International Journal of Engineering & Technology, 9 (1) (2020) 52-58

International Journal of Engineering & Technology

Website: www.sciencepubco.com/index.php/IJET

Research paper

Toxicological properties of activated carbons with saturated by cationic surfactant surface

Artem V. Sharov [1] *, Olga M. Plotnikova [1], Anna I. Rykova [1], Vadim V. Evseev [1]

[1] Institute of Natural Sciences and Mathematics, Kurgan State University, Kurgan, Russia
**Corresponding author E-mail: sharow84@gmail.com*

Abstract

The article discusses the effects of cetyltrimethylammonium bromide, sorbed on activated carbons, on vital signs of some living systems. Extracts from carbon, saturated with cetyltrimethylammonium bromide, were injected into the organisms of laboratory mice and soil samples. The biochemical blood parameters were determined from laboratory mice. In soils was determined the enzymatic activity, as well as the number of major groups of soil microorganisms.
In mice, under the influence of surfactants on active carbons, the activity of enzymes associated with the functioning of the liver changes to a greater extent. The effect on the urease activity of the soil was not detected, the phosphatase activity under the action of surfactants increases, catalase and dehydrogenase - fall. The number of oligonitrophils, oligotrophs and amylolytics is reduced. A decrease in the effect of surfactant bonded to the active carbons surface on the systems as compared with free surfactants has been recorded.
The increase in the number of ammonifiers with the introduction of surfactants can be used for microbiological cleaning of waste active carbone.

Keywords: *Active Carbons; Adsorption; Blood Bio-Chemical Values; Cationic Surfactant; Enzyme Activity of Soils.*

1. Introduction

Cationic surfactants in the form of quaternary ammonium bases are used as fabric softeners or disinfectants, which leads to their discharge into the environment. The toxicological behavior of cationic surfactants on living organisms is recorded.. R. D. Swisher [1] publishes data of calculation of lethal dose of different quaternary ammonium surfactants on living organisms (230 – 730 mg per 1 kg of live weight for rats, 390 – 2000 mg per 1 kg of live weight for mice, 160 – 315 gr per 1 kg of live weight for swine). The significant effect on bio-chemical values of rats is observed while administering 660 mg of cationic surfactants per 1 kg of live weight with food. G. Dumitrescu, L. P. Ciochina [2] describes histologic values of liver and kidney of laboratory mice under the influence of quaternary ammonium surfactants. The phenomenon of surfactants bacterial biodegradation in soils is well-studied [3,4], however there is the negative influence of surfactants on some microorganisms such as phosphate solubilizers, bacteria, oxidizing ammonia, some types of cyanobacteria and etc. [4]. Prolonged introduction of anionic and cationic surfactants into the soil increases the activity of soil phosphatases and reduces the activity of dehydrogenases. [4].
Toxicity to surfactants has led to a number of publications on their sorption binding on various surfaces. The most wide-spread surfactants sorption agents are activated carbons, which have high sorption ability in relation to their molecules in aqueous solutions. The sorption capacity of carbons in relation to cationic surfactants varies within the limits from 0, 03 to 20 mmol/g on cetyltrimethylammonium bromide [5 – 9]. Such a difference is connected with monolayer or multilayer adsorption.
The intensification of the process of activated carbons use for sorption of surfactants actualizes the research of toxicological behavior of activated carbons with the surface saturated with surfactants and the development of methods of their utilization. By reaching the limit of sorption capacity the washing-off of some quantity of pollutant from carbons may be observed. The similar phenomenon may be observed while exhausted agent contacts with water in waste storage sites. In the literature there is a description of the this problems for different sorbents [10 - 15].
Based on the above, the purpose of the study presented in the article was to synthesize and study some toxicological characteristics of activated carbons with a sorption capacity, developed in relation to the cationic surfactant cetitrimethylammonium bromide. Investigated the biochemical parameters of blood of laboratory mice, indicators of the activity of soil microorganisms after the introduction of extracts of waste carbon into these systems.

2. Materials and methods

2.1. Synthesis of sorbents

As a resource for the synthesis of carbons strobilas of Pinus sylvestris (Pinus sylvestris L. sp. kulundensis), collected in Kurgan neighbourhood, Russia, were used. The natural material was comminuted into bits with linear size 0.5 – 1 sm, washed by distilled water and dried in the air. Before the pyrolysis the material was exposed in concentrated phosphorus acid within 24 hours. The received mixture was put into a steel tube with the inner diameter of 3.5 sm, with the length of 30 sm. The pyrolysis was conducted in an electric muffle at the temperature of 600 °C in helium current for three hours. After the pyrolysis the received blocks were washed by distilled water, dried, comminuted and washed in a filter with a lot of distilled water up to a negative reaction to phosphate ions on ammonium molybdate. The carbon was dried at the temperature of 150 °C to a fixed mass and used for the experiment.

2.2. Sorbents characterization

The humidity of sorbents for recalculating onto the mass of dry material was determined by inciderating to a fixed mass at the temperature of 150 °C with the use of the analyzer Sartorius MA 35.
The specific surface area and porosity determined according to the method of nitrogen sorption-desorption at 77 K on the analyzer SORBI MS by dynamic method in helium and nitrogen current. The specific surface area according to BET was stated by analyzing the points of sorption branch within the range of relative pressure of 0.04 – 0.30. To define the size of pores the points of desorption branch were processed according to the method of BJH [16].
The number of the main types of functional groups was determined by Boehm titrating. For this material sample weights of 0.200 g were put into plastic vessels and poured with 20 ml 0.0500 M solutions of sodium hydrocarbonate, carbonate and hydroxide and hydrochlorid acid. After stirring within 24 hours the solutions were filtered, filtrates were titrated with the solutions of hydrochlorid acid and sodium hydroxide with the use of methyl orange and phenolphthalein [17], [18].
The content of amino nitrogen was determined according to the Kjeldahl method. The sample weight of 0,200 g was dissolved in boiling concentrated sulphuric acid with the presence of sodium sulfate, copper sulfate and selenium. Into the received solution sodium hydroxide was added, precipitated ammonia was distilled into the solution of boric acid and titrated by sulphuric acid.

2.3. Measurement of surfactant sorption isotherms

The sorption isotherms of surfactants were measured by the method of separate weights. The weights of sample with the mass of 0,100 gr were poured with surfactant solutions in plastic vessels and held within 24 hours. The surfactant equilibrium concentration was defined by extract-photometric method with bromcresol green and chloroform on the spectrophotometer Specol 1300.
The isotherm of sorption were interpreted with the use of equations Langmuir (1) and Freundlich (2) [19].

$$a = \frac{a_m Kc}{1 + Kc} \tag{1}$$

$$a = kc^{1/n} \tag{2}$$

Here a is sorption value, mmol/g, a_m is maximum sorption value n in the monolayer, mmol/g, K is a constant of sorption equilibrium, k is an empirical constant, connected with sorption capacity of the sorbent, $mg^{(1-1/n)}l^{1/n}/g$, n is an empirical parameter, connected with surface irregularity.

2.4. Sorbents with the surface, saturated with cetyltrimethylammonium bromide obtaining

The 10 mmol/l solution of CTAB in the quantity of 2 l were strained through the layer of sorbent in the mass of 10 g. To remove CTAB out of interparticle solution 200 ml of water was strained through the sorbent. The obtained sorbent was dried at the temperature of 105 °C. The concentration of CTAB was calculated by the method of Kjeldahl, as it is described in paragraph 2.2. It was 0.4 mmol/g.

2.5. Determination of bio-chemical values of laboratory mice blood

To find out the sorbents influence on bio-chemical values of laboratory mice blood water extracts of cationic surfactants from sorbents were obtained. For this the carbons were mixed with the corresponding quantity of distilled water for a week and filtered after that. After the filtration the samples were in the form of suspension of fine carbon.
The blood plasm and red blood cells of laboratory mice CBA-line with the mass of 24-28 g at the age of 3 months, which were kept in standard living conditions, were studied. All the works with mice were held according to the principles of humane treatment to the animals and rules of laboratory practice [20].
For the investigation the mice were divided into 5 groups. For the control group (M-C) physiological solution was injected. The following experimental groups were used. Group M-S was injected with the solution of cationic surfactant with the concentration of 1 mg/ml, which comprises one twentieth of LD50 (410 mg/kg), group M-AC-S – aqueous extract of saturated with surfactant activated carbon. The quantity of water and carbon was calculated in such a way that in conditions of complete desorption, the concentration of surfactant in the water would comprise 1 mg/ml. Group M-AC was injected with aqueous extract of initial carbon. The ratio of water and carbon was taken the same as from group M-AC-S. Every sample was prepared in a three- time repetition and was used for animal injection.
After three-times' injections of the studied solutions on expiry of 24 hours after the last injection the animals were decapitated, the selected blood was centrifuged at 3000 rpm, and blood plasm and packed red cells were separated. According to accepted methods in clinical diagnostics, adapted to small animals, with the help of kit methods of firms «Vector-Best» (Russia) and semi-automatic analyzer Stat Fax 3300 in the blood plasm the following values were determined: concentration of total protein (TP), albumin, urea, glucose, triglycerides (TG), cholesterin (Chol); activity of alanine and aspartate aminotransferase (ALT and AST), lactate dehydrogenase (LDH); analytical methods helped to define substances of low and average molecular weight in blood red cells (SLAMW), the product of lipid peroxygenation – malondialdehyde (MDA) and carbonyl protein derivates (CPD) aldehyde and keto-2,4-dinitrophenylhydrazones (APH and KPH) [21].

2.6. Definition of soil microorganisms vital activity values

Coniferous forest soil of the dark gray forest podsolized type was used. Soil samples were taken from A_1 horizon, which is characterized by the width of 30 sm. The quantities of the cationic surfactant solution and waste sorbent were used with the consideration of the cetyltrimethylammonium bromide total concentration in the samples being 0.4; 4.0 and 40.0 mg/kg of soil. The samples were separated into the following groups. Group S – control. This group is initial soil exhausted to 60%. In groups S-S-1, S-S-2, S-S-3 the soils were soaked with the solution of cetyltrimethylammonium bromide in the 0.4; 4.0 and 40.0 mg of surfactant per the kilo of soil. In groups S-AC-S-1, S-AC-S-2, S-AC-S-3 the soil was soaked with waste sorbent so that the total concentration of surfactant comprised 0.4; 4.0 and 40.0 mg of CTAB per the kilo of soil. In groups S-AC-1, S-AC-2, S-AC-3 initial carbon was introduced to the soil with the same masses as in groups S-AC-S-1, S-AC-S-2, S-AC-S-3. After soaking the soils with active substances, they were exhausted to 60% and composted for some time mixing periodically. Sample temperature was maintained at the level of 24 – 25 °C.

In 15 days the enzyme activity was defined in the soils. Catalase activity was measured with permanganatometric method of Johnson and Temple. As a substrate 0.3 % solution of hydrogen peroxide was used, enzyme activity was determined by measuring the quantity of non-decomposed peroxide by titrating with potassium permanganate. The result was written in ml 0,1 M $KMnO_4$/g·20 min.

At the photometric definition of dehydrogenase activity as a hydrogen acceptor 2,3,5-triphenyl tetrazolium chloride was used. Herewith colourless salts of tetrazolium restored to red compounds of triphenylformazan (TPF). The weight of soil with the mass of 1 g was mixed with $CaCO_3$, The solution of glucose and 2,3,5-triphenyl tetrazolium chloride were added, mixed. The mixtures were temperature-controlled at the level of 37 ^{0}C for 24 hours, after adding spirit and filtrating, the optical density was determined at 440 nm. To define the activity, the calibration curve of the optical density from the concentration of triphenylformazan was used. The activity was expressed in mg of TPF per 1 g of soil for 24 hours.

To state urease activity, phosphate buffer (pH 6,7) and urea solution were added to the soil weight. The mixture was temperature-controlled at the level of 37 ^{0}C for 24 hours. After the incubation period the content was filtered into the volumetric flask with addition of 1 M KCl. The quantitative definition of ammonium was held by photometric method with Nessler's reagent at the wavelength of 400 nm. The quantity of ammonium was calculated according to calibration graph built in advanced. The enzyme activity was expressed in mg NH_3 per 10 of soil for 24 hours.

To definition of phosphatase activity, the soil weight was exhausted to 90% and to it the solution of phenolphthalein phosphate sodium and some drips of toluene were added. The mixture was temperature-controlled at the level of 30 °C for 1 hour and after the addition of aqua ammonia solution, phenolphthalein was checked photometrically at 540 nm. The activity was expressed in mg P_2O_5 per 100 g of soil for 1 hour.

To determine the population dynamics of microorganisms of the main groups the soil samples of series S, S-AC-1, S-AC-S-1 were taken in 15, 30 and 60 days of composting. Sampling was carried out by dilution of soil suspensions and sowing on solid media. The following media were used: meat-peptone agar (MPA) to check ammonifiers, starch ammonia agar (SAA) to check amylolytic group of microorganisms (bacteria and actinomycetes, uptaking mineral forms of nitrogen), hungry agar (HA) to check oligotroph group, Ashbey medium to check oligonitrophil group, as well as free living diazotrophs, Czapek's medium to check the number of soil fungi. After holding for regulated time there was a count of microorganism colonies, their number was defined in a form of the number CFU in 1 g of dry soil [22], [23].

All the experiments were carried out three times.

2.7. Statistical processing of biological experiments results

The results of the research, given below, are presented with median, 0.25 and 0.75 percentiles. The statistical significance among the series of experimental data was estimated with Wilcoxon criterion for independent series. Zero hypothesis of difference uncertainty was rejected at the values of $p<0, 05$ [24].

3. Main results of research

3.1. Characteristics of used carbons

In fig. 1 the isotherms of nitrogen sorption-desorption are presented on initial carbons at 77 K.

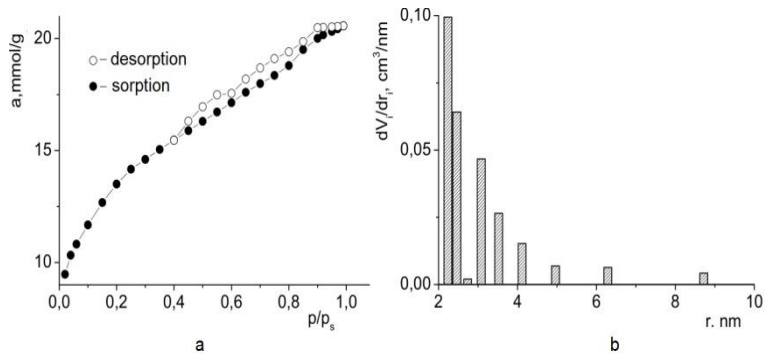

Fig. 1: Characteristics of Porosity of the Studied Sorbents. А – An Isotherm of Sorption-Desorption of Nitrogen at 77К; Б – Pore Radii Distribution.

The isotherms of nitrogen sorption-desorption belong to IV type according to IUPAC classification, based on this the presence of micro- and mesopores may be supposed in the samples. The filling of monolayer happens at p/p_s about 0.2 – 0.3. BET surface area of carbon is equal to 1078±6 m^2/g. Hysteretic loop lies in a range of differential pressures from 0.40 to 0.99, which allows assuming wide pores radius distribution. Dominating pore radii (fig. 1 б) are 2 and 2.5 nm (micropores). The presence of mesopores with radii 4.0; 5.0; 6.0 and 8.0 nm is noticed. Their volume comprises 51% of the total pore volume.

The content of functional groups and atoms on the surface is: carboxylic – 0,90±0,05 mmol/g, lactonic – 0,85±0,04 mmol/g, hydroxylic – 0,80±0,05, base – 0,33±0,33 mmol/g, total nitrogen – 0,09±0,04 mmol/g. As cetyltrimethylammonium bromide is a weak acid, adsorption of surfactant on the base groups can be expected due to a polar part and on hydrophobial surface parts due to hydrocarbon radicals.

The isotherms of cetyltrimethylammonium bromide sorption on carbon are presented in fig. 2, and coefficients of the equations of Langmuir and Freundlich – in table 1.

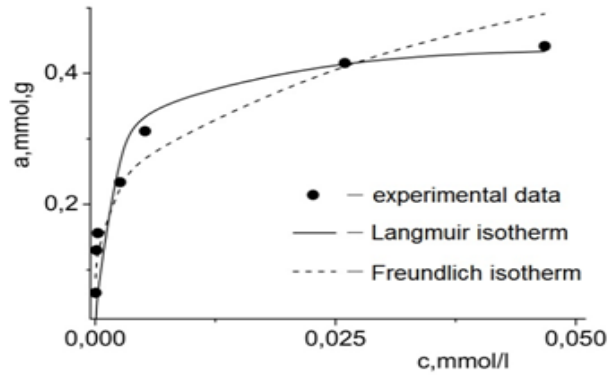

Fig. 2: Isotherm of Cationic Surfactants Adsorption on Activated Carbon.

Isotherms are better described by the Langmuir equation (Table 1). Maximum adsorption (0, 45 mmol/g) coincides with the concentration of surfactant, received as a result of surface saturation (0, 4 mmol/g, paragraph 2.4).

Table 1: Coefficients of Langmuir and Freundlich Equations at Surfactant Adsorption on Carbon (R^2 – Correlation Coefficient of Equation Linear Form)

Langmuir equation			Freundlich equation		
a_m, mmol/g	K	R^2	k	1/n	R^2
0.45	$7.5 \cdot 10^5$	0.9972	6.18	0.25	0.9424

3.2. Bio-chemical values of laboratory mice blood

The results of bio-chemical values definition were processed according to the formula:

$$\delta, \% = \frac{n_e - n_c}{n_c} * 100\% \quad (3)$$

Here $\delta, \%$ is a deviation from control in percent, n_e is an indicator value in the experimental group (M-AC, M-S or M-AC-S), n_c is an indicator value in the control group (M-C). The received results are presented in fig.s 3 and 4.

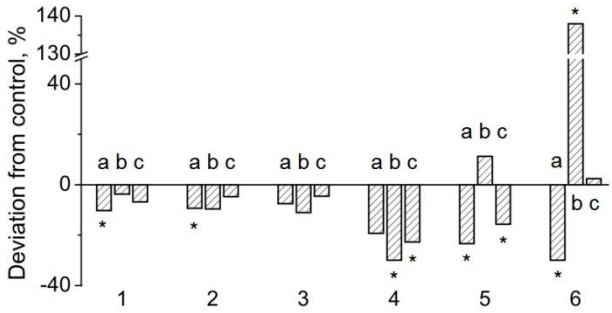

Fig. 3: Change of Bio-Chemical Values of Laboratory Mice Blood (Proteins and Enzymes) in Comparison with the Control Group. 1 – Total Protein, 2 – Albumin, 3 – Alanine Aminotransferase, 4 – Aspartate Aminotransferase, 5 – Cholinesterase, 6 – Lactic Dehydrogenase; A – Group M-AC, B – Group M-S, C – Group M-AC-S. Sign * Marks Significant Differences from Control.

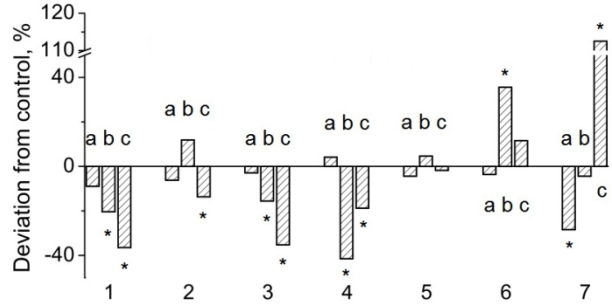

Fig. 4: Change of Bio-Chemical Values of Laboratory Mice Blood (Other Values) In Comparison with the Control Group. 1 – Urea, 2 – Aldehydrophenilhydrazones, 3 – Ketophenilhydrazones, 4 – Malondialdehyde, 5 – Glucose, 6 – Triglycerides, 7 – Substances of Low and Average Molecular Weight In Blood Red Cells; A – Group M-AC, B – Group M-S, C – Group M-AC-S. Sign * Marks Significant Differences from Control.

In the M-AC group, there was a slight decrease in almost all indicators. Significant difference from control was observed only for total protein (10%), albumin (10%), cholinesterase (23%), fig. 3, and substances of low and medium molecular weight (28%), fig. 4. The decline in performance, apparently, is due to the adsorption of substances on particles of activated carbon.

In groups M-S and M-AC-S statistically significant decrease of urea concentration was noted (by 20% and 36% respectively), as well as the decrease of aspartate aminotransferase activity (by 30 and 23% respectively), malondialdehyde level (by 42% and 19% respectively) and products of lipid peroxygenation of proteins in the form of malondialdehyde ketophenilhydrazones (by 12 and 35% respectively). It

is necessary to mention that the change of the values of urea and ketophenilhydrazones in the group M-AC-S is more significant than in group M-S. It is also possible to note the tendency of growth of concentration of aldehydrophenilhydrazones in the group M-AC-S in comparison with the group M-S. The statistically significant decrease of cationic surfactant influence due to carbon combining is observed for the values of activities of aspartate aminotransferase, lactic dehydrogenase, concentrations of malondialdehyde, triglycerides. Moreover, the significant increase of concentration of the substances of low and average molecular weight for the group M-AC-S, whereas the influence of the extract of initial carbon on this value is negative, and for the solution of surfactant the statistically significant influence was not fixed. Full absence of statistically significant changes is noticed only for the values of the activity of alanine aminotransferase and glucose content

3.3. Vital indicators of soil microorganisms

In fig 5 there are diagrams of enzyme activity change in the experimental groups. Deviation from control was calculated according to the formula (1).

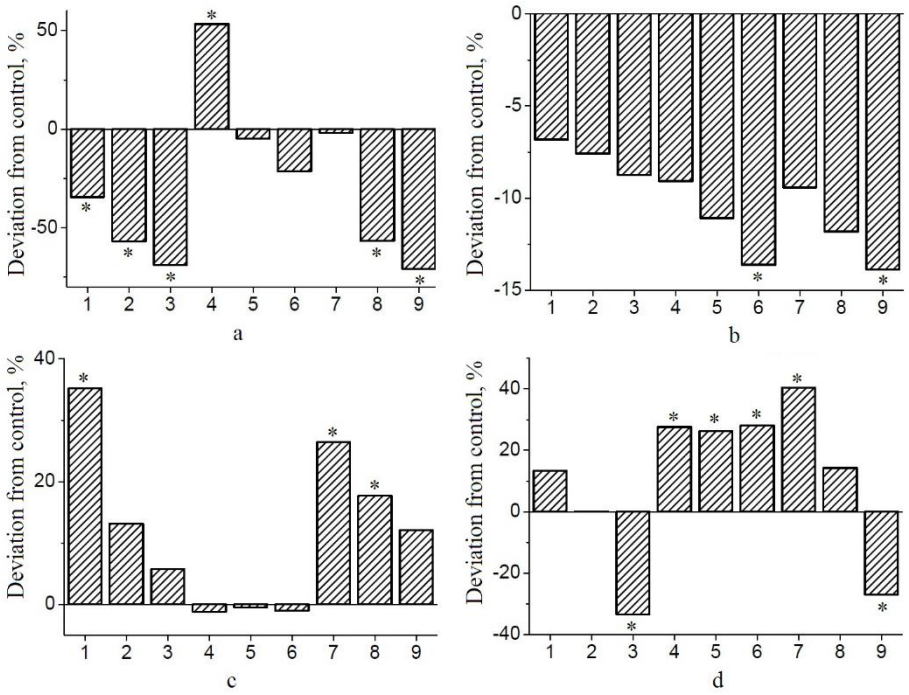

Fig. 5: Change of Soil Enzyme Activity. 1 – Group S-AC-1, 2 – Group S-AC -2, 3 – Group S-AC -3, 4 – Group S-S-1, 5 – Group S-S -2, 6 – Group S-S -3, 7 – Group S-AC-S-1, 8 – Group S-AC-S -2, 9 – Group S-AC-S -3; A - Catalase Activity, B – Dehydrogenase Activity, C – Urease Activity, D – Phosphatase Activity.

In all the cases except for dehydrogenase activity, the influence of the addition of initial carbon on enzyme activity is recorded, which is connected with adsorption of protein substances on it. It is important that in case with urease activity, the deviation from control is increasing with the degrowth of the added carbon. The introduction of surfactant in the concentration 0.4 mg/kg of soil raises catalase activity, which is leveling out by the negative influence of carbon in case with S-AC-S (fig. 5 a). As in the other cases the influence of surfactant on catalase activity is not recorded, negative deviation in sample case S-AC-S-2 and S-AC-S-3 in conditioned by carbon effect. The significant difference on dehydrogenase activity is registered for S-S-3 and S-AC-S-3. At the same time, combining on carbon doesn't influence the effect of cationic surfactant (fig. 5 b). The decrease of surfactant influence at carbon combining is recorded only for phosphatase activity with the concentration of surfactant of 4 and 40 mg/kg (fig. 5 d). So, the general tendency is the influence of the addition of initial carbon on enzyme activity. Carbon binding slightly reduces the effect of surfactants on enzyme activity. Apparently, it is connected with the concentration of soil microorganisms around carbon particles.

The dynamics of soil microorganisms' number in comparison with control is presented in fig. 6.

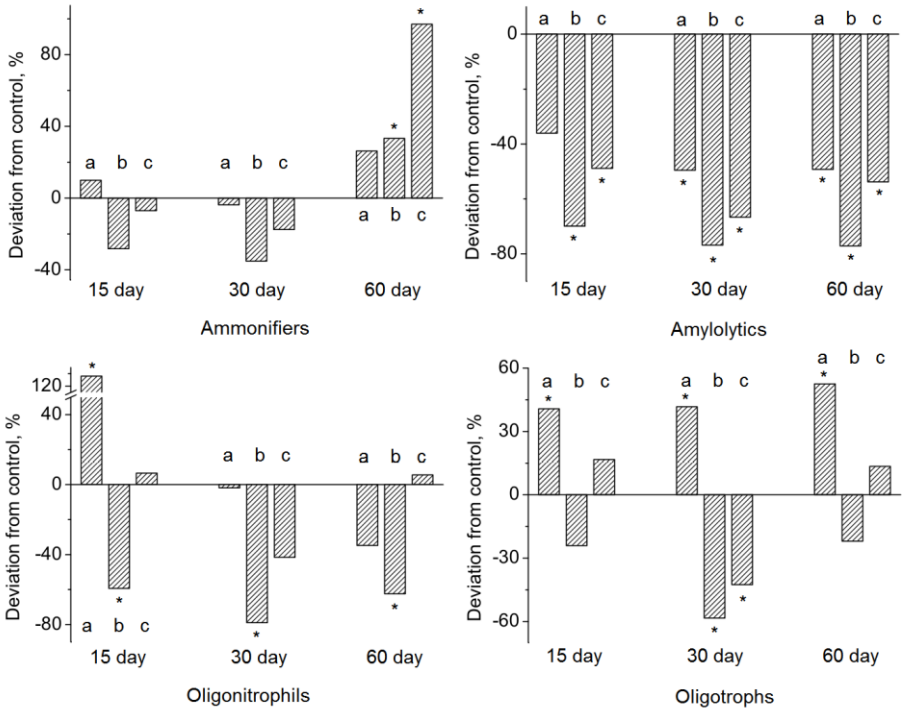

Fig. 6: The Influence of Sorbents on Soil Microorganisms Colony Size Dynamics. Notations: A – S-AC-1, B – S-S-1, C – S-AC-S-1.

The decrease of number is recorded for amylytics, both due to the addition of initial carbon or substances, containing surfactant, almost as soon as surfactant was added into the soil. For oligonitrophils the decrease of negative influence of surfactants is observed in case of its combining with carbon. An interesting fig. is noticed for ammonifiers and oligotrophs. In case with ammonifiers on 60th day of observation there was growth of number for sample S-AC-S-1 by 2 times though there were no significant deviation on days 15 and 30. For oligotrophs on day 60 the group number is building back after a significant fall by 60% on the 15 day.

4. Result discussion

The results, presented in table 1, allow forecasting that if 1 g of carbon saturated with cationic suractant, is put into 1 l of water, the concentration of cationic surfactant in the water will comprise 10 – 15 mg/l. So, it is necessary to expect either the decrease of influence of surfactant in a associated form or peculiar toxicological characteristics of carbons, saturated with surfactants, Both of these theses are proved by data, presented in point 3.2 and 3.3.

In the first place under the influence of CTAB in groups M- S and M-AC-S enzyme activity changes, characterizing the state of liver: AST and ALT, products of lipid peroxygenation and products of deep protein oxidation, registered in the form of ketophenilhydrazones (fig.s 3, 4). The similar data were received for rats while administering the mixture of CTAB, spirulina and CTAB, spirulina, zinc oxide [25]. In the long experiment, a significant decrease of AST activity and insignificant for ALT is noticed, while introducing surfactant-containing solutions. As in our case, the authors [25] recorded a significant decrease of concentration of MDA. In work [26] a certain growth of AST and ALT activities is described while introducing composites CTAB with Cu and Cd. Quite a significant influence of CTAB as a representative of alkyltrimethylammonium salts is connected with the similarity with phospholipid fragment according to construction, and as a consequence with the possibility of influence on cell membranes which leads to dysfunction of membrane bio-layer.

Blood biochemical parameters in mice under the influence of extract from spent carbon as a whole, change to a lesser extent, and their changes in the timing of the experiment are not critical for the body of mice.

The influence of surfactan in free and combining with carbon surface on dehydrogenase (decrease) and phosphatase (increase) activities (fig. 5) is similar to the one, described in literature [4, 27]. The leveling effect of carbon as a sobent is observed only in case with phosphatase activity. Apparently, the influence of activated carbon on these parameters is conditioned by the adsorption of protein substances on its surface and its colonization with bacterial cells.

The decrease of the microorganisms number in the studied groups, especially on the 30 and 60 days, is also natural. The same effects are reflected in literature for different SAAsurfactants [28]. Active reproduction of ammonifiers on S-S-1 и S-AC-S-1 may be used at development of microbiological methods of utilization of exhausted carbons.

In general, the effect of surfactants in a bound form on the studied parameters decreases, reaching for some indicators up to statistically insignificant deviations from the control. But, in most cases, only a certain effect of reducing the effect on the indicator is achieved compared with the control. Fatal deviations from the control have not been identified either for mice or for soil microorganisms.

5. Conclusions

The constant of the sorption equilibrium of CTAB and carbon according to Langmuir is equal to $7.5 \cdot 10^5$.

Under the influence of free and connected surfactant in mice organisms enzyme AST and ALT activity changes in the first place. The presence of surfactant in the soil does not influence urease activity, phosphatase activity rises under the influence of surfactants and catalase and dehydrogenase activities fall. The introduction of surfactant decreases the number of oligonitrophils, oligotrophs and amylolytics. The icrease in the number of ammonifiers on the exhausted carbons may be used in microbiological purification.

For most parameters the surface of activated carbons either decreases the degree of surfactant influence or eliminates this impact. All the same, work out of carbon sorption capacity in relation to CTAB may lead to its desorption while adding new portions of clearing solution or at the influence of atmospheric moisture after the storage of the exhausted sorbent.

Acknowledgements

The research was carried out with the support of the Russian fund of basic researches and the Government of the Kurgan region (grant 17-44-450483 p_ a).

References

[1] R. D. Swisher, Surfactant Effects on Humans and Other Mammals, The Soap and Detergent Association, New York, 1966.
[2] G. Dumitrescu, L. P. Ciochina, Acute effects of tetrabutylammonium chloride ionic liquid on the histological structure of liver and kidney in the mouse, Romanian Biotechnological Letters Vol. 19, No. 1 (2014) pp. 8925-8934.
[3] T. Ivanković, J. Hrenović, Surfactants in the environment, Arh Hig Rada Toksikol, 61 (2010) pp. 95-110, https://doi.org/10.2478/10004-1254-61-2010-1943.
[4] G.-G. Ying, Fate, behavior and effects of surfactants and their degradation products in the environment, Environment International, 32 (2006) 417–431, https://doi.org/10.1016/j.envint.2005.07.004.
[5] J.-X. Xiao, YingZhang, ChenWang et al, Adsorption of cationic–anionic surfactant mixtures on activated carbon, Carbon, 43 (2005) pp. 1032-1038, https://doi.org/10.1016/j.carbon.2004.11.039.
[6] M. Krivova, D.D. Grinshpan, N. Hedin, Adsorption of CnTABr surfactants on activated carbons, Colloids and Surfaces A Physicochemical and Engineering Aspects, 436 (2013) pp. 62-70, https://doi.org/10.1016/j.colsurfa.2013.05.063.
[7] N. A. B. Jamion, Preparation of date seed activation for surfactant recovery, Malaysian Journal of Analytical Sciences, Vol 21, No 5 (2017) pp.1045-1053, https://doi.org/10.17576/mjas-2017-2105-06.
[8] S. M. Yakout, A. A. Nayl Removal of cationic surfactant (CTAB) from aqueous solution on to activated carbon obtained from corncob, Carbon – Sci. Tech, 2 (2009) pp. 107-116, http://www.applied-science-innovations.com/cst-web-site/cst-2-2/CST-24.pdf
[9] P.P. Stevenson, R. Shaw, J. Tulloch, G. M. Evans, The influence of stirring upon the adsorption of a cationic surfactant onto activated carbon particles, Adsorption Science & Technology, Vol. 29, No. 2 (2011) pp. 99-115, https://doi.org/10.1260/0263-6174.29.2.99.
[10] R. Parveen, H. Nawaz, Regeneration of spend activated carbon, Pakistan Journal of Biological Sciences, № 3 (5) (2000) pp. 866-867, https://doi.org/10.3923/pjbs.2000.866.867.
[11] S.-H. Kow, M.R. Fahmi, C.Z.A. Abidin, S.-A. Ong, N. Ibrahim, Regeneration of spent activated carbon from industrial application by NaOH solution and hot water, Desalination and Water Treatment, Vol. 57, Iss. 60 (2016) pp. 29137-29142, https://doi.org/10.1080/19443994.2016.1168133.
[12] E. Da'na, A. Awad Regeneration of spent activated carbon from industrial application by NaOH solution and hot water, Journal of Environmental Chemical Engineering, № (2017) pp. 3091- 3099, https://doi.org/10.1016/j.jece.2017.06.022.
[13] N. Ghasemzadeh, M. Ghadiri, A. Behroozsarand Optimization of chemical regeneration procedures of spent activated carbon, Advances in Environmental Technology, №1 (2017), pp. 45- 51.
[14] V.V. Samonin, M.L Podvyaznikov, V.N. Solov'ev, V.L. Kiseleva, E.D. Khrylova, E.A. Spiridonova, Study of the possibility of regeneration of activated carbon spent in water treatment processes using the chemical regeneration and thermal reactivation, Russian Journal of Applied Chemistry, Vol. 86, Iss. 8 (2013) pp. 1220- 1224, https://doi.org/10.1134/S1070427213080119.
[15] Edy Wibowo, Sutisna, Mamat Rokhmat et al, Utilization of natural zeolite as sorbent material for seawater desalination, Procedia Engineering, Vol. 170 (2017) pp. 8-13, https://doi.org/10.1016/j.proeng.2017.03.002.
[16] V.A. Kucherenko, Shendrik T. G., Khabarova, T. V. et al, Influence of the temperature of chemical activation on the formation of the porous structure of adsorbents from brown coal [Vliyaniye temperatury khimicheskoy aktivatsii na formirovaniye poristoy struktury adsorbentov iz burogo uglya], Journal of Siberian Federal University. Chemistry, No 2 (2009) pp. 223-231, http://elib.sfu-kras.ru/handle/2311/1582
[17] M.S. Shafeeyan, W.M.A. Wan Daud, A. Houshmand, A. Shamiri A review on surface modification of activated carbon for carbon dioxide adsorption, Journal of Analytical and Applied Pyrolysis, No 89 (2010) pp. 143-151, https://doi.org/10.1016/j.jaap.2010.07.006.
[18] R.B. Fidel, D.A. Laird, M.L. Thompson, Evaluation of modified Boehm titration methods for use with biochars, Journal of Environmental Quality, No 42 (2013) pp. 1771-1778, https://doi.org/10.2134/jeq2013.07.0285.
[19] M.R. Samarghandi, M. Hadi, S. Moauedi, F.A. Barjasteh, Two-parameter isotherms of methyl orange sorption by pinecone derived activated carbon, Iran. J. Environ. Health. Sci. Eng., Vol. 6, No. 4 (2009), pp. 285-294 http://hdl.handle.net/1807/62272.
[20] V.E. Chadaev Ethical principles of experiments with laboratory animals [Eticheskiye printsipy pri rabote s laboratornymi zhivotnymi], Bulletin of problems in biology and medicine, Vol. 2, No. 1 (92) (2012) pp. 113-115.
[21] O.M. Plotnikova, A.M. Korepin, N.N. Matveev et al, Markers of endogenous intoxication in the blood of laboratory mice during intoxication by various doses of methylphosphonate [Markery endogennoy intoksikatsii v krovi laboratornykh myshey pri intoksikatsii razlichnymi dozami metilfosfonata], Vestnik Chelyabinskogo Gosudarstvennogo Pedagogicheskogo Universiteta, No. 2, (2011) pp. 346-353 http://www.cspu.ru/nauka/vestnik-chgpu/#archiv.
[22] L. Symochko, V. Patyka, V. Symochko, A. Kalinichenko, Soil microbial activity and functional diversity in primeval beech forests, Journal of Earth Science and Engineering, No. 5 (2015) pp. 363-371 https://doi.org/10.17265/2159-581X/2015.06.004.
[23] F. Hamor, Virgin Forests of Transcarpathia. Inventory and Management, Rakhiv, CBR, 2008.
[24] J.H. McDonald, Biological statistics, Baltimore, Sparky House Publishing, 2014, 299 p.
[25] A.R. Omayma, A. Zaid, A.H. Abdel-maksoud, Y.A. Elsenosy, I.A. Omnia, Biochemical study on the effect of cetyl trimethyl ammonium bromide surfactant coated spirulina zinc oxide nanocomposite as antimammary carcinogenesis in rats, Benha Veterinary Medical Journal, Vol. 29, No. 1 (2015) pp. 170-182. https://doi.org/10.21608/bvmj.2015.31815.
[26] M. Abdelftah, Nadia I. Zakhary, Salwa M. I. Morsy et al, Biochemical study on the effect of metallo-surfactant and its loaded nano-analogue as anticancer drug, Journal of American Science, 8(3) (2012) pp. 763-772, https://doi.org/10.7537/marsjas080312.103.
[27] F. Eivazi, N. Mullings, M.-L. Banks Effect of select surfactants on activities of soil enzymes involved in nutrient cycling, Communications in Soil Science and Plant Analysis, 49(6) (2018) pp. 1-9, https://doi.org/10.1080/00103624.2018.1427263.
[28] M.-L. Banks, A.C. Kennedy, R.J. Kremer, F. Eivazi Soil microbial community response to surfactants and herbicides in two soils, Applied Soil Ecology, 74 (2014) pp. 12-20, https://doi.org/10.1016/j.apsoil.2013.08.018.