Estimation of the Efficiency for Adsorption Purification of Potable Water from Chloroform

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Abstract

The use of chlorination in water treatment system as a basic technique for disinfection often results in secondary contamination of potable water with volatile halogen organic compounds, whereto chloroform belongs as a main component. Results of the studies on the efficiency of the sorptive extraction of chloroform from aqueous solutions by adsorbents of diverse nature are presented in this work. The level of chloroform extraction at various concentrations in aqueous solutions, and the ceiling values of adsorption have been determined. On the basis of complex investigations the most efficient method of regeneration is chosen.

Key words: adsorption, purification, activated coals, chloroform, potable water

INTRODUCTION

For drinking water supply in various regions both superficial and underground water sources are commonly used. The analysis of data concerning the dynamics of superficial water quality all over the territory of the Russian Federation allows one to draw a conclusion about a high level of polluting substances [1] within river basins in Russia. The tolerance parameters are exceeded in various regions with respect to mineral oil, phenols, as well as manganese, copper and iron compounds is observed. Certain areas are characterized by the presence of specific pollutants in water such as lignin, lignin sulphonates, mercaptan, dimethyl disulphide, formaldehyde, hydrogen sulphide and its derivatives, chloroorganic pesticides. The situation with poor quality of potable water is also aggravated by disinfecting methods under common use those result in secondary pollution. The presence of organic substances of natural and artificial origin in river water results in the fact that the disinfection by means of chlorine-containing reagents yields volatile

halogen organic compounds (VHOC) including chloroform therein [2].

Chloroform is characterized by a negative biological action on human organism [3-5]. The experts consider chloroform to belong to the group of carcinogens potentially hazardous for humans, so called group 2B. In order to remove volatile halogen-containing organic compounds most often aeration, sorption and their combination, extraction, alkaline hydrolysis [6, 7] are used. However, at the chloroform concentration lower than 0.1 g/dm³ the extraction method for water purifying from chloroform is nonefficient due to the necessity of energy and solvent consumption, which results in arising the problem of utilizing the secondary waste products. The use of alkaline hydrolysis for water purification from chloroform [6] allows one to decrease the concentration halogen-containing organic compounds by 25-67 % (depending on water pH value). A higher level of VHOC conversion with the formation of inorganic chlorine compounds with 80 % concentration decrease can be provided at the temperature and pressure values elevated up to 150 °C and 475 MPa, respectively.

Physicochemical parameter of activated coals [8]										
Parameter	Adsorbent									
	PFS	SKD-515	KAU	AG-OV-1	AG-3	BAU				
Packed density, g/dm ³	373	526	417	531	465	540				
Durability, %	86	75	90	70	88	60				
Total ash mass fraction, $\%$	1.3	3.1	5.4	15	8.0	7				
pH of aqueous extract	7.8	7.6	9.3	6.80	6.50	7.85				
Total volume of pores, cm^3/g	1.1	0.7 - 1.0	0.97	0.5	0.88	1.65 - 1.8				
Volume of pores, cm ³ /g:										
Micropores	0.34	0.28	0.31	0.2	0.26	0.25				
Mesopores	0.66	0.11	0.4	0.1	0.09	0.08 - 0.1				
Macropores	0.1	0.33	0.26	0.2	0.53	1.35 - 1.4				
Adsorption activity with respect										
to iodine, % (in grain)	80	56	78	65	60	60				

Cylinder

Small

fines

fraction

Irregular

shape

TABLE 1

Shape of granules

F

The analysis of data published allows one to conclude that now there is no high-efficient method for water purifying from chloroform. Novel grades of activated coal with a high specific surface area (industrially produced SKD-515; experimental samples of KAU, PFS) were obtained at the Sorbent JSC (Perm city, Russia), thus it is expedient to consider their application to the adsorption water purification from chloroform. The studies on the adsorption equilibrium allows one to obtain information

Sphere

TABLE 2

Physicochemical parameters of active nonwoven fabric (ANF)

Parameter	Value
Sheet width, mm	400-500
Sheet thickness, mm	3-5
Surface density, g/m^2	50 - 200
Adsorption capacity with respect to benzene, mg/g	more than 280
Adsorption capacity with respect to iodine, %	more than 80
Adsorption capacity with respect to phenol, mg/g	more than 200
Specific surface, m ² /g	more than 1000
Total volume of pores, cm ³ /g	more than 0.8
Fabric humidity, %	less than 5

about the nature of adsorbate-adsorbing surface interaction, to determine the ceiling value of adsorption and other adsorption parameters, as well as to make an assumption concerning the potentialities of spent sorbent regeneration and to determine the level of extraction.

Cylinder

Irregular

shape

CHARACTERISTICS OF THE OBJECTS UNDER INVESTIGATION

The present work deals with the following entities as the objects under investigation:

- activated coal (Sorbent JSC, Perm, Russia), whose physicochemical properties are presented in Table 1;

- activated nonwoven fabric (Neorganika Production Enterprise, Elektrostal city, Russia) whose physicochemical properties are presented in Table 2;

- model aqueous solutions of chloroform with the concentration ranging within $0.2-5000 \text{ mg/dm}^3$.

EXPERIMENTAL

Gas chromatography determination of chloroform in aqueous solutions

For the microquantity of chloroform in water we used the method based on the analysis of equilibrium gas phase [9]. A considerable

473

influence upon the chloroform distribution coefficient between vapour and liquid phases is determined by the following factors: pH value of an aqueous solution, water salinity, the ratio between phase volumes in the system, the temperature of gas extraction process. The constancy of pH was achieved via the addition of phosphate buffer (pH 6.8). The influence of water salinity upon the distribution coefficient was eliminated through adding to water samples an excess amount (in comparison with real salinity) of a salting-out agent such as sodium sulphate. The determination of chloroform concentration was carried out by means of a gas chromatography method with an electron capture detector, the bottom detection limit being of 0.01 mg. The analytical procedure was carried out using a Crystal 2000 gas chromatograph with a packed column 2 m length, d = 0.5 mm, with apiezon L applied onto chromaton ($T_{\rm col}$ = 75 °C, $T_{\rm det}$ = 220 °C, T_{evap} = 80 °C; carrier gas flow rate amounting to $45 \text{ cm}^3/\text{min}$). The retention time value for chloroform under these conditions is equal to 72 s. The calibration curve was obtained using the method of absolute calibration.

Technique for studying the adsorption equilibrium in the aqueous chloroform solution adsorbent system

Each sample of an adsorbent with the same mass (1 g) was loaded to 100.00 cm³ of an aqueous solution with chloroform concentration ranging within $0.2-5000 \text{ mg/dm}^3$, the mixture was shaken during 24 h (preliminary tests demonstrated this time to be enough for establishing the adsorption equilibrium). The constancy of the temperature (T = 298 K) was maintained by means of placing the samples under investigation into a multiplace PE-6410 shaker with heating. The sample was then filtered and the concentration of chloroform in the filtrate was determined. The equilibrium adsorption value was calculated according to the formula $a = V(C_0 - C_{\rm eq})/m$ (1)

Here *a* is the value of adsorption, mmol/g; C_0 , C_{eq} are initial and equilibrium concentration chloroform in the solution, respectively, mmol/dm³; *V* is the volume of the solution, dm³, wherein the adsorption procedure is carried out;

m is the mass of the sample the adsorbent under investigation.

Experimental isotherms were obtained plotting a values against C_{eo} .

Regeneration techniques

Regeneration using the flow of an inert gas (nitrogen). A column filled with a spent adsorbent was connected to a Crystal 2000 gas chromatograph through an adapter. The mass



Fig. 1. Adsorption isotherms for the system of activated coal-aqueous chloroform solution (adsorbent-solution contact time value being 24 h, solution temperature being 298 K): a – initial coals; b – related to linear coordinates determined by the equation of the micropore volume filling theory; 1 – ANM, 2 – KAU, 3 – SKD-515, 4 – AG-3, 5 – AG-OV-1, 6 – PFS, 7 – BAU.

of the adsorbent under regeneration amounted to 50 g. The regeneration was carried out under the following conditions: the column temperature $T_{\rm col} = 150$ °C, the temperature of evaporator $T_{\rm evap} = 150$ °C, the carrier gas temperature after evaporator T = 150 °C; the flow rate of the carrier gas was 20 cm³/min; the procedure duration being 2 h.

Regeneration by hot water (water temperature of 70 °C). A column filled with a spent adsorbent was connected to a vessel filled with water through an adapter, which vessel preliminary heated up to 70 °C was placed into a thermostat. The flow rate of water amounted to made 20 cm³/min. The mass of the adsorbent under regeneration was equal to 50 g, the time of regeneration being 2 h.

Mathematical data treatment

In order to determine the adsorption parameters of the adsorbents under investigation those belong to porous solids, we used the equation of the micropore volume filling theory in the form modified for solutions [10]:

$$\log a = \log a_{\infty} - 2.303 \frac{R^2 T^2}{E^2} \left(\log \frac{C_{\rm s}}{C_{\rm eq}} \right)^2$$
(2)

Here C_s , C_{eq} are the concentration values for saturated and equilibrium solutions, respectively, mmol/dm³; *T* is the temperature, K; *R* is the absolute gas constant; *E* is the characteristic energy, J; a_{∞} is the ceiling adsorption value, mmol/g; *a* is the sorption value, mmol/g.

RESULTS AND DISCUSSION

Figure 1 demonstrates the isotherms of chloroform adsorption from aqueous solutions experimentally obtained for various active carbon grades. The processing of isotherms basing on Dubinin-Radushkevich linear coordinates (see Fig. 1, b) has allowed us to calculate the ceiling values of adsorption (Table 3). The comparison of experimental results (see Fig. 1 and Table 3) and textural properties of active coals under our investigation demonstrates (see Tables 1, 2) that the sorption of chloroform is mainly determined by the volume of micro- and mesopores. The adsorption activity of activated coal BAU should be much lower as compared to other adsorbents under investigation since this sorbent exhibit the fraction of micro- and mesopores equal to 20 % with respect to total amount of pores, whereas the micro- and mesopore fraction value observed for other activated coals is as it follows: SKD-515 - 46 %, AG-3 - 40 %, AG-OV-1 - 60 %, KAU - 95 %. The total volume of micro- and mesopores for active carbon PFS is higher than that for KAU (1.0 and 0.97, respectively), whereas the ceiling adsorption amounts to 57 % the value determined for KAU.

One of the important parameters characterizing the efficiency of either method for water purification from chloroform is the value of extraction level. It is established that at the concentration of the sorbate amounting to 1000 MPC (200 mg/dm³) the extraction level determined under equilibrium sorption conditions at constant values of the concentration, the solution volume and the sorbent-to-solution mass ratio (1 : 100), increases according the following order: BAU < PFS < AG-OV-1 < AG-3 < SKD-515 < KAU < ANM. The further increase in the concentration of chloroform results in a decreases in the level of chloroform extraction from aqueous solutions. For the adsorbents with a higher micropore fraction the decrease in the extraction level value is not so abrupt as it is observed for the adsorbents whose micropore fraction is less than 50 %. For KAU the concentration increase from 1000 up to 6000 mg/dm³ results in the extraction level decreasing from 98.4 down to 92.4 %, whereas

TABLE 3

Ceiling adsorption value calculated for the adsorbent - aqueous chloroform solution system

Parameter	Adsorbent							
	AG-3	AG-OV-1	SKD-515	KAU	PFS	BAU	ANM	
$a_{\rm max}$, mmol/g	6.85	6.54	7.22	7.96	4.56	5.63	8.20	



Fig. 2. Adsorption isotherms for the system of activated coal SKD-515 – aqueous chloroform solution (adsorbent-solution contact time value being 24 h, solution temperature being 298 K): 1 – initial technical grade coal; 2 – coal after the regeneration by means of nitrogen flow heated up to 150 °C; 3 – coal after steam regeneration; 4 – coal after the regeneration by means of hot water (70 °C).



Fig. 3. Adsorption properties recovery level for the sorbents of different grades due to the procedure of regeneration by nitrogen flow heated up to 150 °C. Chloroform concentration in the initial solution being 100 mg/dm³, the solution temperature being at 298 K, sorbent-solution contact time value amounting to 24 h.



Fig. 4. Variation of adsorption properties with respect to chloroform for activated carbon SKD-515 due to its regeneration and reuse. Chloroform concentration in the initial solution being 100 mg/dm^3 , the solution temperature being at 298 K, sorbent-solution contact time value amounting to 24 h.

for BAU the concentration increase from 1500 up to 2500 mg/dm³ results in an 11 % reduction of the extraction level.

An estimation has been performed for the possibility of the recovery the activated carbon adsorption properties with respect to chloroform through the regeneration by steam, by hot water (water temperature amounting to 70 °C) and by the flow of an inert gas (nitrogen) heated up to the temperature of 150 °C. Technical and recovered SKD-515 samples were used as sorbents (the SKD-515-chloroform samples were preliminary exposed to the regeneration by means of one of the three methods). In order to estimate the regeneration completeness, the investigation of chloroform adsorption by regenerated active coals has been carried out (Fig. 2).

The results obtained demonstrate that the decrease in adsorption capacity value for recovered carbon amounts to 5-7 % with steam and heated nitrogen used for the regeneration. Hence, one can consider these methods to be efficient enough. At the same time the isotherm obtained for activated coal after regeneration by hot water indicates that there is a significant decrease in the adsorption capacity amounting to 40 % of the initial value.

A comparison has been carried out for the efficiency of the regeneration of adsorption properties for activated coals such as BAU, KAU, AG-OV-1 and SKD-515 using the flow of an inert gas heated up to 150 °C (Fig. 3). The concentration of the solution wherein the sorption was carried out amounted to 100 mg/dm³

(500 MPC for chloroform). The analysis the results presented in Fig. 3 indicates that there is almost complete recovery of adsorption properties for SKD-515 and KAU grades of activated carbon. For AG-OV-1 and BAU activated carbons a 10 and 15 % decrease in adsorption properties, respectively, is observed.

Endurance test (10 sorption-desorption cycles) was carried out under laboratory conditions for activated coal SKD-515. The adsorption of chloroform by activated coal was measured at chloroform concentration in the initial solution amounting to 100 mg/dm^3 after reiterated regeneration by nitrogen flow heated up to $150 \,^{\circ}\text{C}$ (Fig. 4). The analysis of the data presented indicates that there is almost complete recovery observed for the adsorption capability of coal in six sorption - regeneration cycles, whereas a $30 \,\%$ decrease in the adsorption properties is observed by the 10th cycle.

CONCLUSION

The studies carried out allow one to draw the following conclusions:

1. The process of chloroform sorption by the adsorbents under investigation is determined by the volume of the sorbent micropores and mesopores: the higher the total volume of micro- and mesopores, the higher the sorptive capacity value.

2. The ceiling sorption value with respect to chloroform decreases according to the following order: ANM > KAU > SKD515 > AG-3 > AG-OV-1 > PFS > BAU.

3. At the adsorbed substance concentration amounting to 1000 MPC (maximum permissible concentration), the level of extraction increases in the order: BAU < PFS < AG-OV-1 < AG-3 < SKD-515 < KAU < ANM. With the increase in the concentration of chloroform the level of its extraction from aqueous solutions decreases, whereas for the sorbents wherein whose fraction of micropores is relatively high, the reduction of the extraction level is not so abrupt, as it is observed for the sorbents wherein the fraction of micropores is less than 50 %.

4. The most efficient method for the regeneration of activated carbon after the sorption of chloroform has been revealed to consist in the desorption of chloroform with the help of an inert gas (nitrogen) flow heated up to the temperature of 150 $^{\circ}$ C.

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