

# TECHNOLOGY OF AFTERPURIFICATION OF DRINKING WATER FROM ORGANIC CONTAMINANTS IN PRODUCTION OF FOODSTUFF

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Received April 28, 2016; Accepted in revised form May 30, 2016; Published June 27, 2016

**Abstract:** The technology of afterpurification of drinking water is developed for upgrading of foodstuff from organic contaminants periodically present at natural water or formed on a stage of disinfecting by ozonization. The adsorption research of phenol, formaldehyde and acetic aldehyde from individual water solutions and their mixes on active charcoals (AC) marks AG-3, ABG, KsAU, AG-OV-1, SKD-515 and BAU differing in contents, in the way of reception, structure and chemical state of a surface is carried out. The basic laws, features and the mechanism of adsorption organic contaminants on AC are established. The mechanism of mass carry is shown at adsorption of mixes of phenol and formaldehyde, formaldehyde and acetic aldehyde on AC of different marks. A method to optimise the parametres and modes of continuous absorption cleaning, based on the fundamental equation of external diffusion dynamics of absorption, using Dubinin-Radushkevich constants and kinetic dependences, is offered. The basic parametres of adsorption dynamics which allowed determining the operating period of the column, the quantity of refined water depending on the rate of transmission, height of fixed bed and sizes of a column are stated. According to the results of experimental researches and derivatographic analysis the technology of regeneration of active charcoals after adsorption of mixes by washing AC by water warmed up to 50°C with the subsequent warmup by a stream of air with temperature 200°C within 2 hours that allows to reduce sorptive capacity of sorbents on 95–98% is developed. The technology solution for afterpurification of drinking water from phenol, formaldehyde and acetaldehyde, occasionally presenting in natural water or arising in the stage of ozonation in water processing, was recommended on the basis of the complex analysis of absorption (balance, kinetics and dynamics) of organic substances, optimization of purification modes and parametres of absorption column, using mathematical modelling.

**Keywords:** adsorption, active charcoals, drinking water, phenol, formaldehyde, acetic aldehyde

DOI 10.21179/2308-4057-2016-1-61-69

*Foods and Raw Materials*, 2016, vol. 4, no. 1, pp. 61–69.

## INTRODUCTION

Drinking water playing the major role in maintenance of people's health is one of irreplaceable components in production of much foodstuff: reduced dairy production, meat and bakery goods, alcoholic and soft drinks. Water from system of economic-drinking water supply or prepared of underground water sources is basically used on food industry enterprises.

Kemerovo region – is a large territorial and production complex of the Russian Federation, where the considerable quantity of the metallurgical, chemical enterprises is placed, the mines which are a source of intensive pollution of the main waterway of area, the river Tom'. Therefore in Kuzbas underground waters are also used for water treatment. In the structure of water supply of Kemerovo region underground waters make 37.2%. Practically in all underground waters of Kuzbas there are phenols which are washed away from coal layers and humic connections. So, in Kuzbas in 2015 33.1% of hallmarks of water from sources of the centralized water supply of population mismatched hygienic specifications on sanitarian-chemical indexes,

including from open reservoirs of 13.6%, underground – 33.6% [1, 2].

Underground water is extracted from a source and is exposed to purification directly in a place of extraction with application of modern technologies, including the ozonization, excluding influence of external medium and contact to the person. Ozone is one of the strongest natural oxidants and a good disinfectant agent. Ozone is applied as disinfectant and oxidations of organic contaminants [3]. However as a result of water disinfecting by ozone, oxygen-containing organic compounds mainly aldehydes (formaldehyde, acetic aldehyde) can be formed. Being in water in the concentration exceeding maximum concentration limit, these contaminants damage central nervous system, liver, kidneys, possess toxic and carcinogenic properties [4–9].

So, there is a necessity of working out a technology of water afterpurification from organic contaminants, including phenol, formaldehyde and acetic aldehyde. For water purification from microadmixture of organic compounds it is more expedient to use the

adsorptive methods. The efficiency of water adsorption cleaning from organic compounds is defined by active charcoals on set of researches of balance, kinetics and dynamics of the adsorptive process.

The purpose of the present work is producing the adsorptive technology of afterpurification of drinking water for foodstuff production from phenol, formaldehyde and acetic aldehyde, occasionally presenting in natural water or arising in the stage of ozonation in water processing.

## OBJECTS AND METHODS OF STUDY

Research objects were: active charcoals of marks AG-OV-1, SKD-515, AG-3, BAU (manufacturer "Sor bent", JSC, Perm'), coconut active charcoal KsAU ("Eurocarb", England), ABG (lignite semi-coke, "Karbonika-F", CJSC, Krasnoyarsk), differing in raw materials, in the way of reception, chemical state of a surface, technical characteristics; water solutions of acetic aldehyde, formaldehyde, phenol with variable organic content ( $0.0001\text{--}50\text{ mmol/dm}^3$ ) and their mixes. Balance of mixes adsorption of phenol and formaldehyde is studied in the ratio components  $1 : 50\text{ (mmol/dm}^3\text{)}$ , formaldehyde and acetic aldehyde –  $9 : 1$ . The chosen parities of organic matters correspond to the periodic maintenance of phenol, formaldehyde, acetic aldehyde in water prepared with utilization of ozone. Studying of kinetics and dynamics of adsorption of systems formaldehyde-phenol – water-AC and formaldehyde-acetic aldehyde – water-AC were made on modelling water solutions with the greatest possible real maintenance of components during spring period in water with concentration of formaldehyde of  $0.2000\text{ mg/dm}^3$ , phenol –  $0.0120\text{ mg/dm}^3$ , acetic aldehyde –  $0.0500\text{ mg/dm}^3$ . Production tests were made in the shop of bottled water of "Talinka", LLC using ozonation as disinfecting.

The maintenance of phenol, formaldehyde, acetic aldehyde in samples was defined by method of molecular absorption spectroscopy.

Porous characteristics of active charcoals (total area of surface, area of micropores, volumes) were studied by method of low-temperature adsorption of nitrogen at  $77^\circ\text{C}$  on the device "Sorbtometr M" (production of IR Siberian Branch of the Russian Academy of Science, Novosibirsk).

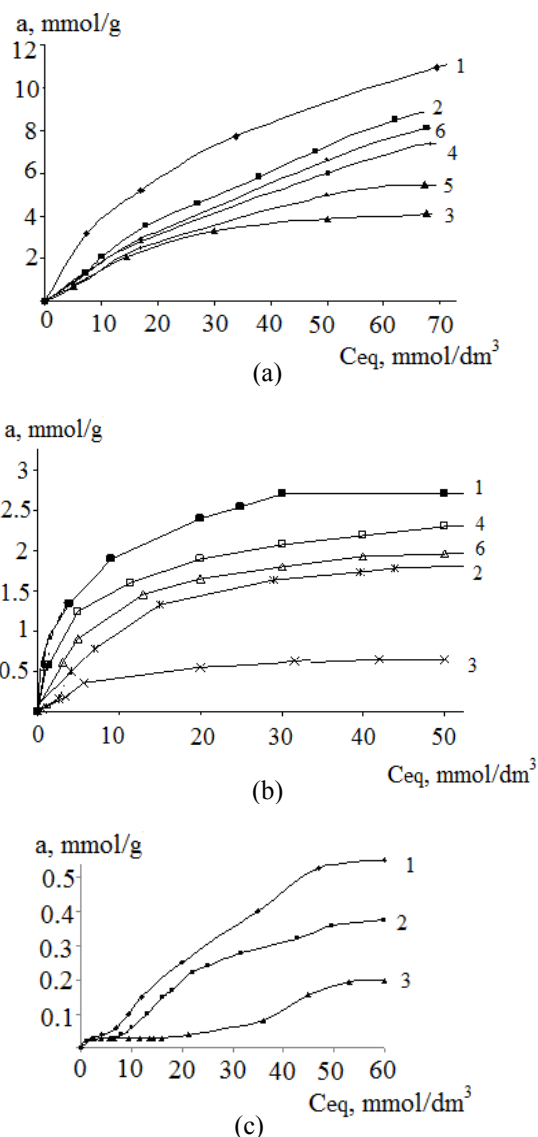
IR-spectroscopic researches were made on samples AC preliminarily slashed to a powdery state and mixed with KBr in the ratio  $1 : 10$ . IR DOFP-spectra were registered on the infra-red Fourier-spectrometer "Infralyum FT-801", production of IFP Siberian Branch of the Russian Academy of Science (Novosibirsk) in the range of  $4000\text{--}500\text{ cm}^{-1}$ , number scans 50.

## RESULTS AND DISCUSSION

One of the basic criteria of estimation of sorbents' adsorption properties are adsorption isotherms. Adsorption isotherms were constructed under the received experimental data of adsorption of formaldehyde, phenol, acetic aldehyde from solutions of individual components in a wide interval of concentration by carbon sorbents (Fig. 1). Various adsorptive capacity of active charcoals at adsorption of

organic matters from solutions is caused by physical and chemical properties of an adsorbent and adsorbate nature.

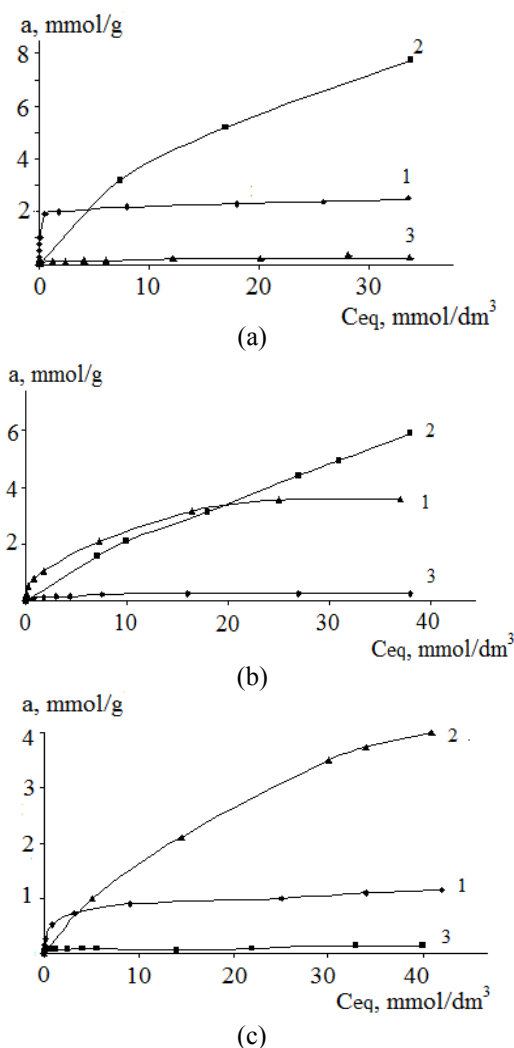
In the field of low concentration (Fig. 1) for all adsorption isotherms is typical the linear site, testifying that the maximum adsorbability has not been reached yet. The isotherms presented in Fig. 1a, 1b have a classical appearance and according to Giles's classification adsorption isotherm of phenol and formaldehyde from water solutions of individual components are isotherms of class L, isotherms of acetic aldehyde adsorption are isotherms of class S. The character of sorption isotherms according to Giles's classification allows to make the conclusion that interaction between the adsorbed molecules is not enough, and critical increment of energy does not depend on degree of fullness of sorbent surface. In case of adsorption of acetic aldehyde the force of interaction between the adsorbed molecules is more than force of interaction between a solute and an adsorbent, and energy activation increases [10, 11].



**Fig. 1.** Adsorption isotherms (a) formaldehyde, (b) phenol, (c) acetic aldehyde from individual water solutions on active charcoals: 1 – KsAU; 2 – AG-3; 3 – ABG; 4 – SKD-515; 5 – BAU; 6 – AG-OV-1.

The analysis of adsorption isotherms of organic contaminants also shows, that the maximum adsorbability of carbon sorbents depends on nature, contents, specific surface and porosity.

The influence of adsorbate properties is presented on Fig. 2.



**Fig. 2.** Adsorption isotherms of organic matters by active charcoal (a) AG-3, (b) KsAU, and (c) ABG: 1 – phenol; 2 – formaldehyde; 3 – acetic aldehyde.

The dependence known from literary data [11] between solubility sorbate and its sorption activity proves to be true for all probed substances. The influence of solubility on the acetic aldehyde adsorption, which limit of solubility is infinite, is especially appreciable. Because of high water solubility it is more favourable for acetic aldehyde thermodynamically to be in solution, than to be adsorbed on AC. Higher solubility of formaldehyde in water ( $12400 \text{ mmol/dm}^3$ ) in comparison with phenol in water ( $925 \text{ mmol/dm}^3$ ) and ability of formaldehyde to form clusters in the solution also reduces sorptive capacity because of dispersive interaction for the yielded component on all probed coals. In the yielded conditions it is more favourable for formaldehyde to be adsorbed on superficial active groups forming the secondary adsorptive centres. In spite of the fact that

formaldehyde and acetic aldehyde have identical functional groups, in this case the influence of solubility prevails and acetic aldehyde practically is not adsorbed. In the field of high concentration formaldehyde adsorption exceeds phenol adsorption, i.e. the yielded dependence is not conserved, because solubility is not the unique factor defining adsorption from water solutions of individual substances. At concentration increasing formaldehyde is adsorbed on the secondary adsorptive centres, forming new active centres for formaldehyde adsorption. Formaldehyde adsorption exceeds phenol adsorption on AC AG-3 in the field of concentration more than  $20 \text{ mmol/dm}^3$ , on AS KsAU more than  $5 \text{ mmol/dm}^3$ , on AC ABG more than  $3 \text{ mmol/dm}^3$ , reflecting features of sorbents behaviour, caused in their various sizes of porosity and chemical surface state, and also adsorbate properties.

For substantiation of adsorption mechanism data of poremetry, potentiometric titration according to Byom and adsorptive curves in the field of low concentration were used. The results of research of a pore structure and titration are presented in Tables 1 and 2. Data of poremetry showed, that the greatest bulk volume of micro- and mesopores at AC KsAU in comparison with other coals (Table 1), assumes higher adsorptive capacity of the yielded sorbent in relation to the substances which adsorption has the physical nature and goes mainly in micropores (Fig. 1a, 1b).

The sorbent of mark ABG possesses the least bulk volume of micro- and mesopores, in comparison with others AC, that causes the least adsorptive capacity of the yielded sorbent in relation to contaminants (Fig. 1). Experimental data also show, that the important factor defining the adsorptive extraction of phenol, formaldehyde and acetic aldehyde is the chemical surface state meaning quantitative and qualitative contents of functional groups.

Potentiometric titration data according to Byom have allowed to explain higher attenuation range of phenol and formaldehyde, at AU KsAU in comparison with ABG and AG-3. A surface of sorbent KsAU (Table 2) contains acid (carboxylic and lacquer) KFG on surface area 3 times more, than ABG, and 2 times more than AG-3. It provides the additional adsorption of organic matters caused by specific interaction because of a hydrogen bridge with KFG of coals.

For the characteristic of carbon materials and calculation of the adsorptive parameters monolayer adsorption theories (Freundlich and Lengmyur's equations), theory of volume filling of micropores (Dubinin-Radushkevich's equation modified for a case of adsorption from water solution) and the generalized theory of polymolecular adsorption Brunauer, Emmet and Teller (BET) are used. Applicability of these equations for calculation of adsorption parameters was defined by pre-award experimental researches. The calculated values of adsorption parameters of phenol and formaldehyde from water solutions for all coals are resulted in Table 3. According to the received parameters theoretical adsorption isotherms of components are calculated.

**Table 1.** The main characteristics of pore structure of probed samples

Sample	$S_{\text{micro}}, \text{m}^2/\text{g}$	$*V_s, \text{cm}^3/\text{g}$	$V_{\text{micro}}, \text{cm}^3/\text{g}$	$**V_{\text{meso}}, \text{cm}^3/\text{g}$
SKD-515	404.0	0.561	0.359	0.202
AG-OV-1	369.0	0.459	0.218	0.241
BAC	586.0	0.455	0.352	0.103
AG-3	490.0	0.340	0.270	0.060
ABG	-	0.260	0.020	0.240
KsAU	1418.7	0.730	0.620	0.110

Note. \* – general volume of pores with diameter less than 150 nm; \*\* – volume of mesopores, got from the balance  $V_s - V_{\text{micro}}$ .

**Table 2.** Surface condition of active charcoals

AC	The maintenance of oxygen active in mmol/g of coal ( $n_{\text{kfg}}, \text{mkmol}/\text{m}^2$ )		
	-OH phenol	-COOH <sub>strong</sub> carboxylic	-COO-lacquer
SKD-515	0.181	-	0.157
AG-OV-1	0.213	0.032	0.078
AG-3	0.321	0.035	0.039
ABG	0.130	0.020	0.040
KsAU	0.194	0.090	0.060

**Table 3.** Parameters of adsorption of organic matters from water solutions, probed active charcoals in static conditions

Coal mark	Type of equitation							
	Freindlikh		Lengmyur	BET		Dubinin-Radushkevich		
	1/n	b, mmol/g	$a_m$ , mmol/g	$a_m$ , mmol/g	-Q, kJ/mmole	$a_{\text{max}}$ , mmol/g	$E_0$ , kJ/mmole	$W$ , dm <sup>3</sup> /kg
formaldehyde								
AG-OV-I	1.34	0.04	13.5	25.0	13.4	21.0	15.9	0.56
SKD-515	0.80	3.80	11.7	20.0	12.5	19.1	13.6	0.51
AG-3	0.99	1.67	11.1	23.8	15.9	20.1	14.7	0.54
BAU	1.00	1.60	8.5	12.8	10.8	15.6	11.3	0.42
KsAU	1.23	2.93	20.8	33.3	17.3	33.1	10.1	0.334
ABG	1.07	0.89	3.92	17.54	16.7	9.2	10.4	0.09
phenol								
AG-3	0.43	10.53	0.75	0.894	13.45	2.14	15.9	0.25
KsAU	0.64	14.30	2.001	2.007	17.42	6.75	14.9	1.115
ABG	0.46	5.83	0.459	0.046	17.7	0.009	15.7	0.086
AG-OV-I	-	-	0.85	1.30	14.9	2.22	15.0	0.310
SKD-515	-	-	0.99	1.58	15.55	2.36	15.2	0.356

In connection with low initial concentration acetic aldehyde is practically completely adsorbed from water solutions on AC, therefore usage of monolayer adsorption theories, theory of volume filling of micropores and generalised theory of polymolecular adsorption BET for calculation of the basic adsorptive parameters of acetic aldehyde is not obviously possible.

Analyzing adsorptive characteristics, it is possible to draw a conclusion, that sizes of limiting adsorptive volume  $W$  for all carbon sorbents are in limits of 0.086–1.115 dm<sup>3</sup>/kg (for phenol), 0.09–0.56 dm<sup>3</sup>/kg (for formaldehyde) and allow to assume, that adsorption of phenol, formaldehyde from solutions of individual substances submits to the volume

mechanism of micropores filling. The values of characteristic energy which are in limits 14.9–15.9 kJ/mole (for phenol), 10.1–15.9 kJ/mole (for formaldehyde), testify that adsorption occurs basically in micro- and mesopores of adsorbents, and for active charcoal ABG in mesopores. Formaldehyde and phenol AC adsorption isotherms assume physical nature of adsorption. The calculated sizes for heats of adsorption 13.42–17.70 kJ (for phenol), 10.8–17.6 kJ (for formaldehyde) confirm the conclusion about the physical nature of interaction of organic matters with a surface of the studied carbon sorbents.

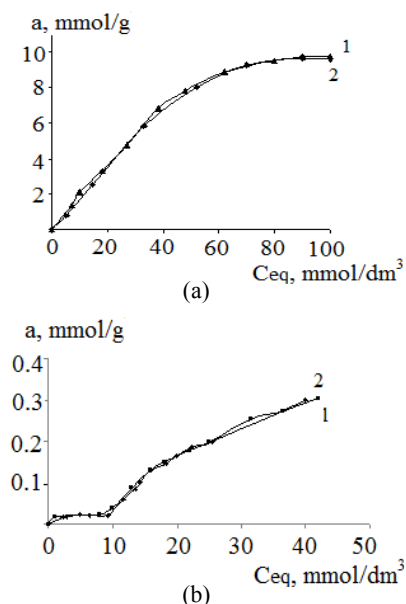
The received experimental data and settlement parameters allow to draw a conclusion, that adsorption of phenol, formaldehyde, acetic aldehyde has physical

nature, and phenol mainly has dispersive (nonspecific) and partially specific interaction because of hydrogen connection, for formaldehyde is more typical specific interaction. The formaldehyde having the highest size of adsorption, besides nonspecific interaction in pores is capable to interact with functional acid groups of surface AC and even to serve for formaldehyde molecules as the secondary centres of adsorption.

The complex estimation of adsorptive characteristics of the probed carbon sorbents in static conditions allowed to arrange them by efficiency of extraction: phenol – KsAU> SKD-515> AG-OV-1> AG-3> ABG; formaldehyde – KsAU> AG-3> AG-OV-1> SKD> 515> BAU> ABG; acetic aldehyde – KsAU> AG-3> ABG.

As in natural water mixes of organic matters usually contain, the balance of adsorption in systems most often meeting in practice of water treatment with application of stage of ozonization is probed: formaldehyde – phenol – water – AC and formaldehyde-acetic aldehyde – water – AC [12].

According to the received experimental data of adsorption of formaldehyde and acetic aldehyde from water solution their mix various carbon sorbents are constructed by adsorption isotherms. Comparison of adsorption isotherms of acetic aldehyde and formaldehyde from water solution their mix with adsorption isotherms from water solutions of individual substances showed absence of components influence on adsorption of each other. At adsorption of formaldehyde and acetic aldehyde from a mix the form of isotherms does not vary, thus acetic aldehyde (Fig. 3) owing to its low initial concentration is adsorbed completely. On the basis of experimental data adsorption key parametres are received.



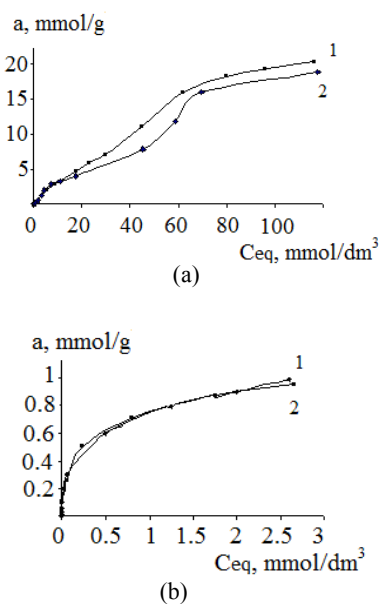
**Fig. 3.** Adsorption isotherms of formaldehyde (a) and acetic aldehyde (b) on AC AG-3: 1 – individual component; 2 – mix of components.

The obtained data allow to draw a conclusion, that adsorption of formaldehyde and weak adsorption of acetic aldehyde from a mix having physical nature, goes independently from each other, and for acetic aldehyde dispersive interaction in micropores prevails,

for formaldehyde – both dispersive in micropores and specific on surface AC with hydrogen connection with oxygen-containing superficial groups of acid type; thus at formaldehyde adsorption some processes proceed: adsorption in accessible size of micropores and specific interaction with active centres (thus sizes of characteristic energies are averaged).

The changing of adsorptive activity of carbon sorbents during formaldehyde and acetic aldehyde extraction at joint presence decreases in KsAU> AG-3> ABG.

The adsorptive behaviour of mix phenol-formaldehyde-water is probed. Under the received experimental data of adsorption of formaldehyde and phenol from water solution their mixes adsorption isotherms are constructed by various carbon sorbents. Comparison of adsorption isotherms of phenol and formaldehyde from water solution of their mix with adsorption isotherms from water solutions of individual components showed, that in the field of low concentration (to 10 mmol/dm<sup>3</sup>) there is no influence of components on adsorption of each other. In the field of high concentration at joint presence of organic matters phenol adsorption does not change, and formaldehyde is adsorbed a little bit poorer, than from its water solution of individual substance (Fig. 4). The form change of an isotherm (reduction of isotherm steepness) is thus observed that can testify about changes of interaction character of components in the solution and with AC surface. The form change of adsorption isotherm of formaldehyde from a mix on AC AG-3 with L on S<sub>4</sub>, means growth of critical increment of energy and bigger force of interaction between adsorbed molecules than between a solute and an adsorbent, and also molecules aspiration of solute to settle down on a surface in the form of chains or clusters. The decrease in adsorption of formaldehyde from water solution of components mix in the field of high concentration (more than 10 mmol/dm<sup>3</sup>) is caused by competitive adsorption on the adsorptive centres.



**Fig. 4.** Adsorption isotherms of formaldehyde (a) and phenol (b) on AC AG-3: 1 – individual component; 2 – components mix.

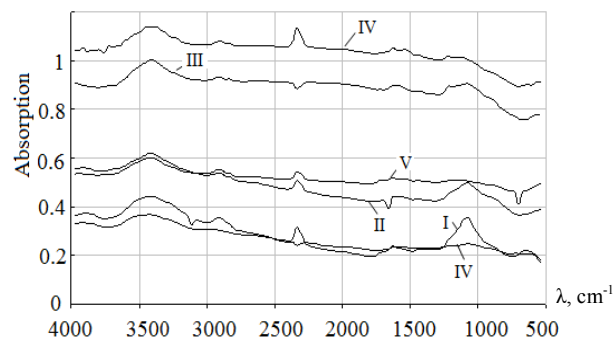
It is experimentally positioned, that Lengmyur's equation is not applicable for the adsorption equilibrium description in system water – phenol – formaldehyde – AC. The adsorption isotherms calculated on the equations of Dubinin-Radushkevich, Freundlich and BET, testify a application possibility of the yielded equations for calculation of equilibrium parameters of adsorption in the system Au – water – phenol – formaldehyde.

The sizes of limiting adsorptive volume  $W$  for all carbon sorbents are in limits of 0.0862–1.0641  $\text{cm}^3/\text{g}$  (for phenol), 0.33–1.231  $\text{cm}^3/\text{g}$  (for formaldehyde) and allow to assume, that phenol and formaldehyde adsorption at joint presence submits to the volume mechanism of micropores filling. The values of characteristic energy which are in limits 14.932–15.902  $\text{kJ}/\text{mole}$  (for phenol) and 13.576–14.668  $\text{kJ}/\text{mole}$  (for formaldehyde), testify, that phenol and formaldehyde sorption at joint presence occurs basically in micro- and mesopores of adsorbents. The value of adsorption heats at a small filling the pores of active charcoals are close among themselves and are in limits 11.282–16.963  $\text{kJ}/\text{mole}$  for phenol, assuming the adsorption caused as Van-der-Vaal'sovy forces (dispersive interaction), and because of formation of hydrogen bridges (specific interaction). The values of adsorption heats for formaldehyde 16.704–22.243  $\text{kJ}/\text{mole}$  give the basis to consider, that at its adsorption specific interaction prevails because of formation of hydrogen bridges with superficial polar functional groups, that is absorption of phenol and formaldehyde by active charcoals is a total process of nonspecific adsorption (in the volume of accessible pores) and specific (on active centres).

For specification of adsorption mechanism of phenol and formaldehyde IR-spectroscopic researches are carried out. The IR-spectroscopy is used for identification of organic matters and their functional groups. The occurrence in a spectrum of characteristic frequency of a functional group is influenced by structure, power constant connections and a molecule environment. The fluctuations change of base units of a molecule because of interaction at formation of intermolecular communication (for example, hydrogen) or dispersive interaction at physical adsorption will also be reflected in a spectrum by change of frequencies and fluctuations intensities of corresponding functional groups that will allow to specify the mechanism of interaction an adsorbent - adsorbate [13]. IR-spectra of active charcoals are studied before and after adsorption of organic matters from water solution.

The analysis of the received results showed (Fig. 5), that for all spectra it is possible to evolve areas of valent and deformation fluctuations -OH of alcohol group, phenols and carboxylic acids (3700–3300 and 1300–1250  $\text{cm}^{-1}$ , accordingly), free and connected hydrogen bridge; area of valent and deformation fluctuations-S-N of aliphatic group (2970–2850 and 1450–1300  $\text{cm}^{-1}$ , accordingly); area of fluctuations  $>C=O$  groups in aldehydes, ketones and carboxylic acids (1780–1600  $\text{cm}^{-1}$ ); fluctuations from group of alcohol

and ethers (1300–1000  $\text{cm}^{-1}$ ); the band corresponding to 2350  $\text{cm}^{-1}$ , falls into to carbon dioxide absorption, this absorption band is visible on all infra-red spectra received on one-beam devices or two-beam device at not enough good indemnification of a working bunch and a bunch of comparison.



**Fig. 5.** IR-DOFP spectra of active charcoals AG-3 and KsAU and their samples after adsorption of organic matters: AG-3 – industrial sample (I), AG-3 after adsorption of phenol (II), AG-3 after adsorption of formaldehyde (III), AG-3 after adsorption of a mix of phenol and formaldehyde in the ratio 1 : 50 ( $\text{mmol}/\text{dm}^3$ ) (IV), KsAU (V), KsAU after adsorption of a mix of phenol and formaldehyde (VI).

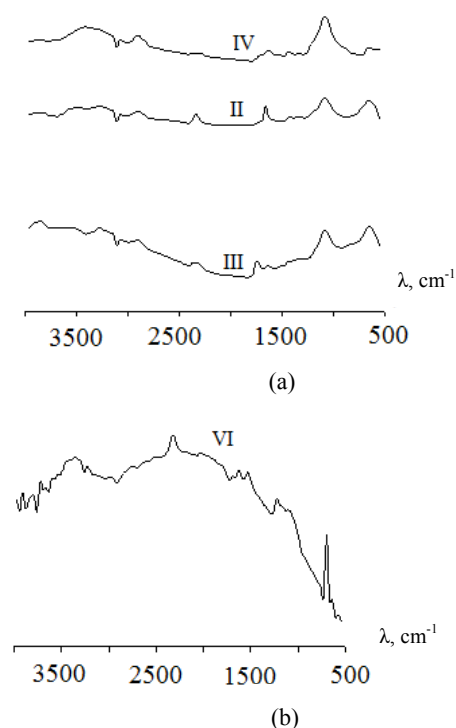
In Fig. 6 different IR – spectra are presented on which the studying of interaction of organic matters with superficial oxygen-containing groups AC is possible. Different spectra are received by subtraction of spectra AC after adsorption by organic matters from spectra AC [14].

On different spectra of samples II-IV and VI a set of bands of average intensity is seen, corresponding to fluctuation of -OH group with formation of an intermolecular hydrogen bridge (3600–3400  $\text{cm}^{-1}$ ). Hydroxyl group presence proves to be true by display of deformation fluctuations of -OH group and valent vibrations from -C-O- group in the field of 1300–1000  $\text{cm}^{-1}$ .

At difference spectrum AG-3 after phenol adsorption there are sets of bands with fluctuations of group -C-O- (1300–1000  $\text{cm}^{-1}$ ), and also a benzene ring (1620 and 1450  $\text{cm}^{-1}$ ) of adsorbed phenol. The set of bands 1790–1640  $\text{cm}^{-1}$ , probably, falls into to fluctuations of a carbonyl group of the carboxylic acids free and connected by a hydrogen bridge on an active charcoal surface.

In difference spectra AG-3 after formaldehyde adsorption there are bands of fluctuations of group -C-O- (1300–1000  $\text{cm}^{-1}$ ), also absorption bands for aliphatic aldehydes of 1230–1100  $\text{cm}^{-1}$  caused by the valent and deformation fluctuations C-C-C in the group  $\text{C}-\overset{\text{O}}{\parallel}-\text{C}-\text{C}$ .

Different spectra AC AG-3 after adsorption of a mix of organic matters at joint presence differs presence of more intensive bands of groups -OH (3600–3400  $\text{cm}^{-1}$ ), -C-O- (1300–1000  $\text{cm}^{-1}$ ) and adsorbed phenol (3650–3520 and 1280–1010  $\text{cm}^{-1}$ ).



**Fig. 6.** Different spectra of active charcoals samples AG-3 (a), KsAU (b) after adsorption of organic matters.

Area expansion of fluctuations to  $3600\text{ cm}^{-1}$ , probably, illustrates hydrogen connection between phenol and formaldehyde. In the field of  $1790\text{--}1630\text{ cm}^{-1}$  fluctuations of a carbonyl group of the carboxylic acids free and connected by a hydrogen bridge, and also quinones are displayed.

In different spectra AC KsAU after adsorption of a mix of phenol and formaldehyde the set of bands  $1870\text{--}1540\text{ cm}^{-1}$  is observed, connected with valence vibrations of group  $\text{C}=\text{O}$ . The field  $1800\text{--}1630\text{ cm}^{-1}$  corresponds to fluctuations of a carbonyl group of carboxylic acids free and connected by a hydrogen bridge, and also quinones. The strengthening of absorption bands in area ( $3600\text{--}3400\text{ cm}^{-1}$ ) in comparison with other samples is specified in occurrence of a hydrogen bridge  $-\text{OH}$  of groups of organic matters with oxygen-containing functional groups on AC surface. The absorption set of bands in area ( $3600\text{--}3400\text{ cm}^{-1}$ ) can be correlated with fluctuations phenolic and carboxyl groups on the active charcoal surface, being hydrolysate in the course of interaction of solvent with a sorbent.

On the basis of experimental researches of the balance, the calculated adsorptive parameters and IR-spectroscopy data, it is possible to consider, that phenol and formaldehyde adsorption both from water solution of individual components, and from a mix has physical character and does not result in to strong linkage with an adsorbent. At joint adsorption of formaldehyde and phenol instead of adsorption of dimer structures on an active charcoal surface the increase aliphatic ( $-\text{CH}$ ) and from  $-\text{C}-\text{O}-$  groups is observed. Hence, between phenol and formaldehyde there is an interaction both in water

solution, and on an active charcoal surface where formaldehyde molecules are capable to represent themselves as the secondary adsorptive centres for phenol molecules. At joint adsorption between these connections, obviously, the effect of hydrogen bonding is displayed which is enough fragile that allows to assume possibility of effective regeneration of active charcoal after adsorption cleaning of water from a phenol and formaldehyde mix.

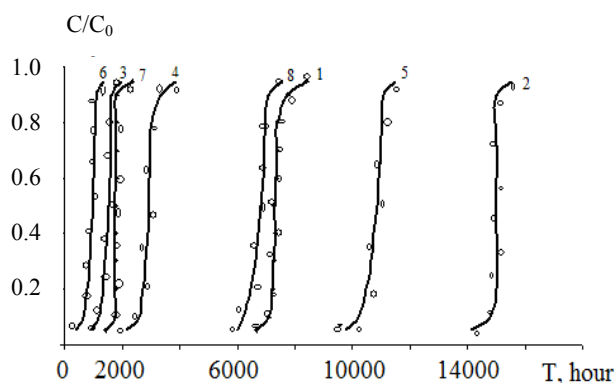
According to kinetic researches it is positioned, that a limiting stage of process of extraction of small concentration organic contaminants from water (phenol, formaldehyde, acetic aldehyde) is external mass carry. Factors of external mass carry, necessary for engineering calculations [15, 16] are calculated.

Experimental studying of adsorption dynamics assumes consecutive selection of parameters (sorbent type, length of fixed bed, rate of flow, etc.) and reception of experimental target curves depending on one varied variable (for example, rates of flow of a solution) at the fixed values of the others. Dynamics research of adsorption of mixes with phenol and formaldehyde, formaldehyde and acetic aldehyde from water on AC were made in columns in diameter of  $1.7\text{ cm}$  with height of bed of loading  $0.5\text{ m}$ , peripheral speed of a stream –  $1\text{ m/h}$ . Experimental researches of dynamics of adsorption showed, that at the continuous water purification containing mixes of organic contaminants, breakthrough of a dominating component is observed as the first from a column: for mixes phenol-formaldehyde and formaldehyde-acetic aldehyde – breakthrough of formaldehyde that allows to model adsorption process on a dominating component. Calculation is executed on the basis of the fundamental equation of external diffusion dynamics of adsorption in the field of low concentration with utilization of experimental data on balance and kinetics of sorption of organic matters on AC [17].

Coincidence of the experimental and theoretically calculated curves confirms legitimacy of the offered approach to modelling of adsorption and possibility of definition of dynamic characteristics of adsorption without additional carrying out of experimental researches (Fig. 7). According to the results of modelling of process of adsorption of the studied mixes dynamic characteristics are received: length of working bed, length of not used bed, protective effect factor, running time of a column and quantity of refined water depending on parameters of a column and a purification mode.

Experimental results confirm possibility of modelling of adsorption process. Engineering calculations for practical adsorptive installation can be made on a dominating component.

While working the efficiency of the adsorptive filters on extraction of pollutants drops, therefore their periodic regeneration is necessary for restoration of sorbents adsorbability. The possibility of utilization of the following methods of regeneration is experimentally studied: a steam, air stream, heated-up to  $200^\circ\text{C}$  and hot water.



**Fig. 7.** Target curves of dynamics of adsorption of formaldehyde in the presence of phenol for dense bed AC AG-3 (on theoretically calculated curves points experimental data are put) at different rates of flow ( $v$ ) and height of bed of a sorbent ( $H$ ): 1 –  $v = 1$  m/h,  $H = 0.5$  m; 2 –  $v = 1$  m/h,  $H = 1$  m; 3 –  $v = 5$  m/h,  $H = 0.5$  m; 4 –  $v = 5$  m/h,  $H = 1$  m; 5 –  $v = 5$  m/h,  $H = 2$  m; 6 –  $v = 8$  m/h,  $H = 0.5$  m; 7 –  $v = 8$  m/h,  $H = 1$  m; 8 –  $v = 8$  m/h,  $H = 2$  m.

For restoration of adsorbability of sorbents the technology of regeneration AC after adsorption of probed mixes – application of washing AC by water warmed up to 50°C, with the subsequent warm-up by a stream of air with temperature 200°C within 2 hours is offered, allowing to reduce sorptive capacity of sorbents on 95–98%. Thermogravimetric researches have preliminarily been made for a choice of temperature of thermal regeneration. The estimation of restoration of adsorption properties of AC after adsorption of aqueous mixes in laboratory conditions showed, that after the fifth cycle regeneration-sorption adsorbability has dropped on 16–22%.

On the basis of theoretical and experimental researches of adsorption process the technology of afterpurification of drinking water from priority organic contaminants and their mixes on AC, providing drinking water upgrading is developed, the carbon sorbent and hardware decor of process is chosen, the way of regeneration of the fulfilled sorbents, allowing to carry out their repeated utilization without decrease in adsorption properties is offered. The production tests on “Talinka”, LLC have shown efficiency of the offered technology.

## REFERENCES

1. Materialy k gosudarstvennomu dokladu «O sostoyanii i okhrane okruzhayushchey sredy Kemerovskoy oblasti v 2015 godu [Materials to the state report “About a state and preservation of the environment of the Kemerovo area in 2015”]. *Committee of preservation of the environment and natural resources of Kemerovo region*, 2015. Available at: [www.kuzbasseco.ru/wp-content/uploads/2016/03/DOKLAD\\_2015.pdf](http://www.kuzbasseco.ru/wp-content/uploads/2016/03/DOKLAD_2015.pdf). (accessed 2 April 2015). (In Russian).
2. Krasnova T.A. and Timoshchuk I.V. Impact of priority water contaminants on the stability of the main components of nectars. *Foods and Raw materials*, 2013, vol. 1, no. 1, pp. 95–107.
3. Nikoladze G.I. *Podgotovka vody dlya pit'evogo i promyshlennogo vodosnabzheniya* [Preparation of water for drinking and industrial water supply]. Moscow: Vysshaya shkola Publ., 1984. 368 p.
4. Sato T., Yamamori H., Matsuda H., et al. An estimation of safety of ozonation and chlorination of water purification plant. *Water Sci. Technol*, 1992, no. 9–11, pp. 2385–2388.
5. Warming to ozone. *Water and Waste Treat*, 1992, vol. 35, no. 4, pp. 12–16.
6. Neale P., Antony A., and Bartkow M. Bioanalytical assessment of the formation of disinfection byproducts in a drinking water treatment plant. *Environmental Science & Technology*, 2012, vol. 46, no. 18, pp. 10317–10325.
7. Itoh S., Gordon B., and Callan P. Regulations and perspectives on disinfection by-products: importance of estimating overall toxicity. *Journal of Water Supply: Research and Technology-Aqua*, 2011, vol. 60, no. 5, pp. 261–274.
8. Jeong C., Wagner E., and Siebert V. Occurrence and toxicity of disinfection byproducts in European drinking water in relation with the HIWATE epidemiology study. *Environmental Science & Technology*, 2012, vol. 46, no. 21, pp. 12120–12128.
9. Grushko Ya.M. *Vrednye organicheskie soedineniya v promyshlennykh stochnykh vodakh* [Harmful organic compounds in industrial sewage: Manual]. Leningrad: Khimiya Publ., 1982. 216 p.
10. Timoshchuk I.V., Ermolaeva N.A., and Proskunov I.V. Adsorption of acetic aldehyde from water solutions carbon sorbents. *Food Processing: Techniques and Technology*, 2012, no. 2, pp. 164–168. (In Russian).
11. Koganovskiy A.M., Klimentko N.A., Levchenko T.M., and Roda I.G. *Adsorbtsiya organicheskikh veshchestv iz vody* [Adsorption of organic matters from water]. Leningrad: Khimiya Publ., 1990. 256 p.
12. Timoshchuk I.V. *Formirovanie kachestva produktov pitaniya na osnove razrabotki i primeneniya adsorbtsionnykh protsessov v tekhnologiyakh ochistki prirodnykh vod*. Diss. dokt. tekhn. nauk [Formation of quality of food products through the development and use of adsorption processes in natural water purification technologies. Dr. eng. sci. diss.]. Kemerovo, 2014. 326 p.
13. Schlücker S., Singh Ranjan K., Asthana B.P., Popp J., and Kiefer W. Hydrogen-Bonded Pyridine – Water Complexes Studied by Density Functional Theory and Raman Spectroscopy. *J. Phys. Chem. A.*, 2001, no. 105, pp. 9983–9989.
14. Timoshchuk I.V., Golubeva N.S., Krasnova T.A., and Tumanova T.A. Studying of surface condition of active charcoal after adsorption of organic compounds. *Ecology and industry of Russia*, 2010, no. 10, pp. 58–59. (In Russian).



15. Fedotkin I.M., Koganovskii A.M., Roda I.G., and Marutovskii R.M. About definition of factor of external mass exchange at adsorption from solutions. *Journal of physical chemistry*, 1974, vol. 48, no. 2, pp. 473–475. (In Russian).
16. Krasnova T.A., Kirsanov M.P., Samoiloa N.A., and Chekannikova I.V. Kinetics of formaldehyde adsorption by activated carbon. *Ecological Congress International journal*, 2001, vol. 4, no. 3, pp. 5–8.
17. Timoshchuk I.V., Krasnova T.A., and Tumanova T.A. Technology of preparation of bottled water. *Food-processing industry. Beer and drinks*, 2009, no. 5, pp. 32–33. (In Russian).



**Please cite this article in press as:** Timoshchuk I.V. Technology of afterpurification of drinking water from organic contaminants in production of foodstuff. *Foods and Raw Materials*, 2016, vol. 4, no. 1, pp. 61–69. doi: 10.21179/2308-4057-2016-1-61-69.

