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Biotransformation of the Active Carbon Layer in Purifying Water of 2-Chlorophenol

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Abstract—The article has investigated regularities of the process of transformation of active carbon into biologically activated carbon in the course of an effective filtration purification of water of 2-chlorophenol. In exploitation of active carbon for more than two years the contribution of the adsorption and biodestructive components to the removal of the target component was marked off. It has been shown that more than 80−85% of chlorophenol is removed biologically after four−five months from the beginning of the process.

INTRODUCTION

Chloroderivatives of phenols are typical representatives of organic substances polluting wastewaters of industrial and agricultural industries. An increase of volumes of dumping of chlorophenols, receptivity and toxicity of these compounds require their profound removal from wastewaters [1−3].

Adsorption on activated carbon (AC) is one of the most effective and technically realized methods of removal of dissolved organic pollutants in modern industry. Expensiveness of carbon sorbents very often makes the use of AC for ecological protection of the water basin economically unbeneficial [4].

Involvement of the biocenosis of microorganisms spontaneously formed in the layer of the adsorbent in the course of water purification makes it possible to substantially make cheaper the latter [5−7].

It is far from the fact that every case of long filtration through the AC layer leads to production of effective biologically active carbon (BAC) whose exploitation results will be economically attractive and correspond to ecological requirements.

Specific conditions of exploitation should ensure enough time of water contact with the AC layer for a successful development of the biocenosis [5, 7−9]. As a rule, operation of biofilters is characterized by medium and low filtration rates. Over time, the adsorption component of removing organic substances by AC diminishes while the effectiveness of the process greater and greater depends on activity and capacity of microbes to destruction of organic matter [7, 8] However, the time of transformation of the sorbent in BAC, regularities of the process and its influence on the efficiency of water purification of synthetic organic mater remain outstanding tasks due to the multifactor nature of the phenomenon and difficulty of dynamic differentiation of the contribution of two components [6, 8−10].

The objective of the present paper is establishing regularities of transformation of activated carbon into biologically active in purification of water of 2-chlophenol by assessing the time of the beginning of manifestation of biodestruction, its contribution to the removal of the target substance in the layer of the medium and impact on AC adsorption properties.

EXPERIMENTAL

The efficiency of water purification of 2-chlorophenol (CP) in stationary AC layers was investigated. The choice of the adsorbent is determined, on one hand, by, the extent and danger of a pollutant, and, on the other, by the possibility of quantitative determination of a part of the substance subjected to destruction [1−3].

Experiments used two filtration systems based on stone fruit activated carbon (KAU) and its analog modified by iron oxides KAU/Fe [11], which had close dimensions and operated under similar conditions. Since the results were identical for simplification of the narration the main attention in our research was given to the data obtained on a filter with KAU. And only in case of differences in them linked to AC features the parall

data for the modified sorbent may be given. The initial general volume of the KAU layer (fraction 0.5–2.0 mm) in a laboratory column constituted 100 cm^3. The volume of the first along the progress filtration layer is 34 cm^3. Layers heights are 39 and 10 cm respectively.

At the initial stage of research ~ 1200 dm^3 of aqueous solution of CP was filtrated. Filtration was done downwards at the average rate of 0.51 m/h. The time of contact in layers constituted respectively 13 and 39 min. Further on the filtration rate through the AC layer was decreased owing to a decrease of the sorbent volume, which was taken in the course of the process as samples.

Mean concentration of 2-chlorophenol in the working input solution prepared on the basis of tap water (city of Kiev) constituted 7.8 mg/dm^3. The control over the efficiency of the operation with BAC was carried out by determining the concentration of the target component and the concentration of chlorides in input and output solutions [12].

The CP concentration was determined on a spectrophotometer Specord UV Vis at the UV wavelength 273 nm. Chemical oxygen demand (COD) was measured according to the technique of the HACH company on a HACH DR/890 colorimeter with a DRV200 module using in this case the set of HACH reagents (0–150 mg/dm^3) heating sample up to 150°C according to the program of two-hour holding.

In filtration AC samples were taken for the control of changes of its structural and sorption parameters. Carbon samples were dried out at 104°C until constant mass, stored in closed exsiccators and used for construction of adsorption–desorption isotherms of nitrogen at 77°K on a Quantachrome NOVA 2200e device. Isotherms by means of a specialized NovaWin software were worked out in accordance with the BET methods, the theory of density functional and the Barret-Joiner-Halender method for calculating main structural and sorption characteristics of the samples of fresh and working AC (Table 1).

Table 1. Changes of KAU structural-porous characteristics

Characteristics	V, dm^3			
	0	500	1200	1574
S_{BET}, m^2/g	1096	520	198	78
S_{eas}, m^2/g	143	130	89	56
V_a, cm^3/g	0.613	0.389	0.219	0.159
V_{mi}, cm^3/g	0.394	0.125	0.051	0.008
V_{me}, cm^3/g	0.260	0.220	0.172	0.134
R_{avr}, nm	1.12	1.84	2.38	4.06

Note: V—volume of filtrate; S_{BET} surface area by the BET method; S_{eas}—external surface area; V_a—adsorption area; V_{mi}—volume of micropores; V_{me}—volume of mesopores, R_{avr}—average radius of pores.

A medium for the second filtration system was KAU/Fe; the content of iron in the sorbent constituted 2% [11]. The initial volume of the filter medium layer—108 cm^3, the first layer—44 cm^3, the height of the layers was respectively 44 and 14 cm. The mean filtration rate—0.42 m/h, the time of contact for the general and the first layer—respectively 43.4 and 11.1 min, the average value of the CP input concentration—9.1 mg/dm^3.

The main difference in operation of the KAU/Fe was in that the sampling of the sorbent samples was started earlier (the first time—after 300 dm^3) and more often (before 1200 dm^3 of filtrate—six times) than for the system with KAU and in this case before passing 1200 dm^3 of the filtrate only one sampling of AC was done.

RESULTS AND DISCUSSION

Efficiency of Purifying Model Solution

In the KAU-CP system 1700 dm^3 of filtrate or 23700 conventional volumes (c.v.) of the column charge were obtained. In the course of research for more than two years the degree of the removal of 2-chlorophenol constituted 100%. Through the layer of KAU/Fe, 1686 dm^3 (24100 c.v.) filtrate were obtained, which did not contain CP.

Figures 1a, 1b gives data on optical density (*D*) and COD of the filtrate compared with indexes of the initial solution. The mean arithmetic values of COD of the initial solution and filtrates after the first and general layer constituted respectively 44; 19 and 12 mgO/dm^3.

(a)

(b)
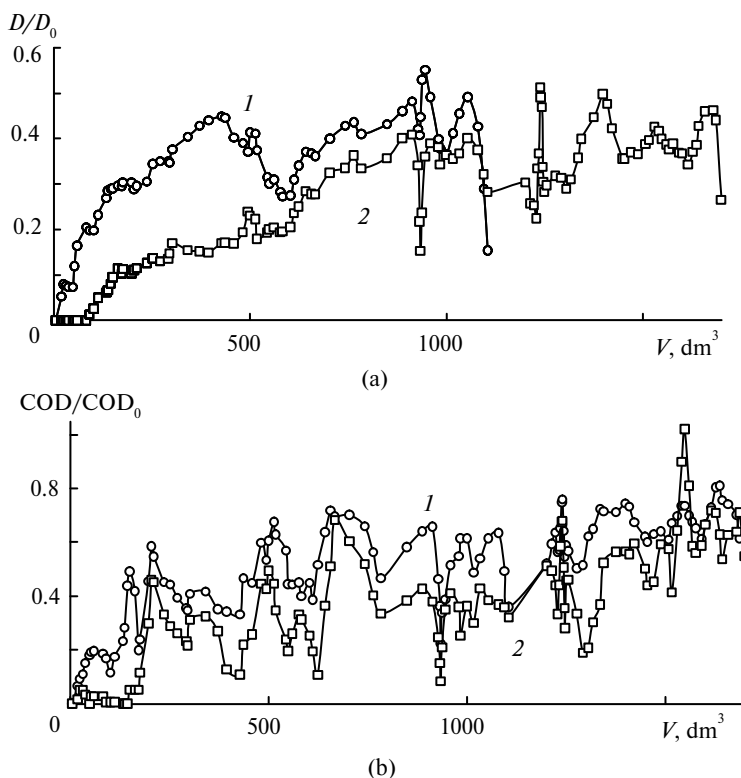
Fig. 1. Efficiency of removing 2-chlorophenol from its model solution in relative units of optical density (a) and COD (b) in the KAU layer of height 10 (*1*) and 39 cm (*2*).

The analysis of the general efficiency of the system showed that the first layer KAU came to a quazistationary mode (see Fig. 1a) and COD (see Fig. 1b) after two and the half month of operation (350–400 dm^3 of filtrate). Before obtaining 1200 dm^3 (35 000 c.v.) the degree of the removal of 2-chlorophenol in the first layer constituted 100%, by optical density—50–60% of the input value, while COD on average decreased by 45–50%.

Emergence and Assessment of the Contribution of CP Biodestruction to the General Process of Water Treatment

Terms of emergence of biodestruction and its intensity in the layer are determined by specific conditions of functioning of the system of purification, in the first place, toxicity and resistivity of substances being removed. The emergence of CP in filtrate corresponds, in the first approximation, the value of equilibrium adsorption at minimal concentration, which may be determined by the control method (0.2 mg/dm^3). According to adsorption isotherm of CP equilibrium concentration constituting 0.2 mg/dm^3 is correspondence of the adsorption value equaling 35 mg/g. Based on the value of arithmetic mean of the CP input concentration (7.8 mg/dm^3) for equilibrium saturation of AC of the whole column 241 dm^3 of the model solution is enough. Thus, in the case of exceptional adsorption nature of CP removal by the AC layer the breakthrough of the target substance should take place on the 54th day. Actually 2-chlorophhenol was not identified in the filtrate until the end of the experiment.

The excess of the value of dynamic adsorption over the equilibrium one is a primary gross-effect allowing one with confidence judge about the presence of microbial activity in the sorbent layer. Achieved working values of the specific dynamic adsorption actually ten times exceed the values of the equilibrium values. Thus, for the first KAU layer after passing 1200 dm^3 of filtrate—a_{d1} = 548 mg/g, while for the whole column—a_{d2} = 297 mg/g (after 1700 dm^3). The values of CP dynamic adsorption on KAU/Fe constituted for the first and general layers respectively 868 and 270 mg/g at the value of the CP equilibrium adsorption (C_{eq} = 0.2 mg/dm^3) 45 mg/g.

Papers [1−3] confirmed stoichiometric correlation between the excess of chloride−ions $(\mathrm{Cl}_i - \mathrm{Cl}_0 > 0)$ and the amount of chloraromatic compounds destroyed by microbes. The beginning of the process of destruction of 2-chlorophenol may be recorded by controlling changes of the concentration of chlorides in the input solution Cl_0 and filtrate Cl_i. The higher redundant concentration of chlorides in filtrate the more intensive is destruction. In the first approximation it may be considered that the emergence moment of the stable excess of chloride−ions is the beginning of the productive operation of the biota in the layer.

The CP concentration (C_{dei}), which is utilized by microbes was calculated by the formula

$$C_{dei} = (\mathrm{Cl}_i - \mathrm{Cl}_0) \times 3.62, \tag{1}$$

where 3.62 is the proportionality coefficient between 1 mg of redundant chlorides and the mass of destroyed chlorophenol.

Biosorption removal of CP by the AC layer m_{off} (summary contributions of adsorption m_a and biodestruction m_{de}) in the case when there is absence of breakthrough to filtrate, is equal to the amount of CP introduced to the system with the input solution, m_{in}:

$$m_{off} = m_a + m_{de} = m_{in} = \Sigma C_{0i} \Delta V_i, \tag{2}$$

where C_{0i} is the input CP concentration on the ith interval of the process; ΔV_i is the volume of filtrate over the ith interval of the process. The value of destroyed 2-chlorophenol m_{de} or the contribution of microbial component to the removal of the target component by the AC layer was calculated in the following way:

$$m_{de} = \Sigma C_{dei} \Delta V_i,$$

where ΔV_i is the volume of filtrate over the ith interval (between neighboring measurements of chlorides).

The main results of the research of the contribution of biodestruction to the removal of CP (for a complete AC layer) are presented in Fig. 2.
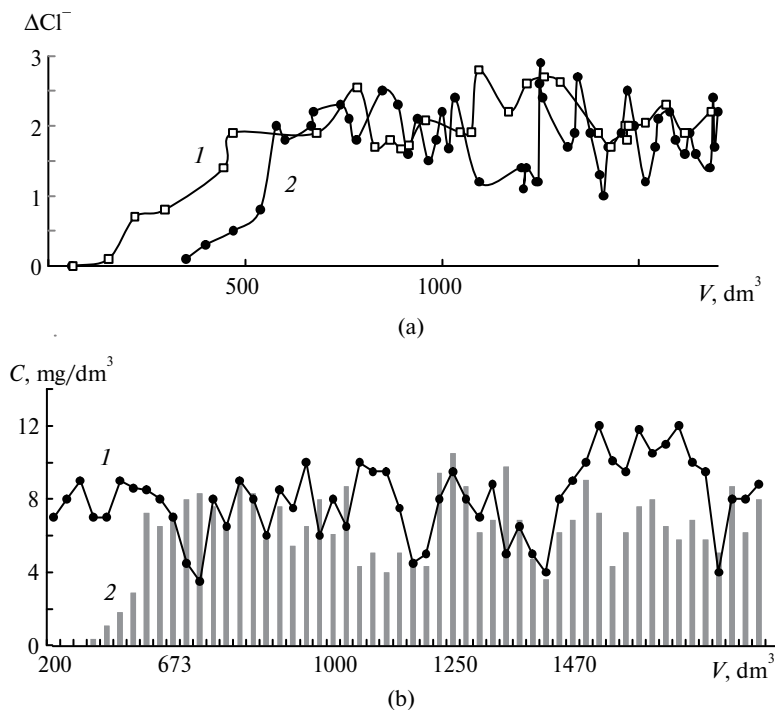

Fig. 2. Relationship between the intensity of biodestruction of chlorophenol in the layer of activated carbon and the volume filtrated solution (the time of the process) evaluated by the redundant concentration of chlorides in filtrate after the layer of modified (*1*) and normal KAU (*2* (a); the same by the concentration of chlorophenol at the exit (*1*) compared with the concentration of biologically destroyed chlorophenol in the layer of KAU (*2*) (b).

From Fig. 2a it follows that for KAU layer the conspicuous redundant concentration of chloride ions is formed after passing 350 dm³ of filtrate. The mean arithmetic value of the increment of the chloride concentration in the course of the experiment constituted 1.79 mg/dm³. The modified sorbent is characterized by a

more earlier appearance of redundant chlorides (150 dm^3) and faster achievement of maximum values. The average value of chloride−ion increment in the course of the experiment constituted 1.89, after the plateau— 2.08 mg/dm^3. The obtained data point to a more intensive proceeding of the process of generation and formation of biocenosis on carbon surface modified by iron oxides.

It should be noted that cases exist of exceeding the amount of destroyed CP over the amount of substance that entered the AC layer during the same time interval (see Fig. 2b). Such facts took place after receiving 500 dm^3 of filtrate and continued to reiterate at various frequency until the completion of the experiment (1700 dm^3). This is an evidence of a parallel process of CP destruction adsorbed earlier on AC. It may be expected that intensive destruction of CP results in partial renewal of AC adsorption places, i.e. leads to regeneration of the sorbent.

Figure 3 shows the contribution of adsorption and destruction to the integral removal of CP by the BAC layer. The contribution of biodestruction assessed by the redundant concentration of chlorides as the process proceeds increases and at the end of the experiment constitutes for usual KAU 62 and for KAU/Fe—76%. The growth of filtration time further on inevitably will increase the summary contribution of destruction. The data of Fig. 3 confirm the dominating role of microbial activity in the removal of the target component. As early as four months of operation (500 dm^3 of filtrate) the current removal of CP in the KAU layer more than by 80% is determined by the biological component.

(a)

(b)
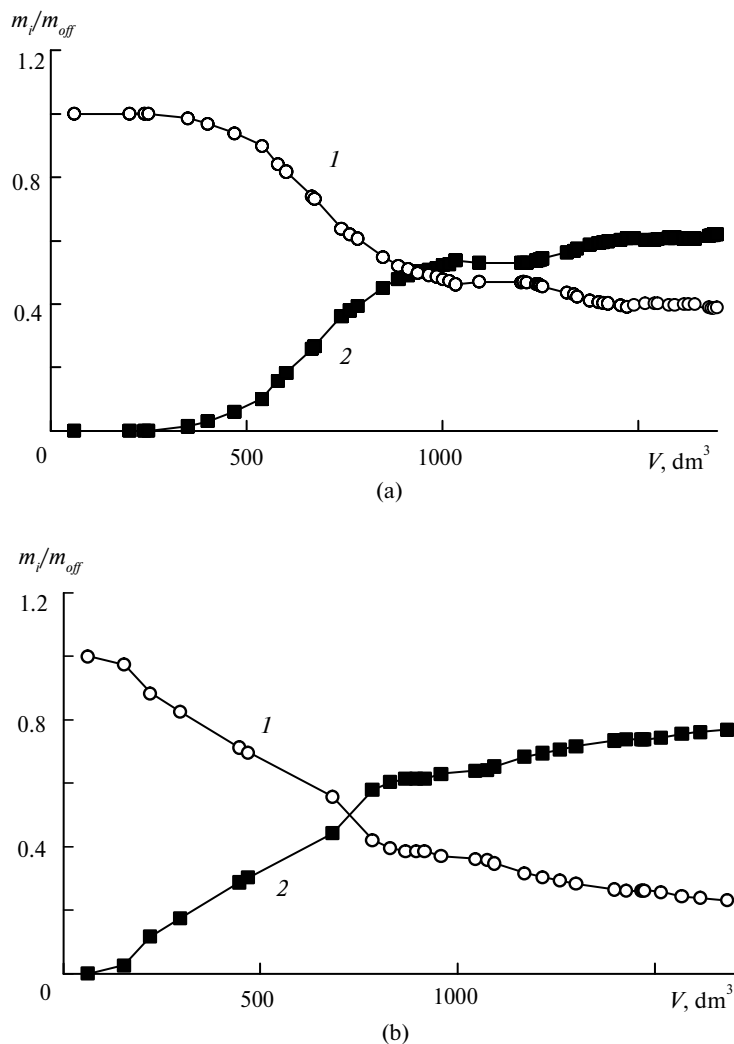
Fig. 3. Contributions of adsorption m_a (*1*) and biodestruction m_{de} (*2*) to integral removing of chlorophenol by the layer of normal KAU (a) and KAU modified by iron oxide (b).

The Change of Structural-Sorption Properties of Activated Carbon

Intensive biodestruction of CP determines the possibility of regeneration of the sorbent (see Fig. 2b), therefore the research investigated changes of structural-sorption characteristics of activated carbon (see Table 1). The data of Table 1 reflect the fact of constant decrease of sorption capacity of AC in the course of the process. Micropores actually are completely absent after the second year of operation (1574 dm^3), meso-pores were filled by 50%. The average radius of free pores R_{avr} increased by 3.6 times, which confirmed the known fact of chiefly adsorption of phenol and its derivatives in micropores. The absence in AC micropores at the final stages of the process (four-time decrease of the adsorption volume) did not allow one to effectively remove chloroderivatives of phenol with initial capacity. High efficiency of BAC at this stage was determined by an increase of time of solution contact with carbon, which intensified CP biodestruction.

Theoretical values of vacant porosity of KAU at equilibrium adsorption and CP adsorption from the aqueous solution in sterile conditions are given in Table 2. In accordance with the formal calculation, which does not take into account CP destruction (the CP quantity removed from 1574 dm^3 of filtrate is considered as located in the AC pores), theoretically vacant porosity in "sterile" conditions of dynamics is much greater than corresponding actual BAC structural-sorption parameters (see Table 1). It should be noted that apart from CP the solution contained other organic compounds, which were input together with tap water. However, these substances are more hydrophilic and less capable to adsorption on a carbon surface than aromatic substance under research. It may be expected that in competitive activity for adsorption organic substances in tap water will be completely ousted from the AC microporous space by 2-chlorophenol.

Table 2. Calculation of vacant porosity of activated carbon for sterile conditions

Conditions	a		V_a occupied	V_{mi}	V_a
				vacant	
	mg/g	mmol/g	cm^3/g		
$C_{eq} = 10$ mg/dm^3	147	1.144	0.119	0.275	0.494
$V = 1574$ dm^3 (the whole column)	242	1.892	0.197	0.197	0.416

Obviously, a decrease of the vacant porous space in the course of filter operation is linked with vital activity of microorganisms. As a matter of fact, dissolved microbe products constitute a part of adsorbates, which fill potentially vacant AC pores. As early as the fourth month of the dynamic process (after 500 dm^3, see Table 1) actually vacant adsorption space was smaller than the equilibrium value (for $C_{eq} = 10$ mg/dm^3, see Table 2) by 0.1 cm^3/g on the 11th month (1200 dm^3) by 0.275 cm^3/g, after two years (1574 dm^3)—by 0.335 cm^3/g.

Thus, blocking of the porous space by microbe products is negative results of bioactivity in the layer. With increased input concentration of organic substances the activated carbon due to microbial fouling of pores will not be capable to use free porosity for adsorption of the increment of the concentration of target component.

CONCLUSIONS

Long (more than two years) effective removal from water of 2-chlorophenol by filtration systems on the basis of KAU was achieved thanks to transformation of activated carbon into a biological analogue. We have established the contribution of the adsorption and biodestruction components in the removal of the target component in the course of the process. Modification of carbon by iron oxides was conducive to earlier energization of microbial activity and the large contribution of destruction in water purification of chlorophenol (76 against 62%), more than 80−85% of which is removed biologically as early as four−five months from the beginning of the process.

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