Original Research

Effects of Granulated Active Carbon Bed Regeneration on Dissolved Organic Matter Removal from Surface Water

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Abstract

This paper presents the effects of thermal regeneration of granulated active carbon (GAC) inhabited by microorganisms on the efficiency of dissolved organic matter removal from surface water. The thermal regeneration of the bed ensured a change in the shares of the particular organic matter fractions. The regeneration of GAC resulted in an increase in refractive organic matter removal and in a considerable reduction in biodegradable dissolved organic carbon (BDOC) removal. However, the process of bringing the deposit back to biological activity was found to be long (about four months) and did not ensure the pre-regeneration efficiency of biodegradable dissolved organic carbon removal.

Keywords: biodegradable dissolved organic carbon, refractive matter, thermal regeneration

Introduction

The organic matter dissolved in the water being purified needs to be removed in order to prevent not only the formation of disinfection byproducts, but also the secondary pollution of the water in the distribution system. If the required reduction in dissolved organic matter content in the water fed into the water supply system is to be achieved, additional processes effectively removing the dissolved organic substances whose molecular mass is smaller than that of the organic substances removed by the conventional unit treatment processes need to be included in the surface water treatment system [1, 2]. Typically, filtration through a biologically aerated filter (BAF) made of granulated/grained active carbon, preceded by ozonation ensuring the transformation of non-biodegradable organic matter to biodegradable forms [3, 4] constituting nutrients for the heterotrophic organisms inhabiting BAF is employed for this purpose [5, 6]. In an adsorptive BAF the adsorption of the biodegradable and refractive dissolved organic matter and the biochemical oxidation of the biodegradable dissolved organic carbon (BDOC) adsorbed on the active carbon and present in the flowing water take place simultaneously [7-9]. The considered filtration process also ensures the removal of some biotoxins, e.g. microcystines [10], and to a small degree trihalomethanes [11].

Since the efficiency of filtering through a BAF bed (and so the efficiency of organic matter removal from water) is the sum of the physical adsorption of the organic matter and its elimination as a result of processes in which the microflora inhabiting the bed participate, it depends on many factors, such as the hydraulic loading and height of the adsorptive bed, the properties of the active carbon (its adsorbing capacity, grain size, specific surface area, pore structure and size, surface chemical properties), the biological activity of the bed (the number of microorganisms and their enzymatic equipment conditioning the biochemical decomposition of BDOC), and the concentration, molecular mass, size, chemical composition, form of occurrence in water and, most of all,

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adsorbability and biodegradability of the organic matter [12-14]. The microorganisms inhabiting the carbon bed by biodegrading and assimilating the BDOC deposited in the pore structure of the adsorbent, on the one hand, cause its bioregeneration and on the other hand, by forming a biological film on the surface of the active carbon grains they limit the availability of the organic adsorbates to the adsorption centres and so reduce the efficiency of physical adsorption [13-15].

The biological oxidation of BDOC is accompanied by the consumption of dissolved oxygen and an increase in the concentration of hydrogen ions in the water after filtration [14, 15]. Despite the bioregeneration of the adsorbent, the bed's adsorptive capacity decreases with its operation time and the rate of its wear increases with the content of organic and inorganic adsorbates in the water being purified [16] and with the percentage of dissolved nonbiodegradable organic carbon (NBDOC) in the dissolved organic carbon (DOC) [15].

The thermal regeneration of the active carbon to some degree restores the adsorptive capacity of the bed, but by destroying the microflora it leads to the total loss of its biological activity. As a result, in the initial period after the regeneration of the bed the latter operates in the adsorption regime. It was also found that this method of regenerating granular activated carbon (GAC) reduced the micropore volume over twofold while increasing the mesopore volume. It was also found that for the first 168 days (24 hour periods) after regeneration the regenerated activated carbon ensured greater (than fresh activated carbon) efficiency of the removal of the total organic carbon (TOC), whereas the opposite dependence was observed in the further period of its service [17]. The time needed to bring the regenerated adsorbent to biological activity depends on the conditions prevailing in the system. If the water being purified is characterized by a low temperature, a low concentration of organic and inorganic nutrients and dissolved oxygen, this time is long (amounting to several months) [14]. A reduction in the biological activity of BAF beds results in them being washed [18, 19], but the time in which they regain this activity after washing is relatively short [4].

The aim of the present research was to determine the effect of the thermal regeneration of the adsorptive bed on the removal of dissolved biodegradable and refractive organic matter from surface water.

Materials and Methods

The studies were conducted in a surface water purification plant with the technological system: volume coagulation, sedimentation, high-rate filtration through sand beds, ozonation, filtration through biologically active adsorption beds (BAF), alkalizing (NaOH), and disinfection (Cl_2+ClO_2).

After ozonation the water was filtered through 12 granulated active carbon (GAC) beds, each having a surface area of 75.4 m^2. Each layer of granulated active carbon (WG Gryfskand) was 1.5 m high. The characteristics of the fresh GAC are presented in Table 1.

2 weeks of sampling mode has been applied. Samples of water before and after filtration through one of the adsorption beds, whichs in the test period (between the taking of water samples Nos. 13 and 14) after 30 months of operation was subjected to thermal regeneration, were investigated. In this way the effect of the regeneration of the bed on its biological activity and effectiveness in removing dissolved organic matter and its fractions from the water being purified was assessed. The water samples would be taken once a month while the same time of flow of water through the filtration bed was maintained. Due to the variable output (1750÷3000 m^3/h) of the water purification system in the test period, the filtration rate ranged from 2.1 m/h to 3.7 m/h and the water/filtration bed contact time was in the range 27.1÷46.4 min.

The analysis of the quality of the water samples covered the following organic pollution indices: absorbance in UV (UV_{254}), oxidation capacity (Oxid.), TOC, DOC, and BDOC. The dissolved nonbiodegradable organic carbon (NBDOC) content was calculated as a difference between DOC and BDOC. In addition, the pH, temperature, dissolved oxygen concentration, and free carbon dioxide content in the water samples were determined.

Also, the inorganic nutrients, i.e. inorganic nitrogen ($N_{Inorg}= NH_4^+ + NO_3^- + NO_2^-$) and phosphate ions, content

Table 1. Parameters of fresh active carbon WG Gryfskand.

No.	Parameter	Unit	Value
1.	Bulk density	g/dm^3	470
2.	Volatile matter content	%	1.50
3.	Ash content	%	11.6
4.	Specific surface area	m^2/g	968
5.	Iodine number	mg/g	1014
6.	CTC – CCI_4 adsorption	%	62.3
7.	< 0.5 mm subfraction content	%	0.0
8.	Mechanical strength	%	97.3

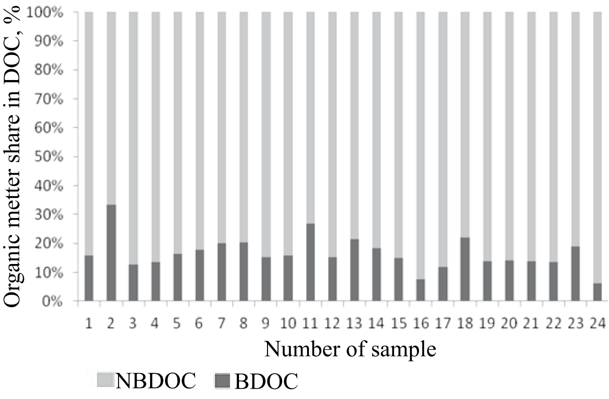

Fig. 1. Percentage of refractive and biodegradable DOC fractions in water flowing onto adsorption bed.

Table 2. Ranges of water quality indices before and after filtration through adsorption bed.

		Before filtration	After filtration	
Index	Unit	Inflow	I	II
TOC	gC/m^3	1.45÷6.15	1.01÷3.58	0.62÷3.22
DOC	gC/m^3	1.32÷5.58	0.82÷3.47	0.59÷3.00
BDOC	gC/m^3	0.260÷0.780	0.078÷0.410	0.088÷0.533
NBDOC	gC/m^3	0.910÷4.820	0.73÷3.06	0.39÷2.47
UV_{254}	m^{-1}	2.25÷9.68	1.34÷6.46	0.92÷2.89
Oxid.	gO_2/m^3	1.60÷7.44	1.30÷4.77	0.75÷3.88
N_{Inorg}	gN/m^3	0.47÷3.89	NT	NT
NH_4^+	gN/m^3	0.01÷0.15	NT	NT
NO_3^-	gN/m^3	0.45÷3.75	NT	NT
NO_2^-	gN/m^3	0.000÷0.003	NT	NT
PO_4^{-3}	gPO_4^{-3}/m^3	0.01÷0.05	NT	NT
pH		6.7÷7.7	7.00÷7.68	6.64÷7.56
Temperature	ºC	0.6÷21.8	0.5÷21.8	4.2÷21.6
O_2	gO_2/m^3	6.76÷14.84	8.64÷13.27	6.16÷14.27
CO_{2w}	gCO_2/m^3	5.00÷14.34	6.10÷11.28	6.70÷15.78
Total number of microorganisms at 22ºC	CFU/cm^3	79÷5700	500-15096	280-14555

NT – not tested; I – bed before regeneration; II – bed after regeneration

in the water flowing onto the filtration bed was determined.

The values of all the indices were determined in accordance with the Polish Standards and the analysis of BDOC was carried out according to the modified Van der Kooij method [6].

The data on the total number of bacteria at 22ºC after 72 h in the water before and after filtration, determined in the Microbiology Laboratory of MPWiK (Municipal Water and Sewerage Company) in Wrocław, were used to interpret the results of the tests.

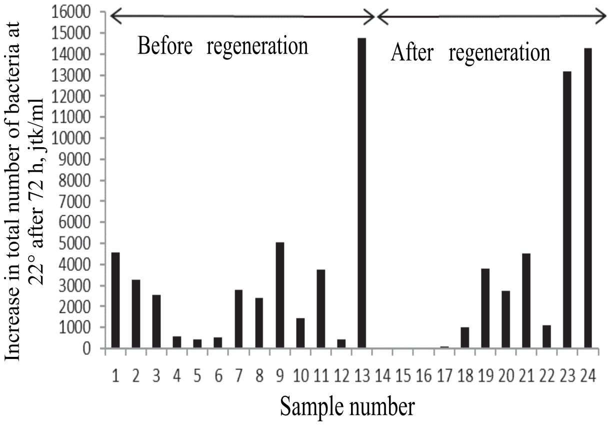

Fig. 2. Changes in total number of bacteria in filtrate samples.

Results and Discussion

In the whole test period the water flowing onto the adsorption bed was characterized by high variability in the investigated quality indices (Table 2).

Dissolved compounds amounting to 79.6-100.0% TOC predominated in the water before filtration. Despite ozonation the share of the biodegradable fraction in DOC was small (close to the one found in natural surface waters [20]), amounting to 6.1÷33.2% DOC (Fig. 1).

In all the samples the NBDOC content was directly proportional to adsorption in UV $(UV_{254})_0$, as illustrated by the following empirical equation ($R = 0.88$, $n = 24$, $p>99.0\%$):

$$[NBDOC]_0=0.300*(UV_{254})_0+0.989 \qquad (1)$$

Besides the organic nutrients, dissolved oxygen (whose concentration was higher than 10 gO_2/m^3 in 23 out of the 24 samples) and inorganic nutrients (inorganic nitrogen and phosphate ions) were found to be present in the water subjected to filtration. Nitrate ions, whose concentration was from 3.8 to 144.0 times higher than the ammonium ions content, predominated among the inorganic forms of nitrogen. Nitrite ions were found to be present in only two water samples, but in minute quantities (Table 2). The concentration of phosphate ions in all the water samples was low (Table 2), but sufficient to sustain the development (at different rates) of microorganisms

Table 3. Ranges of changes in water quality indices during filtration through adsorption bed.

Index	Unit	Change in index value	
		Before regeneration	After regeneration
TOC	gC/m^3	0.27÷0.74	1.06÷3.01
DOC	gC/m^3	0.21÷0.66	0.98÷2.58
BDOC	gC/m^3	0.156÷0.542	0.065÷0.315
NBDOC	gC/m^3	0.010÷0.270	0.910÷2.410
UV_{254}	m^{-1}	0.34÷1.54	1.66÷6.79
Oxid.	gO_2/m^3	0.21÷1.58	1.54÷3.56
O_2	gO_2/m^3	0.93÷2.33	0.19÷0.74
pH		0.0÷0.2	0.0
CO_{2w}	gCO_2/m^3	0.54÷3.35	0.08÷3.22

in the adsorption bed. An additional source of phosphate ions in a filtration bed inhabited by microorganisms is the enzymatic transformation of the organic phosphorous combinations to its biologically assimilable form [21]. This was confirmed by the increase in the biomass of developed biofilm despite the phosphate ions content in the purified water below 0.0062 gPO_4^{-3}/m^3 [22].

The bacterial growth in the bed made of granulated active carbon (GAC) and the subsequent washing out of the bacteria from the deposit are evidenced by the increase in the total number of bacteria in the filtrate samples, varying over the test period (Fig. 2).

The maximum increase in the total number of bacteria, amounting to 14,766 $CFU/cm^3$was found in the last filtrate sample taken before the regeneration of the bed. Whereas in the water samples taken in the first four months after bed regeneration this increase was very small (2÷80 CFU/cm^3), but it would increase with the time of operation of the filtration bed (Fig. 2). An analysis of the test results did not show any dependence between the hydraulic loading

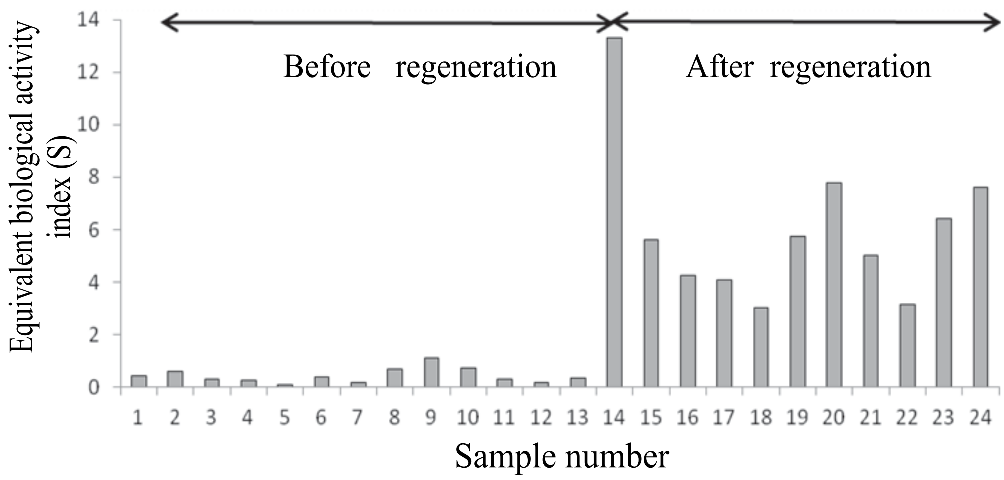

Fig. 3. Effect GAC regeneration on equivalent bed biological activity index values.

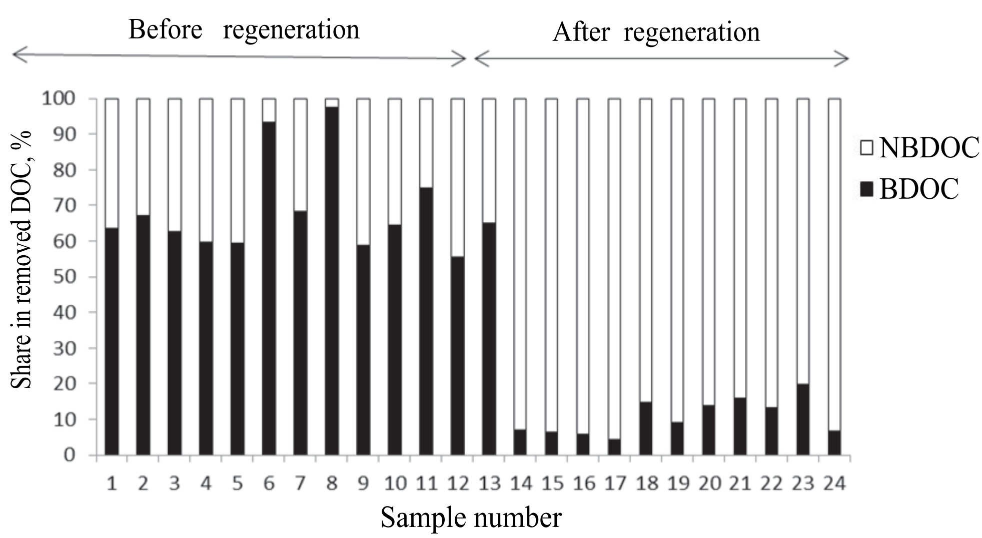

Fig. 4. Share of organic matter fraction in removed DOC.

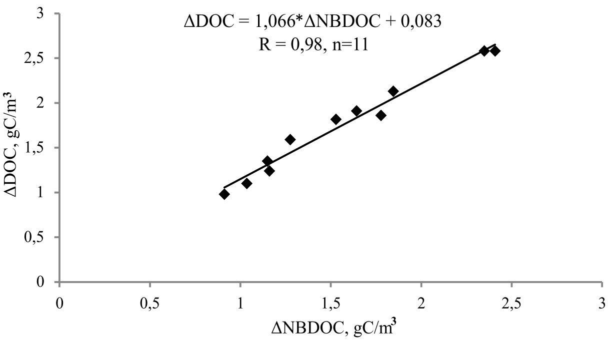

Fig. 5. Dependence between decline in NBDOC and DOC for filtration through the regenerated bed.

of the bed and the intensity with which microorganisms were being washed out of the latter.

The kind and amount of removed organic matter varied in the test period, depending on the biological activity and the degree of depletion of the adsorption capacity of the filtration bed (Table 3).

In the test period preceding regeneration the adsorption bed had been biologically active, as evidenced by the values of the equivalent bed biological activity index:

$$S = \Delta O_{xid}/\Delta O_2 \tag{2}$$

...where:

ΔO_{xid} – difference between oxidability before and after filtration difference between oxidability before and after filtration

ΔO_2 – difference between dissolved oxygen before and after filtration

...which in the case of 12 out of the 13 samples were much below 1.0 (Fig. 3).

In the bed operation period prior to regeneration the adsorption and biological oxidation of BDOC had been mainly responsible for the reduction in DOC content in water (Fig. 4). This had been accompanied by greater (than after bed regeneration) consumption of dissolved oxygen,

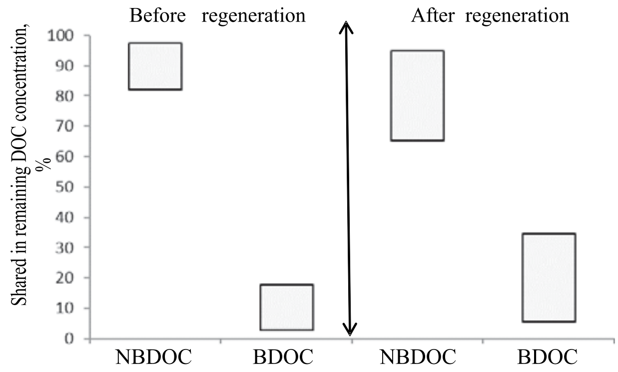

Fig. 7. BDOC and NBDOC shares in remaining DOC concentration.

filtrate acidification, and an increase in free carbon dioxide concentration (Table 3), generally rising with decreasing BDOC content (eq.3) ($R = 0.88$; $n = 13$; $p>90.0\%$)

$$\Delta CO_{2F} = 5.5766*\Delta BDOC;\ R = 0.2261 \tag{3}$$

This regularity, i.e. the depletion of biological activity, was not observed in the test period after regeneration of the filtration bed.

Another result of adsorption (mainly the biological mineralization of BDOC) was a nearly double reduction in the average share of BDOC in DOC (from 18.4% to 8.4%) in the water filtrated through BAF (Figs. 1 and 4). The dominant role of biological processes in the removal of DOC in the first stage of operation of the bed is reflected in the larger amount (gC/m^3) of removed BDOC than NBDOC ($\Delta BDOC/\Delta NBDOC = 1.3\div37.0$), despite the several times higher (2.0÷6.8) content of dissolved refractive organic matter than the biodegradable one in the water samples before filtration. A reverse regularity was found in the stage after the thermal regeneration of the bed, which destroyed the microorganisms inhabiting the surface of the active carbon granules and increased their adsorption capacity. This resulted in a marked increase in

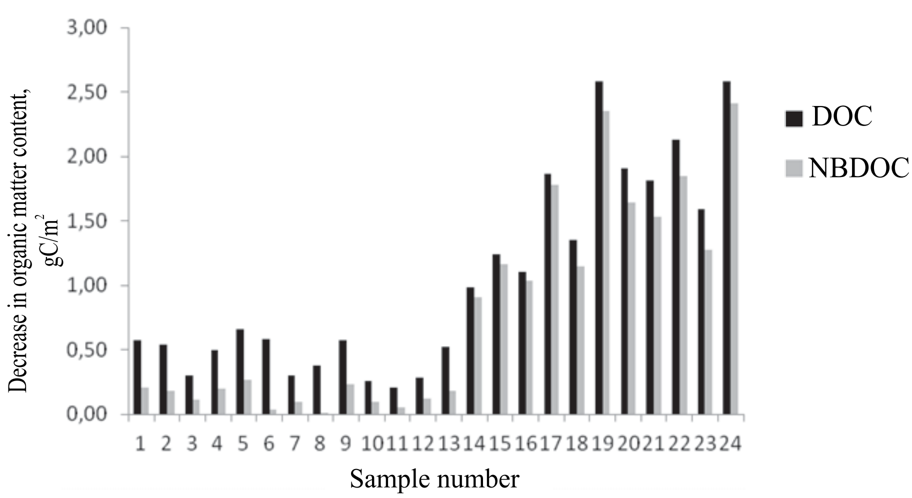

Fig. 6. Comparison of amounts of removed DOC and its refractive fraction.

the adsorbed NBDOC share in the removed DOC (Fig. 4). The much lower efficiency of the biodegradation of BDOC was evidenced by the index S values higher than 1.0, ranging from 3.2 to 13.3 (Fig. 3), no decrease in the pH, and the small decline in dissolved oxygen concentration (ΔO_2 = 0.19÷0.74 gO_2/m^3) in the filtrate samples (Table 3). In the first four months of operation of the regenerated bed the BDOC share in the amount of removed dissolved organic matter was minimal and would slightly increase with the time of bringing GAC to biological activity (Fig. 4). The probable cause of this regularity was the low phosphate ions concentration in the water flowing onto the filtration bed.

The dominant role of NBDOC adsorption in the reduction in DOC content in the filtration through the regenerated adsorption bed is evidenced by the dependence shown in Fig. 5 and by the ΔNBDOC/ΔBDOC values ranging from 4.06 to 21.45.

Because of the much higher NBDOC content than the BDOC content ($[NBDOC_0]/[BDOC_0]$ = 3.53-15.42) in the water flowing onto the regenerated filtration bed (tab. 2) and the efficient adsorption of NBDOC (η = 32.5÷82.1%), the average decrease in the content of dissolved organic carbon and its refractive fraction in the period preceding GAC regeneration had been respectively fourfold and nearly twelvefold lower than after regeneration (Fig. 6).

Regardless of the biological activity of the adsorption bed, in the whole test period the elimination of DOC was co-determined by the content of the organic matter being removed and the degree of its dissociation. The decline in DOC content (gC/m^3) increased with the concentration of DOC_0 and hydrogen ions in the water being purified, i.e. with the decreasing degree of dissociation of the dissolved organic matter. This is expressed by the following equations (respectively: $n = 24$, $R = 0.62$, $p > 95.0\%$ and $n = 24$, $R = 0.58$, $p>90\%$):

$$\Delta DOC = 0.462*[DOC_0] - 0.378 \quad (4)$$

$$\Delta DOC = -1.597* pH_0 + 12.69 \quad (5)$$

The varying biological activity of the adsorption bed in the course of its operation before and after regeneration and the effectiveness of adsorption and biological oxidation in the removal of dissolved organic matter from water resulted in significant differences in the shares of the biodegradable fraction and the refractive fraction in the remaining DOC content in the filtrate samples (Fig. 7).

Conclusions

The kind and amount of dissolved organic matter removed from water depended on the operating regime of the adsorption bed. Filtration through the biologically active adsorption bed (before regeneration) resulted in the elimination of, first of all, biodegradable dissolved organic matter and in a much smaller removal of the refractive fraction of DOC. The reverse regularity was found for filtration through the regenerated adsorption bed. The thermal regeneration of the granulated active carbon resulted in a severalfold (3.99 on average) increase in removed dissolved organic matter, which was mainly determined by the adsorption of DOC refractive components. The time of bringing the regenerated adsorption bed to biological activity was long – it was only after four months of operation of the bed that increased elimination of BDOC from water, amounting to merely 6.7÷19.8% of the reduction in DOC content in the filtrate samples, was observed.

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