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SORPTION AND ION-EXCHANGE PROCESSES

Preparation and Antimicrobial Properties of Chlorinated Carbon Materials

S. S. Stavitskaya, V. E. Goba, and N. T. Kartel'

Institute of Sorption and Endoecology Problems, Ukrainian National Academy of Sciences, Kiev, Ukraine

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Abstract—Antimicrobial preparations based on anthracite and carbon fabric and prepared by chlorination were studied as influenced by the moisture content of sorbent, its bulk weight, chlorination temperature, etc.

Preparation of efficient antimicrobial materials based on solid sorbents, polymers, and fibrous materials is an urgent problem. Such materials can be obtained as granules, powders, pellets, plates, etc. They are especially important for local water treatment and can be used in development of new procedures for the water treatment which would be more progressive than the reagent water treatment, etc.

Materials of this kinds both bactericidal,[1] ensuring death of bacteria upon contact, and bacteriostatic, hindering growth and reproduction of bacteria, antimicrobial composites are based on cellulose and some other fibers, polymers, and activated carbons [1–3]. The antimicrobial efficiency is imparted either by impregnation of appropriate materials with active chemical preparations or by chemical modification of the preparation, introduction of appropriate functional groups, cations, or anions into the sorbent (fiber) skeleton or surface. In the latter case, stronger grafting of antimicrobial material to the support is achieved.

Various antimicrobial modifying agents (silver, copper, and mercury salts, antibiotics, heteroorganic compounds, etc.) have been studied [1]. It has been found that the antimicrobial activity is largely determined by the type of bonding between the modifying agent and support, the highest antimicrobial activity being typical of composites with ionic, labile covalent, or coordination bonding, whereas in the case of strong covalent bonding no antibacterial activity is observed.

The aim of this study was to prepare water disinfectants based on charcoal and other carbon materials (activated carbons, carbon fibers) and to evaluate their antimicrobial effectiveness. It should be noted that the antibacterial activity has been observed previously for pure activated carbons [2, 3], which is probably due to sorption of bacteria onto the developed sorbent surface. To improve the antibacterial effect, activated carbon or carbon fiber was impregnated with drugs (e.g., antibiotics) or some other appropriate compounds [2, 4]. Activated carbon with silver additives is used in the known domestic Rodnik unit for additional purification and disinfection of water, in mobile compact installations, and in special-purpose filters; activated carbons impregnated with silver and other antimicrobial additives are widely used for water treatment on airplanes and ships [2]. The possibility of preparing antimicrobial materials by chlorination of anthracite and other coals has also been studied. As known [5], chlorination is the most widely used procedure for water disinfection. The disinfection effect of chlorine is based on oxidation and breakdown of compounds in the photocytoplasm of bacteria, which causes their death. Water is often treated with gaseous chlorine or compounds containing active chlorine, e.g., chloride lime, hypochlorite, chloramine, etc. Thus, it is believed that the chlorine sorbed or grafted on the carbon surface, or possibly incorporated in the surface compounds or skeleton would also exhibit antimicrobial activity. No published data on biological (bactericidal, bacteriostatic) activity of chlorinated carbon materials could be found. At the same time,

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[1] According to "Regulations concerning Protection of Surface Waters from Pollution," water in sources of potable and public water consumption must contain no pathogenic organisms, and wastewaters should be disinfected after treatment. The permissible content of Saprophyte and Escherichia coli in potable water must not exceed 100 bacteria ml^{-1} and 3 bacteria l^{-1}, respectively [GOST (State Standard) 2374–73 "Potable Water"].

Table 1. Preparation conditions of chlorinated carbon materials

Sample no.	Carbon sorbent	Weight gain, g g^{-1}
1	Air-dry anthracite chlorinated at room temperature	0.40
2	Anthracite preliminarily dried at 200°C for 1.5 h and chlorinated at room temperature	0.44
3	Sample no. 2 treated without air at 900°C for 20 min	Weight loss
4	Wet anthracite chlorinated at room temperature	0.37
5	Initial anthracite without chlorination	–
6	Air-dry BAU chlorinated at room temperature	0.27
7	BAU preliminarily dried at 200°C for 1 h and chlorinated at room temperature	0.37
8	Initial chlorinated anthracite (similar to sample no. 2) for dilution	0.38
	Mixture of sample no. 8 + initial anthracite in indicated ratios:	
9	3 : 1	–
10	2 : 1	–
11	1 : 1	–
	Air-dry DOU chlorinated at indicated temperature, °C:	
12	room	0.26
13	200	0.08
14	450	Weight loss
15	650	″
16	Initial chlorinated activated anthracite for dilution	–
	Mixture of sample no. 16 + sample no. 5 in indicated ratios:	
17	1 : 2	–
18	1 : 3	–
19	Chlorinated sample no. 16 triple treated with distilled water (3 × 200 ml)	–
20	Carbon fabric chlorinated at room temperature	–

the high sorption capacity of activated carbons for chlorine is well known, and even during World War I these materials were used in respirators [2]. Moreover, it has been found [5] that the sorption capacity of carbon materials increases after their chlorination.

In our study, we analyzed for the first time activated anthracite; in our previous experiments we used charcoals commercial with varied surface nature, activated (BAU) and oxidized charcoal (DOU) [4], and AUT carbon fabric.

The chlorination was performed with gaseous chlorine obtained from a reaction of concentrated hydrochloric acid with crystalline potassium permanganate; in all the tests, 100 ml of HCl was added dropwise to 100 g of $KMnO_4$. The chlorine formed was passed through a carbon material (anthracite, charcoal, or fabric) placed in a standard vessel (column), when the experiment was performed at room temperature, or in a tubular reactor, when the experiments were performed on heating to 200–950°C with a furnace. The amount of carbon material was different for each treatment; it was determined by the reactor capacity and bulk weight of the material.

After being passed through a reactor, unchanged chlorine was fed into a vessel with ice-cooled 1 M NaOH. The amount of chlorine sorbed by the carbon material was evaluated from the difference of the concentrations of chlorine in the blank test (without carbon material) and after reaction with a weighed amount of a support. The initial concentration of chlorine was 0.62 mol l^{-1}; both weight and volume concentration of chlorine in the carbon material were estimated.

The time of chlorination varied because of the different reaction rates in each particular case; it was determined by the fact that equal amounts of chlorine were used in each experiment.

Along with chemical analysis, the increase in the coal weight after chlorination was also determined. These data were used only for tentative comparison of the results, because the increase in the material weight may be due to both sorbed chlorine and water vapor, especially when a preliminarily dried carbon material is used.

We prepared more than 20 samples of chlorinated carbons, with the type of carbon, sorbent moisture content (wet, air-dry, and dried at high temperature), and chlorination temperature (room, 200, 450, 650, and 950°C) varied. The preparation conditions of the samples are listed in Table 1.

Table 2. Sorption of chlorine, *A*, by activated anthracite and carbon fabric as influenced by experimental conditions (initial concentration of chlorine c_0 = 0.62 mol g^{-1})

Sample no.	Sample weight, g	c_{eq},* M	*A*		Sample no.	Sample weight, g	c_{eq},* M	*A*	
			mmol g^{-1}	mg g^{-1}				mmol g^{-1}	mg g^{-1}
1	62.8	0.08	8.6	305.3	13	40.9	0.02	14.7	521.8
2	60	0.1	10.1	358.6	14	41.4	0.006	14.8	525.4
4	60	0.14	9.93	352.5	15	40.5	0.004	15.2	539.9
8	64.2	0.08	9.03	320.6	20	45	0.49	2.88	102.2

[*] (c_{eq}) Equilibrium concentration of chlorine.

Table 3. Antimicrobial properties of chlorinated carbons

Sample no.*	Concentration of sorbed chlorine				Disinfecting effect at indicated carbon : water ratio		Chlorine smell
	mmol g^{-1}	mg g^{-1}	mmol ml^{-1}	mg ml^{-1}	50 mg : 100 ml	100 mg : 100 ml	
5	–	–	–	–	5	7	–
2	10.1	358.6	5.77	204.8	100	100	+
3	–	–	–	–	100	100	–
4	–	–	–	–	100	100	+
13	14.7	521.8	–	–	36	100	–
14	14.8	525.8	–	–	100	100	–
15	15.2	539.9	–	–	100	100	–
10	–	–	–	–	25	30	–
11	–	–	–	–	Inactive	Inactive	–
18	–	–	–	–	″	″	–
12	–	–	4.29	152.3	100	100	+
7	–	–	4.79	170.0	100	100	+
20	–	102.3	–	–	35	35	–

[*] Conditions of sample preparation are listed in Table 1.

The data on the sorption capacity for chlorine, recalculated to the weight and volume of the carbon material, are listed in Tables 2 and 3. As seen, sorption of chlorine is rather high, but depends strongly on the experimental conditions. The smallest sorption (102 mg g^{-1}) is observed for carbon fabric; anthracite samples exhibited high sorption capacity (A = 300–550 mg g^{-1}), similar results were recorded for commercial charcoals.

As seen from Table 2, the amount of sorbed chlorine increases, (from about 300 to 350 mg g^{-1}) with increasing treatment temperature, which indicates chemical interaction of chlorine with carbons, and the mechanism of such an interaction may be rather complex [6, 7]. Various processes (e.g., chemical sorption, substitution reactions, addition reactions, etc.) may proceed simultaneously; the composition of the carbon material and chemical nature of the surface can also affect the process.

Taking into account the possible use of chlorinated carbons as antimicrobial materials, we evaluated (even if approximately) the strength of chlorine binding in the samples of carbon materials prepared. For this purpose, we determined the amount of active chlorine easily removed from the surface with water (Table 4); 1-g sample was shaken with distilled water (100 ml) for 1.5 h , then the solid phase was filtered off, and the concentration of chlorine in the filtrate was determined [8]. In some cases, we used 0.1-g samples and 50-ml water portions (conditions similar to those when the antimicrobial activity was determined). It should be noted that the amount of chlorine desorbed

Table 4. Desorption of chlorine from chlorinated carbons (carbon sample $m = 1$ g, water portion $V = 100$ ml, contact time $\tau = 1.5$ h)

Sample no.	Equilibrium concentration of chlorine after desorption c_{eq}		Sample no.	Equilibrium concentration of chlorine after desorption c_{eq}	
	mmol l^{-1}	mg ml^{-1}		mmol l^{-1}	mg ml^{-1}
2	1.52×10^{-4}	5.39	14	1.04×10^{-4}	3.69
3	4.0×10^{-5}	1.70	15	4.0×10^{-6}	0.14
4	1.42×10^{-4}	5.04	16	0.9×10^{-4}	3.20
7	0.0	0.0	16a*	1.16×10^{-4}	4.12
10	1.28×10^{-4}	4.54	17	8.00×10^{-6}	0.28
11	1.00×10^{-4}	3.55	18	2.00×10^{-6}	0.07
12	8.00×10^{-6}	0.28	20	0.0	0.0
13	1.52×10^{-4}	5.39			

* Carbon sample $m = 0.1$ g, $V = 150$ ml.

from samples of chlorinated charcoals (BAU, DOU) and carbon fabric is 10–20 times smaller compared to that in the case of chlorinated anthracite (Table 4).

Moreover, we determined in some cases the rate of chlorine desorption from the carbons (see figure); the desorption was effected by triple treatment of a sample with distilled water (3 × 200 ml).

Our results showed that, under such conditions, only insignificant amount of chlorine is desorbed; however, the resulting concentration of chlorine in the solution is comparable with that used in at common water treatment. Actually, the initial concentration of chlorine for efficient water disinfection is 1–10 mg l^{-1} [8], and after the reaction with bacteria and impurities, the residual concentration decreases to 0.3–0.5 mg l^{-1}.

As seen from the figure, most of weakly bound chlorine is removed after first treatment with water, and then its amount decreases fast.

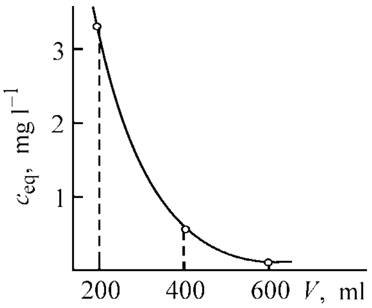
We also studied mixed samples of carbon materials, in which a chlorinated sample was diluted with pure anthracite in various ratios to decrease their activity and amount of desorbed chlorine (sample nos. 10, 11, etc; Table 1), and a sample three times washed with distilled water (sample no. 19).

The antimicrobial activity was evaluated with respect to *E.coli* K12, because the coli-index (content of bacteria per liter of water) is a standard characteristic of the water quality [2, 8].[2]

Data on the antimicrobial properties of the samples studied are listed in Table 3. As seen, unmodified activated anthracite exhibits zero antimicrobial activity; a similar behavior is observed for carbon fabric. At the same time, almost all samples of chlorinated anthracite and charcoals possess strong disinfection activity. Dilution of chlorinated samples with straight anthracite decreases the recovery of available chlorine into water (Table 4) and completely eliminates antimicrobial activity (Table 3).

Correlation of the disinfection effect with the amount of the sorbed and desorbed weakly bound chlorine (Table 4) shows no direct dependence between these parameters. In our opinion, sample nos. 2, 4, 7, 12 cannot be used in practice because of the strong smell of chlorine.

Some samples, including those chlorinated at high temperatures (e.g., sample nos. 3, 15 and charcoals BAU and DOU), possess the strongest disinfection activity and liberate insignificant amount of chlorine into solution.



Chlorine desorption after triple treatment with water (3 × 200 ml) of anthracite sample no. 16; $m = 15$ g and $\tau = 15$ min. (c_{eq}) Equilibrium chlorine concentration and (V) distilled water volume.

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[2] These tests were performed at the Kiev Research Institute of General and Public Hygiene, Kiev, Ukraine.

CONCLUSIONS

(1) Chlorinated carbon materials are promising antimicrobial agents. Several samples with strongly bound chlorine were prepared, which possess high antimicrobial activity with respect to *E.coli* K12 (bacteria commonly used in evaluation of hygienic requirements); the amount of chlorine desorbed from these materials into water is close to that satisfying sanitary requirements to potable water (GOST 2874–54).

(2) In some cases, chlorinated anthracene and charcoals can be used to replace water treatment with gaseous chlorine, which is especially important in water treatment at remote installations; their use does not require any special equipment, the necessary concentrations can be easily obtained, etc. Some of chlorinated anthracite samples exhibit acceptable (with respect to sorption capacity, stability, energy consumption, cost, antimicrobial activity, etc.) properties.

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