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Biocide Filters Based on Betulin for Cleaning Drinking Water

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Abstract—A technology for applying biocidal agents, betulin and silver, in the amount of 1% on the surface of carbon sorbents has been developed. The effect of the plant steroid betulin on the inhibition of *E. coli* reproduction on the surface of carbon filter sorbents in comparison with silver coating was evaluated. It is shown that graphite sorbents coated with silver and betulin are practically identical in the number of colonies formed and suppress their multiplication by a factor of 6–7. A composition including a carbon sorbent (active coal and/or foamed graphite) and betulin is obtained, which is recommended as a biocidal agent to replace silver in the manufacture of filters for post-treatment of drinking water.

Keywords: foamed graphite, betulin, water purification, filters

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At present citizens of many regions of the country do not have access to a quality drinking water. Therefore, design of systems for purifying water from toxic impurities for small communities is of practical interest for their health and well-being.

Carbon sorbents with a highly developed surface (active coal, carbon fiber, or foamed graphite) are widely used in water treatment [1–3].

Silver-containing components are used to prevent bacterial development in the filter. Silver is a costly metal and this makes expensive silver-coated filter sorbents.

Silver metal is insoluble in water, but oxygen dissolver in water oxidizes the surface silver layer to silver oxide. The water solubility of the latter is poor but sufficient to form chemical or physicochemical bonds with bacteria. Silver ions (maximum allowable concentration in water is 0.05 mg/L) as heavy metal ions related to hazard class 2 (highly hazardous substances) inhibit bacterial activity. Even though silver-containing filters are quite expensive, their service life is as short as a few months, after which they are thrown away.

Therefore, search for new nontoxic biocidal materials from renewable sources is quite an urgent problem.

Fullerene is among new nontoxic biocidal substances suggested as substitutes of silver. A technology for the preparation of a sorbent involving treatment of active coal with an aqueous solution containing fullerene and a stabilizer (crown ether, cyclic diether, tetralkylammonium hydroxide, tetra-alkylammonium halide, ethylene glycol or propylene glycol dimer, trimer, or tetramer, mono- and diether of ethylene glycol or their mono- or diether, C_1–C_6 alcohol mono- or diether, calixarene, or a mixture of the listed compounds) at concentrations of 1–100 μg/g active coal has been patented [4]. At present fullerenes are produced on a limited scale, primarily for scientific research, and are quite expensive. Therefore, fullerenes, in spite of their efficiency, are unlikely to provide keen and tough competition to silver in the near future.

At present one plant antiseptic, betulin (birch bark extract), is known. This substance has been protected birchbark letters from biodegradation in the ground for over a thousand years. Betulin is a plant steroid. According to international classification of toxic chemicals, betulin belongs to hazard class 4 (low-toxic substances): LD_{50} 9000 mg/kg. Betulin does no show allergenic, carcinogenic, skin irritant, cumulative, mutagenic, sensitizing, and embryotoxic activity [5].

In the present work we have studied the use of betulin, a renewable plant raw material, for preventing

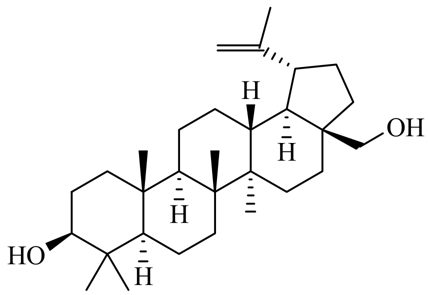

Fig. 1. Empirical formula of betulin.

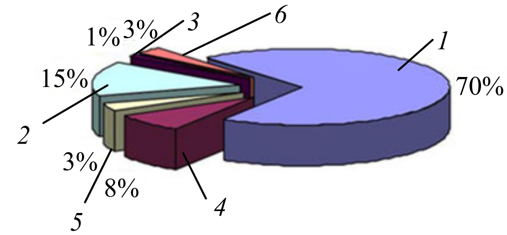

Fig. 2. Surface layer of birch bark (*betula alba*): (*1*) betulin, (*2*) polyoxyphenols, (*3*) lupeol, (*4*) phytosterols, (*5*) betulin acid, and (*6*) others.

bacterial growth in drinking water filters, using *E. coli* as an example.

Betulin is triterpene alcohol of the lupane series with the chemical formula is $C_{30}H_{50}O_2$, empirical formula shown in Fig. 1, and chemical name betulenol. It is contained as great number of plants (hazel, calendula, licorice, etc.) but in industry it is produced by extraction of birch bark (Fig. 2).

The main advantages of betulin, which differentiate it from other related compounds, include an accessible raw materials base, high content of the product in the raw material, and facility of isolation of the product. Betulin is an odorless white power with a slightly astringent taste, it is resistant to oxygen and sun light. Betulin is a nontoxic substance (hazard class 4).

The priority in studying the chemical properties of birch bark extract belongs to the Russian chemist Tovii Egorovich Lovits (Johann Tobias Lowitz), a colleague of M.V. Lomonosov. In 1788 he isolated by sublimation from birch bark a white substance which showed high efficiency in the therapy of burns and superficial wounds. Lowitz was also the first to describe its chemical properties. Later, in 1831, the prominent chemist Mason gave the name betulin [from the latin word *betula* (birch)]. Further study of betulin as an extractive substance revealed its multicomponent nature [6].

Physicochemical characteristics of the graphene sorbent

Parameter	Value
Appearance	Light powder
Carbon content, %	99
Bulk density, g/cm^3	0.1–0.01
Specific surface area, m^2/g	800–1000
Working temperature range, °C	–60 to +300
Crude oil adsorption capacity, g/g, no less than	1 : 50
Water absorption, %	70–90

As the filler for filters we used a graphene sorbent (GS) obtained, according to the patent [7], by the destruction of interlayer bonds in graphite with organic oxidants. The sorbent appears as a light dark gray powder.

At present intercalated (foamed) graphite is produced by impregnation of graphite flakes with strong oxidants followed by their heating to a high temperature. Oxidant molecules are small, which allows them to penetrate between graphite layers. When impregnated graphite is exposed to high temperatures, oxidant molecules decompose forming a lot of vapors and gases. The developed gas pressure destroys interlayer carbon–carbon bonds.

As oxidants we used organic peroxides. Under heating they decompose with oxygen evolution, and their residues burn out as carbon dioxide or undergo carbonization (see table).

To prepare the sorbent, betulin is applied on the carbon substrate (active carbon or foamed graphite, particle size 200–1000 nm) as a solution in an organic solvent or as a suspension (1–5% with respect to sorbent). Alternatively, betulin is applied on the surface from a 1–5% solution in an organic solvent, for example, alcohol, or from an aqueous suspension prepared according to the patent [8]. The specific feature of the procedure is that the hydrophobic substance betulin is first dissolved in a low-boiling organic solvent (1 to 10%). This solution is then mixed and homogenized with an aqueous solution of a surfactant in the working body of a colloid mill under vigorous stirring, and the solvent is removed by boiling away. To this end, the aqueous surfactant solution heated to 40–95°C (depending on the boiling point of the chosen solvent) and the organic solution of betulin are passed in a cyclic mode through the working body of the colloid

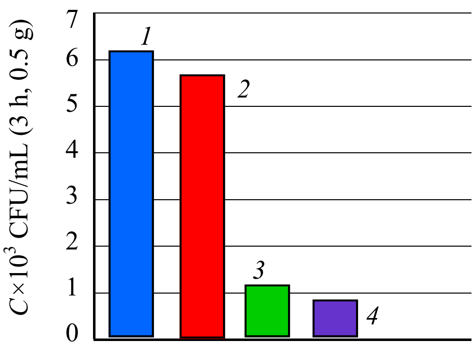

Fig. 3. Concentrations of *E. coli* colonies *scherichia coli* at different natures, sorbent concetrations, and culturing times: (*1*) medium, (*2*) carbon, (*3*) silver, and (*4*) 1% betulin.

mill at the rotor speed 15000–28000 rpm. Therewith, droplets and bubbles of the boiled-over solvent are broken up into microscale ones. The boiled-over solvent evaporates, while the solid solute particles (>1 μm) form a micro suspension. Thus formed aqueous suspension of betulin is mixed with the carbon sorbent at a preset ratio and dried at above 100°C to remove water and residual solvent.

For comparison, the cost of Betulin is 15 rubles per gram, i.e. to make 1 kg of carbon sorbent you will spend 150 rubles, instead of 875 rubles for silver nitrate.

For bacterial tests *E. coli* were grown in tubes on a dry nutrient agar at (28–30)°C for 3 days. Submerged culturing was performed in Erlenmeyer flasks (0.75 L) with 100 mL of the medium on a rotary shaker (230 min^{-1}) at (28–30)°C.

The results of bacterial tests, specifically, the effect of biocide additives (silver salt and betulin) on the growth of bacterial colonies on the GS surface, are presented in Fig. 3. As seen, the uncoated sorbent does not have any effect on bacterial growth. The results for silver- and betulin-coated sorbents are almost the same in terms of both the number of the formed colonies, and they both inhibit growth of bacteria by a factor of 6–7. The increase of the culturing time from 3 to 5 h did not have any effect on the concentration of colonies. The decrease of the sorbent portion from 0.5 to 0.3 g did not have any statistically significant effect. The betulin-containing sorbent decreased the titer of micro-organism by an order of magnitude, like that with silver.

CONCLUSIONS

Carbon sorbents (active coal and/or foamed graphite) and the plant biocide products betulin were used to obtain compositions which can be recommended for application in drinking water filters as a substitute of silver-containing sorbents [9]. The characteristic features of betulin are that its insensitive to air oxygen dissolved in water, insensitive to sun light, nontoxic, and cheaper than silver.

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