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PHYSICAL CHEMSTRY OF WATER TREATMENT PROCESSES

Chemical Regeneration of Biological Activated Carbon in Removing Nitrophenol

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Abstract—Investigated are changes of the porous structure of biological activated carbon in filtration and after chemical regeneration. It is shown that 71–84 vol % of recovered pores were blocked by the products of microbe vital activity. Alkaline treatment of the bed of biological activated carbon (during several days) makes it possible to prolong efficient nitrophenols removal from water by 10–11 months.

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INTRODUCTION

Systems of water treatment based on fixed beds of biological activated carbon (BAC) is efficient with correct selection of the rate of organic load and sizes of the bed of adsorption material. The efficiency of the system is achieved in the case if a decrease of the value of adsorption over time is completely compensated by the growth of the biodestruction contribution. Prolongation of the of the BAC resource is ensured at the sake of intensive biodestruction of organic matter leading to the appearance in the bed of the medium simultaneously with filtration of bioregeneration phenomena. Economic advantages of using activated carbon (AC) in the biofiltration process manifest themselves after excess of the adsorption resource of the bed. Therefore the maximum prolongation of the term of using the sorbent is extremely important for economic attraction of the method [1–4].

Experimental data show that for BAC with an "old" biofilm gradual decrease of its efficiency takes place, which is characterized by the following negative tendencies [3, 5–8]:

– a decrease of the active part of the biofilm and an increase of the density of the matrix (due to kinetic difficulties when transporting nutrients and oxygen; accumulation of poisons and inhibitors);

– a decrease of the accessible porous space due to adsorption of target organic substances and products of vital activity of microorganisms blocking pores.

Self-regeneration of BAC is of random nature and is poorly controlled. It appears as a result of the change of intensity of abiotic and biotic factors, which cause the growth of metabolic activity of microorganisms on the surface of carbon leading to a reverse (desorption) gradient of concentration of organic substances from the kernel of the sorbent to the external solution. The efficiency of BAC may be stabilized by conducting special operations helping to intensify desorption phenomena and resulting in partial restoration of the porous space of carbon. Directional treatment with a certain periodicity is necessary to maintain the active state of the biofilm and set filter capacity. Thus aeration of the BAC bed with the addition of mineral substances in many cases makes it possible to speed up the reconstruction of biocenosis in that measure which is necessary for achieving the required degree of removing phenol derivatives [9].

Adsorption of nitrohenols by activated carbon depends on the pH of the aqueous solution. An increase of alkalinity of the medium by several points creates prerequisites for ionization of adsorbed molecules and diminished values of equilibrium adsorption. Changes of biotic conditions increasing the pH in the system will be conducive to desorption of nitrophenols and regeneration of AC pores from proteins and other biological products [2].

On the other hand, high values of the pH negatively affect the biofilm: they destroy living cells of microorgnisms i.e., actually they are aimed at liquidation of biological activity in the medium bed. As a matter of fact, alkaline treatment is one of the methods of fighting undesirable microbial infection of filtration systems. However, using the preliminary procedure of "washing out" the biofilm with AC we may save and subsequently

regenerate part of adapted bed biomass both for repeated conversion of restored sorbent into the biologically activated state and for utilization regeneration wastewaters in separate biological reactors.

Thus, the objective of the present paper is the study of the influence of chemical regeneration on the degree of removing nitrophenol by biological activated carbon for which purpose it was necessary to determine an increase of the resource of the stationary BAC bed after chemical treatment and also the impact of regeneration procedures on an increase of porous space of AC as a result of desorption of the target product and products of metabolism of microbes.

EXPERIMENT

Before the start of the experiment BAC has been in operation for three years out of which 27 months—directly in the mode of filtration of aqueous solutions of 2-nitrophenols (NP). The experiment consisted of three stages including stages of chemical regeneration—adsorption under dynamic conditions. The efficient operation of a biosorption filter corresponded to the concentration of filtrate not exceeding the maximum value of the direct spectrophotometric determination of NP (0.2 mg/dm^3). The degree of chemical regeneration was assessed by the additional resource of BAC, by the additional time of operation or the volume of filtrate obtained before the appearance of the breakthrough of NP. The change of the parameters of the structural-sorption space of AC pores was controlled before and after chemical treatment with the isotherm of nitrogen adsorption [7].

The filling of AC pores by the target substance was assessed on the basis on dynamic concentration curves of NP and the account of the contribution of biodestruction of the latter. The contribution of destruction to the removal of NP in the course of biofiltration after chemical regeneration I was determined based on concentration of excessive nitrates in filtrate, whereas for chemical regeneration II and III—from the data of efficiency of the process conducted in parallel, the process of biofiltration through the bed of inert medium (sand) with adapted biomass.

Biofiltration of NP was done on a laboratory unit (biosorber) [9] representing a glass column of 2.1 cm in diameter, filled by 113 cm^3 of activated carbon KAU modified by iron oxides [7]. The fraction of the medium was 0.5–2.0 mm. The volume of the AC volume of the bed decreased as the process goes on due to the necessity of using samples of the medium for other research. The decrease of the mass and volume of the bed was taken into account when calculating the parameters of the process. The average rate of filtration was 0.32 m/h, the NP concentration in the initial model solution—$7.5 \pm 3.$ mg/dm^3.

The efficiency of the BAC operation was controlled determining in the input and output solutions the NP concentration, indices of optical density and COD [9].

It is known [10] that an excess of nitrate–nitrites is a result of destruction of nitroderivatives of synthetic aromatic compounds. The concentration of nitrates and nitrites at the input and output from the AC bed was determined by means of special sets of portion reagents according to the technique of the HACH company [11] on a photocolorimeter HACH DR/890.

Chemical regeneration of BAC included the following operations: wash-out of the biofilm, chemical treatment by an alkaline solution, neutralization and repeated biological immobilization of the bed.

The wash-out of the biofilm was done by a 0.8% solution of sodium chloride. Preliminary water from the column was drained and the column was filled from bottom to top with two volumes of physiological solution. Using a microcompressor air (10 dm^3/min) for 0.5 h was passed through a bed of AC then tap water (2–3 min) with a 30–50% expansion of the bed. Wash waters were collected into a reactor for preservation of biomass (a container with aeration and nutrients).

Chemical treatment by an alkaline solution was done in the following way: the solution of NaOH (1M, 2 volumes of the bed heated to 55–60°C) was fed to the column by a peristaltic pump and was held for 4 h. During next 4 h the 0.002 M alkaline solution (45–50°C) was passed through AC at the expenditure 2 volumes per 1 h. The procedure was completed with a wash-out of the bed with tap water (15 min, 40–45°C) at the rate of 8 volumes per 1 h. Wastewaters obtained in chemical treatment were gathered portion by portion.

For neutralization of AC through its bed acidified tap water was circulated up to the pH of filtrate 6.5–8. The stage time—2 h. The volume of neutralization waters—up to 3 volumes of the bed. The total volume of wastewaters after chemical treatment by the alkaline solution and neutralization constituted about 15 volumes of the bed.

Repeated biological immobilization of AC bed was conducted in the following way: suspended biomass (from the reactor preservation of biomass) by the peristaltic pump was made to circulate through the AC bed, at first from bottom to top (2.5 h) and then from top to bottom (0.5 h) at the consumption 2–4 volume per 1 h.

The operation was completed by washing carbon with tap water from top to bottom for 0.15 h until the clarification of wasewaters. Wastewaters (3–5 volumes of the AC bed) was channeled to the bioreactor.

The total volume of wastewaters after chemical regeneration constituted 24–26 volumes of the bed. The total time of operations for the treatment of AC (without the account of the time for regeneration of washed–out biomass)—14–15 h. Actual residence of the bed outside filtration with the account of downtimes constituted from one to three weeks. The described technique provided basis for chemical regenerations I and II.

As a result of a shortened time and simplification of the stages of chemical regenerations III and IV were carried out expeditiously—in all for 4 hours. Soaking of the bed in the solution of alkaline lasted 1 h. The volume of the 1M of NaOH solution constituted 2.4 volumes of the medium, the solution temperature before entering the column—40°C. Washing off carbon was conducted only in tap water (3 volumes of the bed) for half an hour. The ratio of the total volume of wastewaters after the chemical treatment to the volume of regenerated AC constituted 8 : 1. Neutralization was done by two volumes of acidified tap water (0.25–0.33 h). A repeated biological immobilization of the bed was conducted by biomass preliminary regenerated and adapted to increased concentrations of NP (from the bioreactor of preservation). All operation together with the bed wash-off from top to bottom constituted 1 h. The total volume of wastewaters after chemical regeneration (III, IV)—13–14 volumes of the bed.

The control of regeneration waters was done by operations, in this case the volume of waters and concentration of NP were determined. Additionally in waters after the wash-off the biofilm and repeated biological immobilization of the bed (cultered liquid) turbidity and suspended matter were analyzed.

RESULTS AND DISCUSION

The main data of the investigation of the efficiency of BAC before and after chemical regeneration are given in Table 1. As may be seen the efficiency of BAC at the third year of operation ($\tau_{tot} = 915$ day) constitute 100%. Actually complete removal of NP during two last years was maintained in great measure at the sake of periodic aeration treatments including addition of nutrients. The refusal of systematic aeration effects on BAC, contributing to increased biomass activity and restoration of adsorbent porosity, subsequently led to a gradual decline of the quality of water purification from NP ($\tau_{tot} = 1203$ days). Chemical treatment of AC by the solution of alkaline has allowed to raise the degree of NP removal in the first filtrated bed and stabilize the degree of purification in the column on the whole: after regeneration I and II—during 10–11 months and after regeneration III and IV—for 4 months (see Table 1).

Table 1. Results of the dynamics of biofiltration of 2-nitrophenol solution through fixed BAC bed subjected to chemical regeneration

Index	18.08. 2011	22.05. 2012	25.05. 2012*	03.04. 2013	24.04. 2013*	26.03. 2014	17.06. 2014	25.06. 2014*	25.10. 2014	15.12. 2014	21.02. 2015*	26.06. 2015
τ_{tot}, day	915	1203	1206*	1520	1541*	1876	1957	1965*	2072	2122	2190*	2315
τ_{act}, day	550	824	825	1134	1135	1473	1547	1555	1662	1712	1747	1868
V_f, dm^3	1343	1811	1850	2492	2493	2810	2913	2926	3093	3192	3231	3360
C_1/C_0	0.54	0.71	0.01	0.67	0.06	0.47	–	–	–	–	–	–
COD_1/COD_0	0.82	0.83	0.75	0.88	0.98	0.82	–	–	–	–	–	–
V_2, c.v.	12686	20970	21570	33010	33047	44787	52027	52480	57650	63187	64747	69923
C_2/C_0	0	0.63	0	0	0	0.04	0.63	0	0.06	0.5	0	0.2
COD_2/COD_0	0.5	0.44	0.42	0.59	0.23	0.53	0.75	0.45	0.65	0.70	0.47	0.68

* Data after chemical regeneration. τ_{tot}—total time of the experiment; τ_{act}—actual time of biofiltration of the model solution of NP; V_f and V_2—volumes of filtrate respectively in actual and conventional (bed volume) units.

The data on the change of the main parameters of the BAC porous structure depending on the duration of filtration and the presence of chemical treatment by the alkaline solution are given in Table 2. Before the moment of chemical regeneration I the main parameters reflecting the vacant volume of pores and the area of the surface with the growth of the duration of biofiltration were steadily decreasing. Alkaline treatments (see Table 2) substantially increased porosity and accordingly restored AC adsorption properties. However, from regeneration to regeneration the values of the porosity parameters achieved are inferior to the previous values. The data of Table 2 point to a high efficiency of regeneration I as a result of which an increment of AC porosity

exceeded the value of losses for the previous year of filtration. Regeneration II allowed to restore up to 80–90% of micropores and the surface of mesopores spent over the time of the effective removal of NP.

Table 2. Change of the structural-sorption characteristics of BAC in the course of chemical treatment by the alkaline solution

Parameters of porous structure	Fresh AC (V_f = 0 dm^3)	One year before regeneration I (V_f = 1152 dm^3)	Regeneration I		Δ	Δ, %	Regeneration II		Δ	Δ, %	Regeneration III		Δ	Δ, %
			before	after			before	after			before	after		
S_{BET}, m^2/g	991	404	204	547	343	172	186	469	283	78	120	327	207	59
S_{me}, m^2/g	119	105	89	106	17	106	68	103	35	92	79	99	20	83
V_s, cm^3/g	0.532	0.296	0.191	0.362	0.171	163	0.166	0.311	0.145	74	0.109	0.22	0.111	55
V_{mi}, cm^3/g	0.359	0.121	0.049	0.187	0.138	192	0.051	0.168	0.117	86	0.017	0.111	0.094	62
V_{me}, cm^3/g	0.204	0.157	0.108	0.175	0.067	137	0.073	0.139	0.066	65	0.085	0.114	0.029	54
R_{av}, nm	1.075	1.42	1.64	1.32	–0.32	–	2.22	1.37	–0.85	–	2.37	1.47	–0.9	–

Note. Δ—increment of the value of the parameter as a result of chemical regeneration; Δ, %—relationship between the increment of the parameter after regeneration and the value of its diminishing during filtration; S_{BET}, S_{me}—specific surfaces of pores and mesopores of AC, respectively; V_s, V_{mi}, V_{me}—respectively specific volumes of pores and mesopores of AC, respectively; R_{av}—average radius of pores.

Regeneration III shows a fairly complete (> 80%) recovery of the outer porosity represented by the surface of wide mesopores, whereas restoration of micropores constitutes ~60% of the used value in the course of biofiltration. It is obvious, the intensity and duration of regeneration III is not enough for freeing the AC pores exhausted over the preceding 10 months of the bed operation.

The restored resource of BAC of the filter constituted after regeneration I and II accordingly 11440 and 11740 of conventional volumes (c.v.) (see Table 1). Despite the decreased porosity of repeatedly restored carbon the length of the efficient operation of the regenerated bed was preserved. Additional resources of the filter ensured by conduction of regeneration III and IV were also practically identical (respectively 5170 and 5176 of bed volume).

Since in filters with BAC losses of free porosity of carbon are bound mainly with non-target filling of the pores with products of vital activity of microorganisms, the degree of regeneration is the sum of restored pores from NP and bioproducts. Based of the technique of determination of the volume of pores of non-target filling [8] contributions of NP and biologically soluble products (of metabolism and growth of microorganisms) in the change of porosity of BAC were separated. The obtained data are given in Table 3.

Table 3. Change of volumes of BAC pores in the course of filtration–regeneration due to adsorption–desorption of 2-nitrohenol and biological products

Stage	V_f, dm^3	$\pm \Delta V_s$, cm^3/g	$\pm \Delta a_{NP}$, mg/g	a_D, %	$\pm \Delta V_{NP}$, cm^3/g	NP	BP
						%	
Filtration	1152	–0.105	+87.1	95	0.003	3	97
Regeneration I	1850	+0.171	–71.7	–	0.049	29	71
Filtration	2492	–0.196	+157.1	77	0.024	12	88
Regeneration II	2493	+0.145	–40.8	–	0.028	19	81
Filtration	2913	–0.202	+231.0	65	0.054	27	73
Regeneration III	2924	+0.111	–26.8	–	0.018	16	84
Filtration	3093	–0.093	+106.0	60	0.026	28	72

Note. a_D—destruction of NP in BAC bed during biofiltration, %; $\pm \Delta a_{NP}$—specific values of removing NP during filtration and regeneration; $\pm \Delta V_{NP}$—specific volume of removing NP; NP, BP—restored or filled pores ($\pm \Delta V_s$) respectively by nitrophenol and bioproducts, %.

From Tables 2 and 3 one can see that the efficiency of regeneration decreases if the efficiency is understood exceptionally the volume of the porous space, which is freed as a result of treatment. The data of Table 3 shows that the bulk of used pores in filtration is occupied by bioproducts. Non-targeted pore filling of BAC in the long absence of activation treatments of the bed reaches 97%. Chemical regenerations increase subsequently the share (from 3 to 28%) of NP being filled. Chemical treatment by the alkaline solution helps to remove both

NP and soluble microbic products. The relative volume of pores being freed as a result of desorption of bioproducts, from treatment to treatment of AC increases (see Table 3).

It should be noted that regeneration I is the most productive in terms of the amount and specific share of the washed-off target organic substance. The volume of the regenerate being used for the first treatments was by 80% larger while the time of contact was in fact five times higher than for regeneration III. It is obvious the longer and larger specific volume of the regenerate are used for chemical treatment the higher is amount of desorbed NP. The aspiration to limit the volume of wastewaters at the chemical treatment of the AC bed (up to 12–14 volumes of the bed) during the regeneration III and conduct the process for 4 h decreases the efficiency of restoring the porous structure and accordingly limit the length of the following stage of biofiltration. Actual chemical treatment for 1.5–2 h is not enough at kinetic point of view for mass desorption of NP. This time is also not enough for complete washing off biological products of vital activity, adsorbed in large AC mesopores (0.093 cm^3 against 0.121–0.117 cm^3—for two first regenerations) (see Table 3).

It appears possible to achieve higher results of regeneration than those obtained at last stages of the experiment. In order to increase the desorption current of NP and bioproducts and to increase the efficiency of single regeneration it is necessary to raise temperature, to increase the time of contact and volume of the regenerate per unit of BAC volume. For the efficient biosorption process, it is necessary to balance the degree of regeneration with the duration of the subsequent filtration stage, i.e. maximally bring together the values of recovery and loss of porous structure per cycle.

As a matter of fact fulfillment of regenerations I and II in laboratory conditions takes less than one day. Due to the necessity of repeated immobilization of biomass on carbon the filtration was resumed after a week. In the case of regeneration III and IV the duration of the procedure was decreased up to one hour since activated biomass from the reactor of preservation was used. Biomass was no less active than after the first treatments, but the efficiency of the effective operation of the bed was substantially lower because in fact only 50% of the occupied porous space was freed in the course of a short-time treatment (see Table 3). The degree of NP removing after regeneration increased thanks to an increase of the contribution of adsorption. Adsorption removal of NP occurred due to filling of freed micropores. Obviously, as the ordinal number of regeneration increases, the processing time for maintaining the duration of effective filtering should increase. Treatment is necessary for ensuring desorption and reverse diffusion of NP from microporous region. Desorption currents of the target substance may be braked by diffusion "corks"of biological products therefore the intensive and prolonged abrasive effect on BAU in many cases is necessary.

CONCLUSIONS

Technological approaches for development of the method of chemical regeneration of biological activated carbon are proposed and tested. Changes of the BAC porous structure as a result of chemical regeneration and subsequent filtration were investigated. It was established that 71–84% of volume of restored pores is filled with products of microbial vital activity. It was shown that alkaline treatment of carbon performed in the course of several days prolongs the effective removal of NP from water for 10–11 months.

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