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ORGANIC MATTER REMOVAL FROM SURFACE RIVER WATERS BY MEANS OF A BIOSORPTION SYSTEM AND THE EFFECT OF PHENOL ON ITS FUNCTIONING

The work deals with the application of a biosorption system with granular active carbon for the removal of pollutants from surface river waters. The system was tested under conditions of the appearance of a shock concentration of phenol in the water. It was found that during 3–6 days of operation of the system a stable microflora is formed on the activated carbon surface and the heterotrophs count on this surface is much higher than that in the imbuing water. The results show that the microbiological oxidation of pollutants takes place primarily on the surface of the solid phase. A satisfactory agreement of the results was obtained in calculation of the total rate coefficients of pollutants removal by employing a modified equation for biofiltration. A shock concentration of an agent inhibiting the microbiological processes (phenol) did not cause a lasting destabilization of the biosorption system.

1. INTRODUCTION

A number of new technological procedures for preparation of pure water [1]–[4] has been recently developed. Oxidation of water pollutants by means of various oxidizing agents and the adsorption of the resulting products is frequently employed. Active carbon as the adsorbent appears to be the most suitable material for removal of different micropollutants from water. For the economic reasons, active carbon has to be regenerated after its usage. Therefore, the development of new regeneration methods has promoted an increased application of granular active carbon for production of pure water from the increasingly polluted surface waters. Studies on the long-term (lasting several years) usage of granular active carbon for removal of the organic matter, bad odour, and flavour from water indicate the occurrence of certain bioregeneration processes.

The importance of microorganisms present in a biosorption system with granular active carbon has been pointed out by many authors [4]–[9]. It has been established that, under some favourable technological conditions, the adsorption of organic

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micropollutants and their microbiological oxidation take place simultaneously, which results in regeneration of the active carbon [10]. Thus, the two processes can be carried out in one technological system. In this way, it is possible to remove a wide range of organic micropollutants from water.

The objective of this work is to study the application of a biosorption system with granular active carbon for removal of pollutants from surface river waters. An especially important aspect is to examine the system operation under conditions of the appearance of a shock concentration of phenol in the influent.

2. EXPERIMENTAL

The biosorption system with granular active carbon is shown in fig. 1.

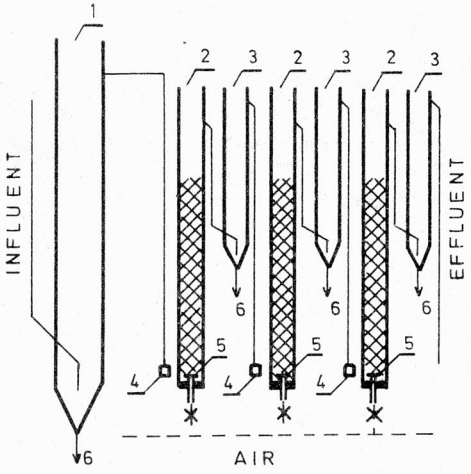

Fig. 1. Schematic diagram of the apparatus
1 – primary precipitator, *2* – columns with activated carbon, *3* – precipitators, *4* – pumps, *5* – sintered glass plates, *6* – taps for sludge removal

It consisted of one primary precipitator, 3 columns, and 3 precipitators. Each column contained 1300 g of granular activated carbon "Karbozak H". Air was introduced into columns through the sintered glass plates at their bottom. The river water was pumped up-flow.

Two series of experiments were carried out at the hydraulic load in the range of 0.20–2.11 $dm^3/dm^3 \cdot h$. The first series was completed during the time when adsorption was the prevailing process, whereas for the second series the process of microbiological oxidation of organic matter was predominant. After that, the possibility of appearance of phenol in the river water (at a hydraulic load of 1.17 $dm^3/dm^3 \cdot h$) was simulated. Phenol was added gradually to the influent to

a concentration limit of 5.73 mg/dm^3, which was achieved after 25 h. Afterwards, the biosorption system was operated as before the addition of phenol.

Concentrations of organic matter and phenol were determined by standard methods [11]. Standard microbiological analyses were employed to determine the heterotrophs count both in water and on carbon [11]. Counts of the phenol-oxidizing bacteria were determined on a modified agar-containing medium, proposed by ROLSTON and VELA [12].

The oxygen consumption by biologically activated carbon was determined by the manometric method. The measurements were carried out on a Warburg apparatus (model V 166, B. Braun Melsungen) at 20°C, using the 140 cm^3 bottles. About 2 g of carbon from the columns was added to each bottle together with 40 cm^3 of the river water, effluent, and model solution, respectively. The corresponding experiments with no carbon in the bottles (blank) were set up in parallel. The iodine number of the activated carbon was determined at the beginning and several times during the experiment.

3. RESULTS AND DISCUSSION

It has been found that the count of heterotrophic bacteria becomes fairly constant during the first 3–6 days of the set-up operation (fig. 2). An increase in bacteria count on the carbon is observed only at the increased water flow-rate. As seen from fig. 2, the bacteria count on carbon is always higher than in the imbuing water.

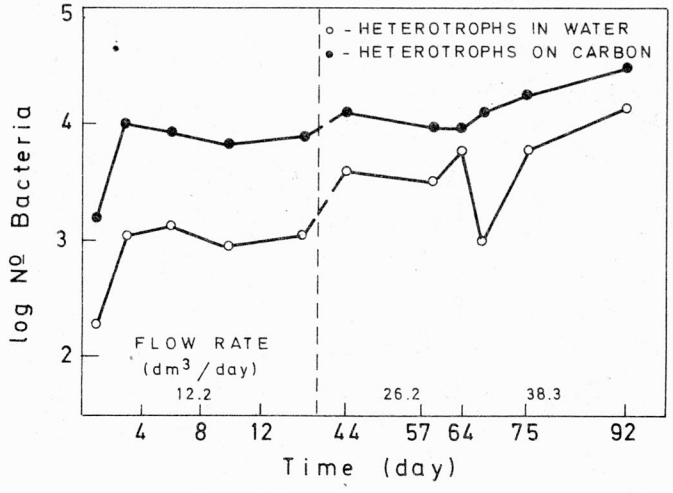

Fig. 2. Bacteria count on activated carbon vs. time

A comparison of bacteria counts for different compartments of the set-up at the highest hydraulic load (fig. 3) shows that activated carbon is always richer in bacteria colonies. Therefore, the carbon surface together with the organic matter adsorbed on it represents a suitable medium for survival and metabolic activity of bacteria. The natural ability of bacteria cells to stick on different materials (in this case, on the

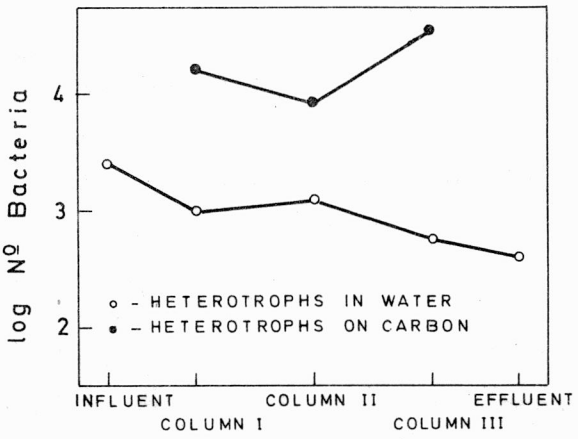

Fig. 3. Population of heterotrophic bacteria on activated carbon and in water at different stages of the set-up operation

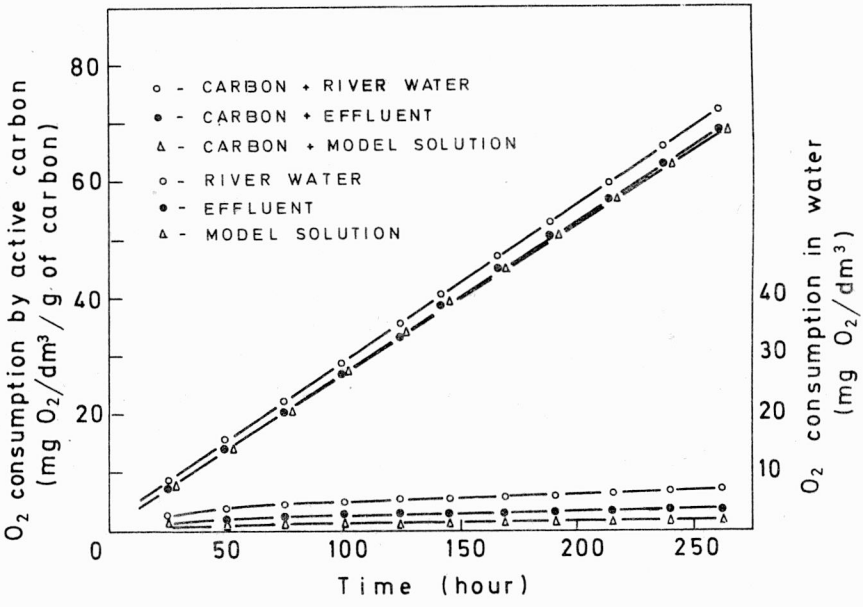

Fig. 4. Oxygen consumption vs. time

active carbon) is of great importance. Due to their metabolic activity, the bacteria colonized onto carbon are involved in regeneration of its surface. At the same time, a higher bacteria count on the activated carbon means their lower count in the effluent.

Activities of microorganisms on activated carbon were measured by the respirometric method. A typical dependence of the oxygen consumption on time for biologically activated carbon is presented in fig. 4. The oxygen consumption increased by several times after addition of activated carbon from the columns to the river water, effluent, and model solution, respectively. The close values of oxygen consumption in all three cases indicate that an increased oxygen consumption (if

Table 1

Oxygen consumption rate coefficients K. R – river water, E – effluent, M – model solution

Flow rate		Column I		Column II		Column III	
		K	K_1	K	K_1	K	K_1
dm^3/day		mg O_2/g·h	mg O_2/g·h	mg O_2/g·h	mg O_2/g·h	mg O_2/g·h	mg O_2/g·h
First series							
25.6	R	–	–	0.0054	0.0047	0.0053	0.0049
	E	0.0039	0.0039	0.0033	0.0035	0.0053	0.0053
26.2	R	0.0054	0.0050	0.0050	0.0047	0.0049	0.0045
	E	0.0049	0.0046	0.0045	0.0043	0.0045	0.0041
72.5	R	0.0108	0.0107	0.0103	0.0101	–	–
	E	0.0106	0.0105	0.0084	0.0084	0.0107	0.0107
114.5	R	0.0108	0.0105	0.0097	0.0094	0.0109	0.0107
	E	0.0111	0.0109	0.0096	0.0094	0.0100	0.0079
Second series							
	R	0.0087	0.0084	0.0093	0.0091	0.0103	0.0101
28.4	E	0.0094	0.0092	–	–	0.0099	0.0097
	M	0.0090	0.0090	0.0099	0.0099	0.0094	0.0094
	R	0.0095	0.0092	0.0108	0.0105	0.0115	0.0111
39.0	E	0.0097	0.0080	–	–	0.0104	0.0101
	M	0.0096	0.0096	0.0113	0.0112	0.0109	0.0109
	R	0.0094	0.0092	0.0107	0.0105	0.0102	0.0099
42.2	E	0.0089	0.0086	–	–	0.0106	0.0103
	M	0.0092	0.0092	0.0113	0.0113	0.0106	0.0106
	R	0.0098	0.0097	0.0125	0.0124	0.0115	0.0115
72.5	E	0.0094	0.0094	–	–	0.0107	0.0107
	M	0.0096	0.0095	0.0121	0.0121	–	–
	R	0.0107	0.0106	0.0125	0.0124	0.0119	0.0119
118.5	E	0.0103	0.0102	–	–	0.0117	0.0115
	M	0.0107	0.0105	0.0122	0.0120	0.0110	0.0108

compared to the blank) is a consequence of the presence of both organic matter and microorganisms on the activated carbon.

A statistical treatment of the results yielded a linear dependence of oxygen consumption by biologically activated carbon (in mg 0_2/g carbon) on time and a coefficient of determination (r^2) in the range of 0.96–0.99. The corresponding oxygen consumption rate coefficients are given in tab. 1.

Coefficient K is related to oxygen consumption in microbiological degradation of the organic matter, both adsorbed on the activated carbon and introduced with the river water and effluent, respectively. On the other hand, coefficient K_1 was calculated as the difference between the total oxygen consumption and the consumption due to the river water, effluent, and model solution, respectively, added to the probe (blank). In this way, it was possible to determine the oxygen consumption in degradation of the organic matter adsorbed. The close values of K and K_1 indicate that the largest part of the organic matter is oxidized at the activated carbon surface.

Coefficients K and K_1 depend on the organic load on biologically activated carbon. An example is given in fig. 5, where coefficient K, calculated for the model

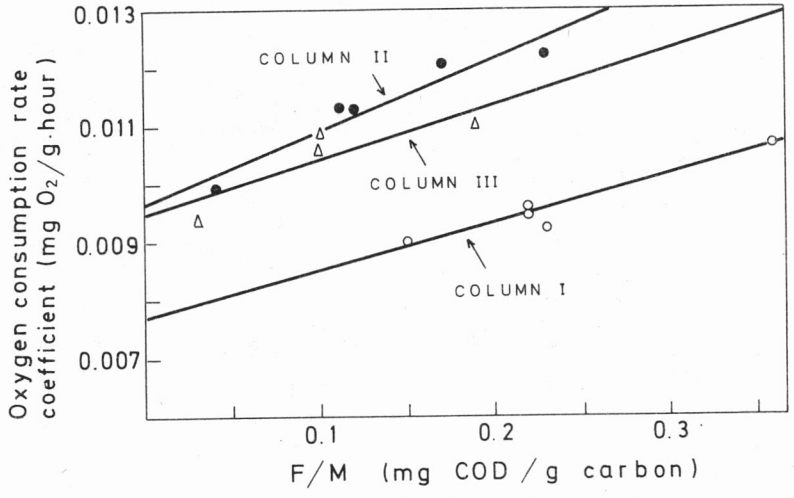

Fig. 5. Dependence of coefficient K on organic load of biologically activated carbon

solution and active carbon, is presented as a function of the organic load on the active carbon. It should be noticed that the experiment with the model solution gives the most reliable data on oxygen consumption for microbiological oxidation of the adsorbed organic matter.

The results of both microbiological studies and oxygen consumption indicate that a simultaneous presence of both the organic matter adsorbed and microor-

ganisms results in a microbiological activity on the activated carbon surface. Another support to this statement are the data concerning the adsorption degree of organic matter and the free surface degree of activated carbon, given in tab. 2. The adsorption degree is defined as the ratio of the amount of organic matter actually adsorbed and the adsorption capacity. On the other hand, the free surface degree is expressed as the ratio of iodine number for activated carbon at the particular stage of the experiment and the iodine number corresponding to its beginning.

Table 2

Characteristics of active carbon in the columns as a function of the water flow rate

Flow rate dm^3/day	Total volume passed m^3	Adsorption degree Column			Free surface degree Column		
		I	II	III	I	II	III
First series							
70.1	0.51	0.98	0.32	0.34	0.85	0.68	0.94
126.8	11.11	1.65	0.60	0.62	0.42	0.35	0.41
Second series							
27.5	14.62	3.36	0.83	0.78	0.77	0.85	0.81
38.6	15.14	3.50	0.85	0.82	0.63	0.79	0.77
70.1	15.91	3.63	0.90	0.84	0.55	0.74	0.62
115.1	17.96	4.12	0.93	0.89	0.64	0.72	0.53

It has been observed that the free surface degree of activated carbon shows a decrease with an increase in hydraulic load in the column. This decrease is not proportional to the organic matter introduced, but is always lower. However, the free surface degree was never below 41%, regardless of the hydraulic load in the column and adsorption degree of organic matter.

The adsorption capacity of each column was 10.192 g COD units, and it was calculated from the values given in tab. 3. All the above results indicate the possibility of calculation of the optimal hydraulic load in the biosorption system, at which the rate of microbiological oxidation of the organic matter adsorbed is equal to the rate of its accumulation on the carbon surface. In order to choose the optimal hydraulic retention time in the biosorption system it was necessary to calculate the total rate coefficient for pollutants removal. This was done by using a modified Eckenfelder equation for biofiltration:

$$\frac{S_e}{S_0} = e^{-k_s \frac{S_a \cdot Z \cdot A}{Q}}$$

Table 3

Adsorption characteristics of activated carbon "Karbozak H"

Parameters	Values
Adsorption capacity, mg COD/g	7.84
Iodine number, mg/g	503
Specific surface area, cm^2/cm^3	2.666×10^6

where S_0 is the COD for the influent (mg $0_2/dm^3$), S_e the COD for the effluent (mg $0_2/dm^3$), S_a the specific surface of activated carbon (cm^2/cm^3), Z the adsorber height (cm), A the adsorber cross-section area (cm^2), Q the flow rate (cm^3/day), k_s the coefficient of total rate of the organic matter removal (cm/s).

The values of k_s in both series of experiments were dtermined from the diagram presented in fig. 6.

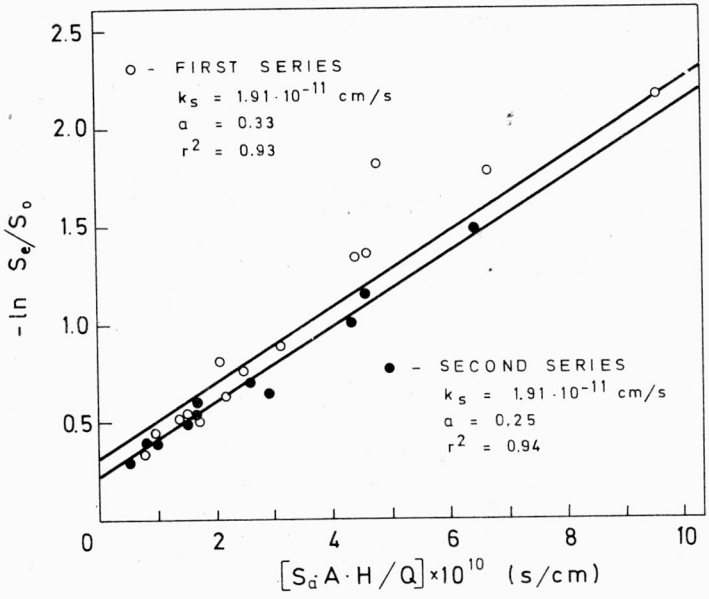

Fig. 6. Determination of coefficient k_s

In the first series, when the adsorption degree of organic matter was 0.60–1.65, the intercept is 0.33, whereas in the second series, corresponding to an adsorption degree of 0.89–4.12, the intercept is 0.25. Thus, the intercept shows a decrease with an increase in the adsorption degree but it does not reach its theoretical value of zero. It can be assumed that a positive value for the intercept is due to the fact that the

organic matter adsorbed is not oxidized completely, but partly remains on the carbon surface. On the basis of the free surface degree it can be concluded that there is a correlation between the free surface of carbon and the corresponding microbiological activity. It has been found that there is always some free surface, formed as a result of the activity of microorganisms. This enables adsorption of new amounts of organic matter. On the other hand, the organic matter accumulated on carbon serves as a good substrate for microorganisms. Thus, a continuous process of the organic matter adsorption and its microbiological degradation takes place on the activated carbon surface.

It can be concluded from the k_s values (fig. 6) that the system studied behaves in a similar manner as during the treatment of a mixture of oil refinery and municipal wastewaters in the ratio 30:70 [10].

The results of studies of the phenol effect on the biosorption system functioning are presented in tab. 4 and fig. 7.

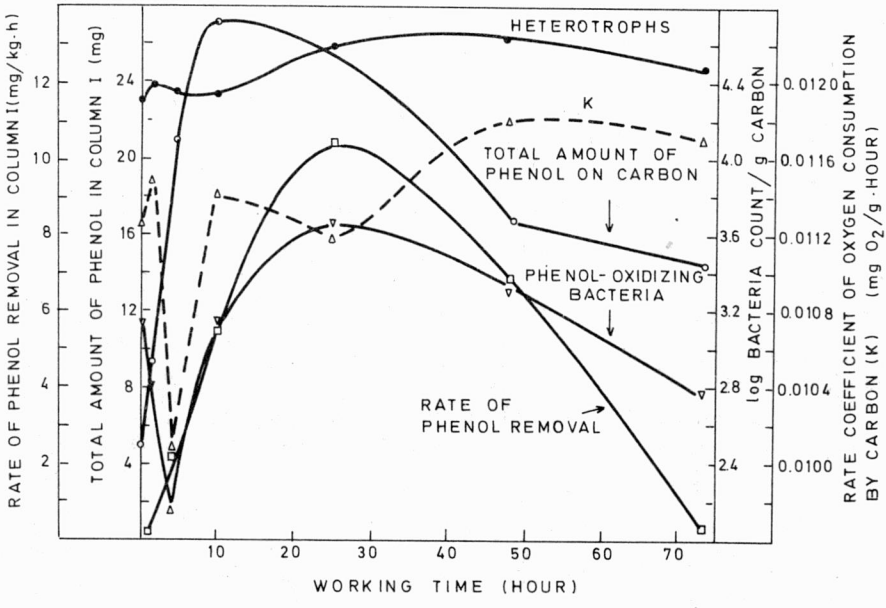

Fig. 7. Effect of phenol on microbiological activity of activated carbon in column I of the biosorption system

When phenol concentration in the influent reached 2.42 mg/dm^3 (1.5 h after its addition), the slow increases in the oxygen consumption in column I, the rate of phenol removal from columns I and II, and in the number of heterotrophic bacteria on carbon were observed. At this stage, no phenol was detected in the effluent by standard methods.

Table 4

Effect of phenol on functioning of the biosorption system

Sampling time h	Total volume passed dm^3	Concentration of phenol in water mg/dm^3				Concentration of phenol on carbon mg/kg Column		
		Influ-ent	Precipi-tator (after column I)	Percipi-tator (after column II)	Efflu-ent	I	II	III
0	0	0.010	0.001	0.001	0.001	0.34	0.25	0.20
1.5	4.4	2.42	0.015	0.014	0.001	0.72	0.25	0.20
4.5	13.3	2.58	0.27	0.068	0.017	1.63	0.31	0.22
10.0	29.6	3.51	0.091	0.044	0.015	2.10	0.45	0.25
25	71.0	5.73	0.007	0.005	0.001	1.98	0.44	0.27
48	141.5	0.010	0.005	0.001	0.001	1.30	0.31	0.13
72	214.0	0.004	0.006	0.001	0.002	1.11	0.28	0.14
144	439.5	0.004	0.002	0.002	0.001	0.78	0.22	0.13
192	587.5	0.001	0.001	0.001	0.001	0.56	0.21	0.13
360	1067.0	0.006	0.001	0.001	0.001	0.52	0.20	0.07
480	1405.5	0.003	0.001	0.001	0.001	0.42	0.20	0.04

After 4.5 h (phenol concentration in the influent was 2.50 mg/dm^3) the oxygen consumption, as well as the counts of the heterotroph and phenol-oxidizing bacteria showed a decrease. At the same time, phenol appeared in the effluent. Afterwards, when phenol concentration reached 3.51 mg/dm^3 (10 h from the moment of phenol addition), all three parameters, i.e., the oxygen consumption, the count of phenol-oxidizing bacteria, and the rate of phenol removal, showed an increase. This stage was characterized by the highest concentration of phenol on carbon in columns I and II. At the same time, phenol concentration in the effluent exhibited a decrease.

After 25 h, when phenol concentration in the influent reached its peak (5.73 mg/dm^3), the system attained certain stability: counts of the heterotroph and phenol-oxidizing bacteria increased in both the influent and column I, which caused an enhancement of the rate of phenol oxidation, and, consequently, a decrease in its concentration on carbon. Since the corresponding phenol concentration in the effluent was below the detection limit of standard methods, it can be concluded that the microorganisms involved were accommodated to use phenol for their nutrition.

Finally, when the influent was surface river water with no phenol added, the result was a decrease in the rate of phenol removal, and the phenol concentration on carbon, as well as in count of the phenol-oxidizing bacteria. At the same time, the count of heterotrophs as well as oxygen consumption showed an increase. The last two parameters were somewhat higher than at the beginning of the experiment. This was probably due to an enhanced concentration of organic matter (phenol to which the microorganisms were adapted, as well as the metabolic products of phenol oxidation) on the activated carbon surface.

The above results indicate that a shock concentration of an inhibitor of microbiological processes (phenol) did not cause a lasting destabilization of the biosorption system.

4. CONCLUSIONS

A stable microflora on the carbon surface is formed during first 3–6 days of operation of the biosorption system. The heterotrophic bacteria count is always higher for the carbon than for the imbuing water. The findings of oxygen consumption by biologically activated carbon indicate that the microbiological oxidation of organic pollutants takes place mainly on carbon surface.

The kinetics of processes in the biosorption system can be successfully described by a modified equation for biofiltration. Its use enables one to calculate the total rate coefficient of pollutants removal.

The biosorption system with activated carbon can be effectively employed for removal of phenol from surface river waters in possible accidental cases. A critical period (at a hydraulic load of 1.17 dm^3/dm^3. h and phenol concentration in the range 2.50–3.51 mg/dm^3) is 4.5–10 h from the moment phenol entered the biosorption system. After that the system attains stability, even at enhanced phenol concentrations in the influent.

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USUWANIE ZANIECZYSZCZEŃ ORGANICZNYCH Z WODY RZECZNEJ ZA POMOCĄ SYSTEMU BIOSORPCJI ORAZ WPŁYW FENOLU NA EFEKTYWNOŚĆ PROCESU

System biosorpcji z granulowanym węglem aktywnym zastosowano do usuwania zanieczyszczeń z wody rzecznej. System ten został zbadany w warunkach uderzeniowej dawki fenolu w wodzie. Stwierdzono, że po 3–6 dniach działania systemu na powierzchni węgla aktywnego formuje się stabilna mikroflora, a liczba heterotrofów jest znacznie większa na powierzchni węgla niż w wodzie. Badania wykazały, że mikrobiologiczne utlenianie zanieczyszczeń odbywa się głównie na powierzchni fazy stałej. Do obliczenia współczynników całkowitej szybkości usuwania zanieczyszczeń zastosowano zmodyfikowane równanie biofiltracji i uzyskano dobrą zgodność wyników. Uderzeniowa dawka czynnika hamującego mikrobiologiczny proces (fenolu) nie powodowała trwałej destabilizacji systemu biosorpcji.

УДАЛЕНИЕ ОРГАНИЧЕСКИХ ЗАГРЯЗНЕНИЙ ИЗ РЕЧНОЙ ВОДЫ ПРИ ПОМОЩИ СИСТЕМЫ БИОСОРБЦИИ, А ТАКЖЕ ВЛИЯНИЕ ФЕНОЛА НА ЭФФЕКТИВНОСТЬ ПРОЦЕССА

Система биосорбции с гранулированным активированным углем была применена для удаления загрязнений из речной воды. Эта система была исследована в условиях ударной дозы фенола в воде. Установили, что после 3–6 дней работы на поверхности активированного угля образуется стабильная микрофлора а число гетеротрофов значительно больше на поверхности угля, чем в воде. Исследования обнаружили, что микробиологическое окисление загрязнений происходит, главным образом, на поверхности постоянной фазы. Для вычисления коэффициентов полной быстроты удаления загрязнений применили модифицированное уравнение биофильтрации и получили хорошее согласование результатов. Ударная доза агента, тормозящего микробиологический процесс (фенола), не вызывала постоянной дестабилизации системы биосорбции.