) make them unique and ideal adsorption materials, which helps in solving a big number of questions connected with chemical and biological safety of man, environment and infrastructure. Activated carbons are highly porous carbonic materials having extremely developed inner surfaces (1000-2000 m^2/g). In the activated carbon porous structure (micro- and mesopore volume) adsorption of any type of trace organic contaminants takes place by means of adsorption forces (surface interaction forces). Table 1 shows globally essential ecological technologies of activated carbons application. It is necessary to mention about constantly arising threats for prevention from which we need AC.

Thus, solvents losses and emissions at the beginning of 1990th were evaluated as 600-800 thousands tons per year. In the majority of cases, solvent vapour concentration in fumes is low (several grams per 1 m^3), that mainly predetermines the exclusive method of their recuperation by means of activated carbons. For example, activated carbon AG-PR with the following structural characteristics: Limiting adsorption volume W_o = 0,32 cm^3/g, size of micropores X_o= 0,67 nm, volume of mesopores V_{me}= 0,10 cm^3/g provides an effective recuperation of a wide range of vapours and solvents.

MATERIALS, RESULTS AND DISCUSSION

A great number of sanitary carbon adsorption purification technologies_includes, in particular, processes of trapping ammonia, chlorine, carbon bisulfide, sulfur dioxide, hydrogen sulphide, mercury, hydrocarbons, organic and chlororganic solvents of low concentration (<1 g/m^3) from air. All these problems are solved with the help of activated carbons, catalysts and chemical absorbents on their base. Sanitary purification processes may be divided into the following branches: gas desulfurizing, removal of radioactive gases and evil-smelling substances. These processes are described well enough in the monographs of professor Keltsev N.V., E. Bader and H. Kinle [2, 3].

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Table 1. Globally essential ecological technologies of activated carbons application

Biosphere constituent	Carbon adsorption technologies
Atmosphere	Solvents recuperation Fume sanitary purification, including desulphurization System of purification of air of AES Evolved by motor transport benzene vapor recovery Chemical weapon demolition Solid domestic wastes demolition Purification of air going into quarters and workrooms (air conditioning)
Hydrosphere	Drinking water purification Sewage sterilization Liquid radioactive wastes processing Gold and non-ferrous metals mining
Lithosphere	Soil protection from xenobiotics, including pesticides Soil remediation Zones of irrigation heads protection
Human	Devices of personal and collective protection of filtering type Chim-pharm preparation, vitamins, antibiotics producing Entero- and hemo sorption Ecologically pure food producing

Environmental pollution by motor transportation recently attracts more and more attention. Along with emission of hydrocarbons with waste gases from combustion engines, the essential quantity of them gets into the atmosphere as a result of many reasons like fuel evaporation from engine feed systems (gas tanks, carburets and other units).

On the basis of investigation results, we formulated technical requirements to crush carbonic adsorbents on coal base USK-DB for benzene vapour absorption: total pore volume ≥ 1,2 cm^3/g, effective pore volume >0,38 cm^3/g, abrasion strength ≥ 55%, air flow resistance of 5cm carbon layer – 17-24 mm w.c.

Testing of adsorber, equipped with activated carbon USK-DB on VAZ car according the standard method of the USA, showed that this adsorbent demonstrates 35-39% higher desorption ability in comparison with American carbon "Rochester". Later we improved adsorption system, having manufactured adsorber working element in the form of drum, using fine-grain polyethylene of low pressure as a binder.

These benzene vapour recovery adsorbers application in VAZ 2110-2115 cars prevented vapor emission in the quantity of 10000 t, which essentially improved ecological situation in RF cities. The technology of mustard gas, lewisite, their mixtures and organophosphorus toxic agents (OTA) demolition, adopted and realized in Russia by Federal Agency of chemical weapon storing and destruction, are accompanied with vent emission formation, containing these toxic agents in low but potentially dangerous concentrations. In connection with that, these emissions are directed to catalyst chambers which are vertical adsorbers with an activated carbon layer. Experiments showed that activated carbon AG-PR-1 with developed micropore volume (more than 0,35 cm^3/g) may be used as such an adsorbent. The waters of surface water supply sources are very often polluted with oil products, pesticides and other stable enough agents, mainly of organic nature.

One of the methods of drinking water purification is its treatment with powdered activated carbon (PAC). Usually, in advance, a suspension of 3-7% PAC by weight in water is prepared, which is then measured out into the polluted water flow. During the last years, for such purposes, activated carbon OU on wood base was usually used. Yet, the requirements for improvement of sorption process efficiency stipulated for reworking of PAC (on coal UAF base) quality parameters. That raised an absorptance on especially toxic compounds (chlorophenols and pesticides).

It is possible to raise water purification depth by means of traditional technology added with stages of water ozonation and following treatment by granulated activated carbons. Ozone-sorption treatment is foreseen by projects of new waterworks treatment facilities. In 2002 in Russia new modern ozone-sorption purification block on Rublevskaya waterworks with 240 thousand m^3/day capacity was planned to be put into operation. In this connection it was necessary to develop native granulated carbons (GAC).

Properties of new activated carbon "Hydrosorb" and exploitation order provide its effective application in drinking water preparation. It is confirmed by data of water quality control after the 4^{th} block and traditional installations of RWS: according to organic pollution generalized data (organic carbon content, permanganate oxidability) water purification efficiency exceeds the analogue in traditional technology for 40-50%; in case of unpleasant smells appearance in the water of Moskva river reliable deodorization can be made; waste products of ozonation (formaldehyde) are absent in water after carbonic filters.

This carbon was directed to Water Technologies Center (t. Karlsruhe, Germany) for possibility evaluation of its application at Germany waterworks taking water from open sources. Evaluation data of carbon adsorption capacity, given in table 2, show that carbon "Hydrosorb" iodine number is a little lower than of carbon ROW 08 S, but is high enough to meet the requirements of DIN-EN 12915. Along with this, "Hydrosorb" essentially surpasses a standard and demonstrates the most important advantage for water purification in adsorption capacity on organic polluters; difference between DOC values before and after the water treatment with carbon, besides this difference is an index of organic polluters extraction from water. Moreover, plant putting in operation stipulates for halogen hydrocarbons absence in water treated with carbon "Hydrosorb".

On the whole, experiments held at the Hostervitz waterworks (T. Dresden) state that activated carbon "Hydrosorb" meets the requirement of German standard and may be recommended to be applied in the process of drinking water preparation in Western Europe.

Among the problems of nuclear power engineering and nuclear and radiation technologies application, connected with radioactive wastes, the problem of liquid radioactive wastes (LRW) is the most actual. By the present moment only at the plants of Russian Nuclear Industry Ministry, there are more than 500 mln.m^3 of LRW with a total activity of 7,3 * 10^{19}Bq. The essential amount of LRW (more than 10 thousand m^3 with the activity of 10^{13}Bq) is accumulated at shipyards and dockyards of Russian Navy [4]. In connection with it, we got a task to find methods of effective LRW treatment with the help of sorption technologies based on activated carbons with improved strength properties.

For solving of radiation safety problems we developed two types of high-strength activated carbons: AG-95 on coal base and FAS-3 on polymer base. During in-process tests and commercial operation of LRW treatment systems, begun in 2001, we provided stable project index and confirmed activated carbon AG-95 efficiency in all technological components.

Sorption technologies for gold extraction from ores and concentrates recently occupied leading positions thanks to the possibility of their application at any type ore treatment, to high level of metal extraction, to minimal losses of the last (with "tails") process and to important ecological advantages in comparison with gravity method. Sorption technologies in gold hydrometallurgy don't lead to Siberia, the Far East, and the Ural water resources pollution. According to Federal program of gold-mining branch development in the Russian Federation the part of carbon-sorption technologies in ore treatment must increase to 73%. Already in 2000 gold-mining industry need in granulated activated carbons was valued for 1000 t/year.

Special character of gold sorption extraction required the development of native carbonic adsorbent of special type, which combine high-strength properties and good capacity on gold and don't yield to activated carbons of the same application made in the USA, Holland, Belgium, Japan, China (table 3). Russian requirements to activated carbons for noble metals hydrometallurgy are formulated by SPE "IRGIREDMET": capacity on gold at its balanced concentration in solution of 1 mg/l – no less than 8mg/g; strength at abrasion according to GOST 16188-70 - no less than 85%; grain-size composition – 90% of 2,5-1,0 class. Activated carbons AG-90 and AG-95 are already introduced at 5 gold-mining enterprises of Russia.

As it was said above, the main threats to biosphere consist in soils fertility decrease and even full exhaustion of them as a result of technogeneous activity. But soils constitute only 6% of the whole land and 30% of them belong to Russia. Taking into account that at the end of XXI century more than 10 billion people will live on the planet, we must pay great attention to protection and rehabilitation of soils.

Wide-ranging application of different chemicals, including pesticides, in the world agricultural practice, intensified medical-biological problems, caused by pollution of plant cultivation, cattle-breeding products and biosphere as a whole. At present, an assortment of pest-killers, applied in different countries, counts about thousand items (on reactants), about 3 hundred items are widely used [5].

At solving ecological tasks of agricultural complex (ACC) activated carbons are characterized with such advantages as sorption selectivity of organic toxicants, sorption properties universality, high absorbing capacity, hydrophobic property, handy preparative shape (grains, powder) and low cost. Till recently, in spite of task urgency, carbonic adsorbents for soils detoxication were not produced. That's why at first we theoretically substantiated the requirements for porous structure and preparative shape of such activated carbons (agri-sorbents) and also for technology of their bringing in soil. It is ascertained that agri-sorbents must have micropore volume no less than 0,2-0,3 cm^3/g with essential development of thin pores (0,6-0,8 nm), providing firm keeping not only of pesticides molecules but also their destruction products. Besides, transport porosity must also be well developed for providing of these agents absorption good kinetics. Such structures are easily formed at use of raw coal and its vapor-gas activation.

Given in table 4 experiment results, got in the laboratory of artificial climate (LAC) with different types and concentrations (corresponding to different residual quantities) of herbicides in soils, show that activated carbon is really a universal thing for fertility recovery of polluted soils irrespective of herbicide type and residual content, increasing crop capacity for 20-100%.

Another important result of carbon-adsorption soil detoxication is getting of ecologically pure plant cultivation and vegetable-growing products. Table 5 shows the results of contrastive experimental investigation on crops at their cultivating according to usual technology and with the use of adsorbent. As it is seen, activated carbons carrying into polluted zones in quantity of 100 kg/hec (in case of barley grain – 200 kg/hec) provide an extreme decrease, and sometimes complete exclusion, of herbicides accumulation in products of plant cultivation and vegetable-growing. Thus, AC application directly influences on nutrition and life quality of a man.

According to data of RSII of phytopathology, prospective ecologic-economic effect from soil detoxication achieves USA $500 from 1 hectare and only in Moscow region it may consist of 30 million USA dollars/year. It is also important because in Russia 50 million hectares of arable land is mentioned to be polluted with pesticides in dozes, leading to suppression of culture plants growing. At the condition of forced activated carbons application in agricultural practice, in the nearest years only Krasnodarsky region – a region of intensive agriculture – will need 25-30 thousand tons/year [1, 6].

And, at last, gasmask technique: gas masks, respirators and collective protection devices production is impossible without high quality activated carbons and sorption materials on their base: catalysts and chemical absorbents. Effective functioning of many important industries in Russia is impossible without this aspect of carbon-adsorption technologies. All system of population protection from man-caused catastrophes bases on application of personal protective devices of filtering type on AC base.

CONCLUSION

Special field of AC application, directly providing man's health, is medicine and health-care. Table 6 shows AC application in Russian medical industry. Total volume of AC production in the world comes to 400 thousand t/year. However the main index, characterizing country ecologic protection, is a rate of AC use by a person per year. In countries of Western Europe, USA and Japan this standard comes to 0,5 kg/person. In the Soviet Union it was about 0,15 kg/person.

Thus, the obvious advantages of active carbons as unique materials for the environmental protection are showed. To solve the most important ecological problems it is necessary to built plants of activated carbons based on different raw types, and reach to general AC output in the world more than 1,5 million tons/year till 2020. For example, new technologies of receiving of AC from straw of wheat, rye, oats, rape and other agricultural crops, the abundance of which, including renewal yearly, is the high innovated source, are being developed.

Table 2. Adsorption properties of activated carbons for water purification

Activated carbon	Iodine number, mg/g	Adsorption capacity on DOC at C=1,0 mg/l	Concentration in water after filter, mcg/l	
			1,2-cis-dichloroethene	1,2-cis-dichloroethane
Hydrosorb	850	24,0	<0,1	<0,1
ROW 08 S (standard)	1000	12,0	<0,1	<0,1
DIN-EN 12915	>600	-	<0,1	<0,1

Table 3. Characteristics of Russian and foreign activated carbons for noble metals extraction (data of SPE "IRGIREDMET")

AC type	Strength on GOST 16188-70, %	Activity on gold, mg/g	C_{rem}, mg/l
AG-90	85-88	12,2	1,1
AG-95	88-90	18,0	1,1
FAS-3	96,0	22,4	1,1
Taiko GW 612 (Japan)	91,5	19,6	1,3
Chemviron FFW-A (USA)	88,6	14,4	1,3
Norit R-2529 (Holland)	88,0	25,8	1,3
Jx-102 (China)	89,0	13,5	-

Note: C_{Au} = 16,8 mg/l – initial concentration.

Table 4. Efficiency of recovery of soil fertility, polluted with herbicide remains, by means of modified activated carbons at application rate of 100kg/hectare.

Herbicide remains in soil	Culture	Indices of kept test-cultures crop, % to polluted control
Chlorosulforon, 0,2g/hec	Cucumber	16-20
	Beet	58-63
	Radish	23-28
Terbasil, 1,4kg/hec	Cucumber	23-27
	Beet	64-69
	Radish	30-39
Picloram, 2g/hec	Cucumber	22-24
Simasin, 50g/hec	Tomato	22-26
Chlorosulfuron, 0,4g/hec	Tomato	98-100
	Beet	98-99
	Radish	98-100

Table 5. Herbicides accumulation by crops

Herbicide doze, kg/hec	Activated carbon doze, kg/hec	Test-culture	Herbicide content in crops, mcg/kg
Treflan -1	-	Tomato	28
Treflan -1	100	The same	0,6
Treflan -1	-	Carrot	95
Treflan -1	100	The same	Absent
2,4-D-5	-	Barley	220
2,4-D-5	200	Barley	Absent
2,4-D-10	-	Barley	670
2,4-D-10	200	Barley	Absent
2,4 - dichlorphenoxiacetic acid			

Table 6. Activated carbons application in medical industry (1992)

Application field	Volume, t/year	Mark
1. Production of chemical-pharmaceutical items	2368	OU-A, OU-B, UAM
2. Production of antibiotics	940	OU-A, OU-B
3. Production of vitamins	420	OU-A, UAM, AR-A
4. Production of remedies	240	OU-A, OU-B
5. Production of blood substitutes	80	OU-A, OU-B
6. Hemo- and enterosorption	5	SKT-6A, FAS, FAS-E, MeKS
Total:	4053	

These sorbents have a big potential if one looks at the initial investigation data [7]. The future of the environmental protection is with active carbons.

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