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SORPTION PURIFICATION OF POLLUTANTS IN THE FORM OF MICROORGANISMS AND THEIR NUTRIENT MEDIA IN A SOLITARY PORE SYSTEM OF A CARBON SORBENT

Research article

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Abstract

The article considers the sorption of pollutants on a carbon sorbent. The study of recycled and purified water samples was carried out using photometric equipment. By modeling, it was found that pollutants (in the form of microorganisms and their nutrient media) are mainly immobilized in micropores and, in the future, their study was carried out using electronic optics. With the help of bioinformatic interpretation, sorption interaction of microorganisms subdivided by size factor in a solitary pore system consisting of three types of subsystems: macro-, meso- and micropores is modelled. For a theoretical description of a pore system, an oriented graph is constructed using network theory. Then, using the Roy-Warshall algorithm in a matrix representation, the problem of its optimal routing is solved, with the calculation of a path element for an example. In the future, considering sorption as a single process of transportation and purification of pollutants, the phenomenon of their slip, which inevitably occurs in these cases, was predicted. The determination of the probability of the passage of pollutants using the Bayes theorem, often used in bioinformatics, made it possible to predict, in general, such an equilibrium phenomenon as desorption.

Keywords: pollutants, microorganisms and their nutrient media, sorption purification, carbon sorbent, solitary pore system, macro-, meso-, micropores, digraph, dimensional subsystem of microorganisms, adjacency matrix, Roy-Warshall algorithm, Bayes theorem.

СОРБЦИОННАЯ ОЧИСТКА ЗАГРЯЗНИТЕЛЕЙ В ВИДЕ МИКРООРГАНИЗМОВ И ИХ ПИТАТЕЛЬНЫХ СРЕД В УЕДИНЕННОЙ ПОРОВОЙ СИСТЕМЕ УГЛЕРОДНОГО СОРБЕНТА

Научная статья

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Аннотация

В статье рассмотрена сорбция загрязнителей на углеродном сорбенте. Исследование образцов оборотных и очищенных вод выполнено с помощью фотометрического оборудования. Путем моделирования установлено, что загрязнители (в виде микроорганизмов и их питательных сред), преимущественно иммобилизованы в микропорах и, в дальнейшем, проведено их изучение с помощью электронной оптики. С помощью биоинформационной интерпретации смоделировано сорбционное взаимодействие микроорганизмов, подразделяемых по размерному фактору в уединенной поровой системой, состоящей из трех типов подсистем: макро-, мезо- и микропор. Для теоретического описания поровой системы, с помощью теории сетей построен ориентированный граф. Затем, с помощью алгоритма Роя-Уоршолла в матричном представлении, решена задача его оптимальной маршрутизации, с вычислением для примера элемента пути. В дальнейшем, рассматривая сорбцию как единый процесс транспортировки и очистки загрязнителей, было спрогнозировано явление их проскока, неизбежно возникающее в этих случаях. Определение вероятности проскока загрязнителей с применением часто употребляемой в биоинформатике теоремы Байеса дало возможность в общем случае спрогнозировать такое равновесное явление как десорбция.

Ключевые слова: загрязнители, микроорганизмы и их питательные среды, сорбционная очистка, углеродный сорбент, уединенная поровая система, макро-, мезо-, микропоры, орграф, линейная подсистема микроорганизмов, матрица смежности, алгоритм Роя-Уоршолла, теорема Байеса.

Introduction

Recycled (waste) water as a nutrient medium for numerous microorganisms (blue-green algae, protozoa, bacteria and viruses) it causes many harmful phenomena, such as turbidity and unpleasant odor, corrosion of concrete and metals, even such as stainless steels, and also, due to the transfer of a number of serious diseases, poses a real threat to human health. Municipal wastewater containing an increased concentration of iron oxides and phosphates, in general, are excessive nutrient media for the development of algae and protozoa, as well as bacteria and viruses. Thus, due to the widespread use in everyday life of synthetic detergents containing phosphates in high concentrations, the growth and reproduction of blue-green algae occurs in wastewater, causing its active flowering, accompanied by a drop in dissolved oxygen in the water [1]. When the dissolved oxygen content decreases to critical values, many aquatic inhabitants (for example, fish) begin to die, so flowering can lead to the formation of overseas zones. One of the most effective methods of wastewater treatment from such pollutants is the use of carbon sorbents. Close attention is paid to the study of the nature of the adsorption interaction, porosity, as well as the specific surface area of sorbents, since the strengths of the use of these substances are their high absorbing and brightening ability, repeated use, as well as availability and cheapness [2].

Experiment and methods

Before conducting a series of experiments on wastewater treatment from pollutants representing various microorganisms and their nutrient media, the synthesis of carbon sorbents was developed and adjusted, with the development of technology for their use for wastewater treatment [3]. Then the porosity of the obtained sorbents was studied [4]. Thus, it was found that the average size of macropores was about 4-8 microns, mesopores had dimensional indicators comparable to 0.2-0.6 microns, and the size of micropores (determined using electronic optics) was assumed to be 0.03-0.2 microns. Sorption purification of wastewater from pollutants consisted in its passage through a column filled with a carbon sorbent and analysis of the degree of purification upon completion of sorption filtration (fig. 1).

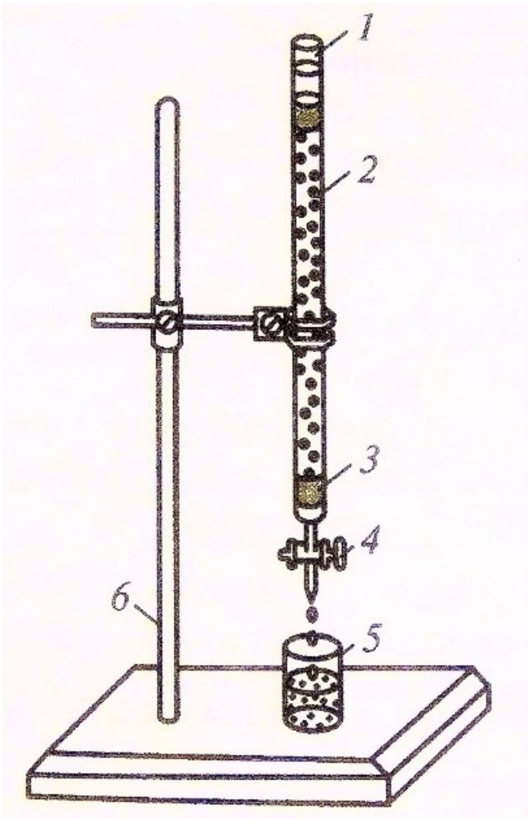

Figure 1 - Filtration column with carbon sorbent
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Note: 1 – glass burette; 2 – sorbent layer; 3 – glass wool or fiberglass layer;

4 – a tap to adjust the filtration rate; 5 – a glass for collecting filtrate;

6 – metal tripod with foot

Photometric equipment in the form of single-parameter colorimeters from Milwaukee (USA) of the MW 12 (phosphates) and MW 14 (common iron) series was used in conducting research on sorption wastewater treatment.

The essence of the method for determining phosphates was to adapt the standard method of "Water and wastewater Research", 20th edition, ascorbic acid method [5]. During the analysis, as a result of the reaction of phosphates and reagent, the measured liquid (wastewater and purified water) was colored blue, the intensity of which was recorded by a highly sensitive silicon photodetector. The radiation source was a point LED with a wavelength of 525 nm. Wastewater according to the results of a series of tests showed an overestimated phosphate content, averaging 5.0 mg/l (ppm), which is explained by the widespread use of various synthetic detergents based on phosphate salts by the population as highly effective water softening reagents. During the filtration of wastewater on the sorbent, in the sorption column, the phosphate content was reduced by almost an order of magnitude, to a value of 0.55 mg/l (ppm).

The essence of the method for determining total iron was the use of EPA-phenanthroline, also known as method 315B [6]. During the analysis, as a result of the reaction of common iron and reagent, the measured sample (wastewater and purified water) was colored orange, the intensity of which was recorded by a highly sensitive silicon photodetector. The radiation source also served as a point LED with a wavelength of 535 nm. Wastewater according to the results of a series of tests showed a total iron content averaging 1.54 mg/l (ppm). During the filtration of wastewater on the sorbent, in the sorption column, the total iron content was reduced by more than an order of magnitude, to a value of 0.14 mg/l (ppm).

Thus, the pore system of the carbon sorbent, effectively retaining various microorganisms in itself, makes the water safer biologically, and also works as an effective means of absorbing phosphates and total iron, which, in turn, are nutrient media for the origin and development of foci of secondary bioorganic pollution of recycled and wastewater.

Calculation algorithm and discussion of the results

When carrying out all calculations, the main condition of the described processes is that sorption (immobilization) in this case takes on an exclusively physical (dimensional) character, i.e. the retention of such microbiological particles as blue-green algae, protozoa, bacteria, viruses, etc. in a solitary pore system, occurs without destroying the shaped (membrane) integrity of these microorganisms.

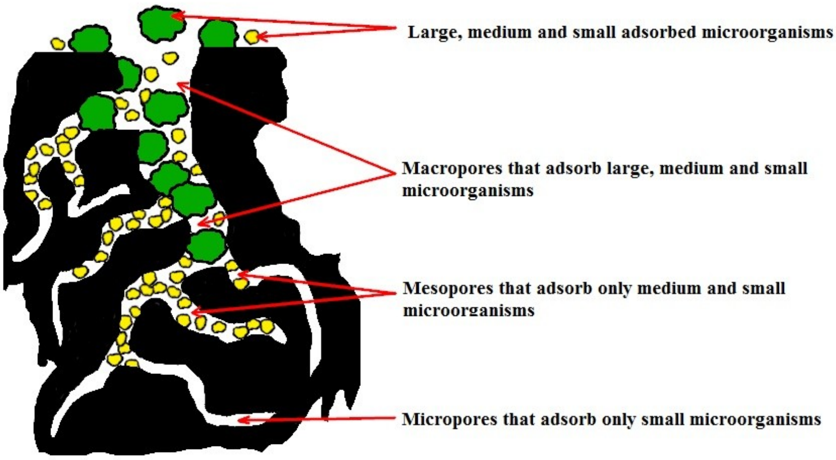

Figure 2 - Model of a solitary pore system

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Consider a solitary pore system consisting of subsystems such as macro-, meso- and micropores (fig. 2). Now imagine it as a transporting system through whose capillaries water contaminated with microorganisms (blue-green algae and protozoa, bacteria and viruses) flows, passing from one point of the subsystem to another. Using this representation, using network theory, we will represent this transporting system in the form of an oriented graph, the edges of which are microcapillaries between points (subsystems of pores), in turn, represented by the vertices of the graph (fig. 3) [7]. We introduce the concept of flow as a measure of the number of microorganisms passing through the capillaries of a solitary pore system for their retention (sorption), and the flow in question will be directed only in one direction (from the liquid to the pores) and has constancy. Thus, there is some fixed flow, the source of which is the entrance (A) to the pore system through the macropore, the mesopore (B, D, E) will be an intermediate (connecting) link, and the micropore (C, F, Z), in turn, will become a drain. Then it becomes obvious that the amount of flow cannot exceed the throughput capacity of micropore capillaries. Thus, sorption in the most general case is limited by the filtration rate in micropores.

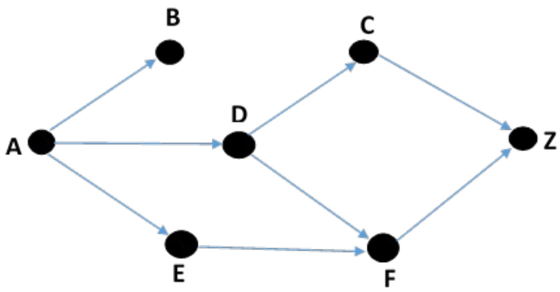

Figure 3 - Digraph describing a solitary pore system

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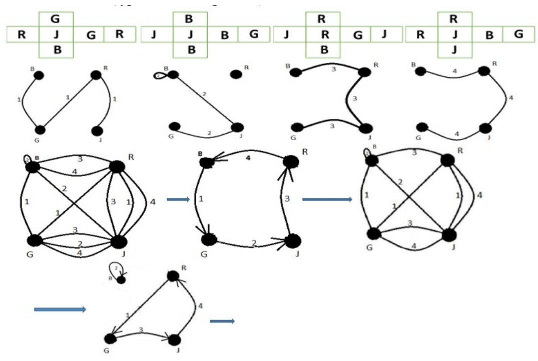
Let there be a solitary pore system, which (for clarity) can be formally described using four cubes, with the assignment of an individual name to each: "total porosity"; "macropores"; "mesopores"; "micropores". Cubes as congruent figures will have six faces, each of which will be represented as one of four dimensional types of microorganisms: "blue-green algae"; "protozoa"; "bacteria"; "viruses" and, for greater clarity, we will assign each of them its own color (color) [8]. Let the red color denote bacteria, blue – protozoa, green – blue-green algae, and finally yellow – will be responsible for viruses. The purpose of this simulation interpretation is to obtain a dimensional subsystem with one of the four inherent types of microorganisms from a general–solitic porous system. The solutions (if they exist) depend on the choice of the type of microorganism (color) for the faces of the cube. Therefore, there may be one solution, there may be several, or the solution may not exist at all. The solution of the proposed interpretation is displayed in the form of a sweep, on which the faces of the cube are designated as the front (F), back (H), upper (B), lower (H), left (L) and right (N) surfaces. The parts of the cube that should form the desired subsystem are called the Left, Right, Front and Back (to distinguish them from the originally appearing faces of the cube). Thus, the front and back, as well as the left and right parts of the cube will be mutually opposite to each other. Now let's consider an example of a given interpretation: let there be cubes whose faces are represented by the following color combination (types of microorganisms):



L	N
R	G
B	B
G	J
J	R

F	H
B	G
G	J
J	R
R	B

Figure 4 - The cubes
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Since the digraph describing a solitary pore system, being its graphical representation, is very limited in the possibilities of its storage and transmission, the necessary measure for its operational reproduction is the translation of the graphic image into digital form. For this, the most suitable form of mapping is a Boolean matrix, as a universal array whose elements are 0 or 1. In this case, the adjacency matrix can perform an exact description of the digraph [9]. Her task makes it possible to quickly restore the digraph. In addition, the adjacency matrix coincides with the matrix of the relation defined by this graph. Therefore, an undeniable advantage in using a matrix form is the ability to store its array in computer memory [10].

The adjacency matrix describing the digraph characterizing the pore system takes the following form:

$$\begin{bmatrix} 0101100 \\ 0010000 \\ 0000001 \\ 0010010 \\ 0000010 \\ 0000001 \\ 0000000 \end{bmatrix}$$

Figure 5 - The adjacency matrix describing the digraph characterizing the pore system
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Insofar as there are no loops, all elements of the diagonal of the matrix are equal to 0. It follows from this that the presented adjacency matrix is symmetric, since the graph is represented by a symmetric relation. An important application of this matrix is also the ability to find a path of fixed length k. For example, consider this case:

$$A^{\odot 2} = \begin{bmatrix} 0101100 \\ 0010000 \\ 0000001 \\ 0010010 \\ 0000010 \\ 0000001 \\ 0000000 \end{bmatrix} \odot \begin{bmatrix} 0101100 \\ 0010000 \\ 0000001 \\ 0010010 \\ 0000010 \\ 0000001 \\ 0000000 \end{bmatrix}$$

Figure 6 - Case 1
DOI: https://doi.org/10.23649/JAE.2023.40.6.6

and calculate, for example, the element $A_{13}^{\odot 2}$

$$A_{13}^{\Theta 2} = \{(A_{11} \wedge A_{13}) \vee (A_{12} \wedge A_{23}) \vee (A_{13} \wedge A_{33}) \vee$$
$$\vee (A_{14} \wedge A_{43}) \vee (A_{15} \wedge A_{53}) \vee (A_{16} \wedge A_{63}) \vee (A_{17} \wedge A_{73}) =$$
$$= (0 \wedge 0) \vee (1 \wedge 1) \vee (1 \wedge 0) \vee (1 \wedge 1) \vee (1 \wedge 0) \vee (0 \wedge 0) \vee (0 \wedge 0) =$$
$$= 0 \vee 1 \vee 0 \vee 1 \vee 0 \vee 0 \vee 0 = 1.$$

So, there is a path of length 2 from vertex V_1 to vertex V_3.

Matrix $\hat{A}$ can be computed as $\hat{A} = A \bigvee A^{\odot 2} \bigvee A^{\odot 3} \bigvee A^{\odot 4} \bigvee \ldots \bigvee A^{\odot n}$ but this method is ineffective. Therefore, we will apply a much better method implemented in the form of the Roy-Warshall algorithm for manual counting:

$$\begin{bmatrix} 0101100 \\ 0010000 \\ 0000001 \\ 0010010 \\ 0000010 \\ 0000001 \\ 0000000 \end{bmatrix} \Rightarrow \begin{bmatrix} 0111100 \\ 0010000 \\ 0000001 \\ 0010010 \\ 0000010 \\ 0000001 \\ 0000000 \end{bmatrix} \Rightarrow \begin{bmatrix} 0111101 \\ 0010001 \\ 0000001 \\ 0010011 \\ 0000010 \\ 0000001 \\ 0000000 \end{bmatrix} \Rightarrow \begin{bmatrix} 0111111 \\ 0010001 \\ 0000001 \\ 0010011 \\ 0000010 \\ 0000001 \\ 0000000 \end{bmatrix} \Rightarrow \begin{bmatrix} 0111111 \\ 0010001 \\ 0000001 \\ 0010011 \\ 0000011 \\ 0000001 \\ 0000000 \end{bmatrix}$$

Figure 7 - The form of the Roy-Warshall algorithm for manual counting

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A matrix constructed on a transitive closure using the Roy-Warshall algorithm displays the following deterministic digraph (fig. 8) [11]:

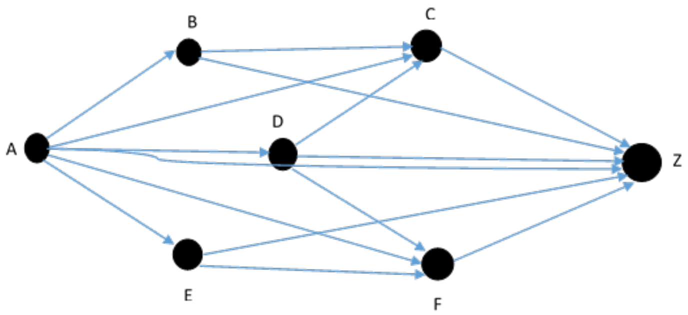

Figure 8 - Deterministic digraph based on transitive closure

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From this structure it can be seen that the macropore, being the source (input) in the pore system, contacts all the pores or, in other words, the flow of pollutants (wastewater + microorganisms) penetrates through it into each subsystem, regardless of the dimension of the latter. Mesopores, as nodal elements (vertices of the graph) of the system have a larger source, but a smaller drain, which means that the filtration rate in these elements will be sharply reduced relative to macropores. And, finally, micropores at the vertices of which all flows converge, take (as can be seen from the digraph) the greatest value in filtering, further reducing its speed. In connection with the above, for greater clarity and purity of the experiment, it was decided to visualize (using electronic optics) only the element of the pore system that, based on the calculation carried out, has the highest degree of filtration, which means that significant amounts of contamination could be concentrated in it. Technically, this was implemented in the following way: the spent coal sorbent was drained under vacuum and frozen in a Dewar vessel to the temperature of liquid nitrogen. Then thin sections were obtained from its surface to expose pore systems. After that, their surfaces were microscoped with electron optics at high resolution (fig. 9).

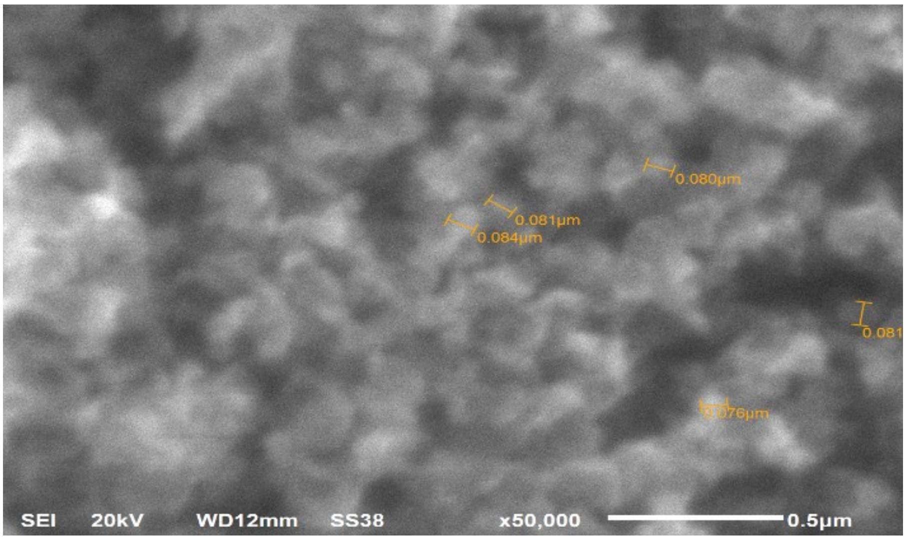

Figure 9 - Electronic photo of microorganisms localized in micropores of the pore system (micropore section, large and small bacteria + viral particles)
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In the future, considering sorption as a one-time process of transportation and purification of liquid media, the phenomenon of the passage of pollutants (microorganisms and their nutrient media) inevitably arising in these cases was predicted. The determination of the probability of the passage of pollutants both in the pore subsystems and in the external environment makes it possible, in general, to predict the equilibrium phenomenon of desorption. The calculations assumed that a solitary pore system is divided into three subsystems according to its size factor: macropores (large pores), mesopores (medium pores) and micropores (small pores). It was assumed that 20% of the total number of pollutants were retained (sorbed) macropores (*a*), 30% passed and were retained by mesopores (*b*), and the remaining 50% - after passing the above subsystems were retained by micropores (*c*). We assume the probability that during the sorption cycle, the leakage of pollutants from macropores will be 0.2; for mesopores, this probability will be 0.03; the slip from the micropores will be taken equal to 0.01. Then it will be necessary to consider the probability of leakage of pollutants separately for each subsystem of the pore system. To solve this problem, Bayes' theorem was applied to study the effect and determine its cause. So, this theorem is generally recognized today and is often used in bioinformatics, as it is very useful for determining the causes of many serious diseases (for example, cancer), as well as prognoses of their treatment and recovery [12], [13]. It follows from the condition that P_1=0,2; P_2=0,3; P_3=0,5 – the probability that any types of pollutants will be retained in the pore system. Then, by the condition $\widetilde{P_1} = 0,2; \widetilde{P_2} = 0,03; \widetilde{P_3} = 0,01$ – the probability of the passage of pollutants from the pores. We use the full probability formula:

$$P = P_1\widetilde{P_1} + P_2\widetilde{P_2} + P_3\widetilde{P_3} = 0,2 \times 0,2 + 0,3 \times 0,03 + 0,5 \times 0,01 = 0,054$$

Then, by Bayes' theorem, we have:

$P_a = \frac{P_1\widetilde{P_1}}{P} = \frac{0,04}{0,054} = 0,74$ – the probability that pollutants will make a slip from macropores;

$P_b = \frac{P_2\widetilde{P_2}}{P} = \frac{0,009}{0,054} = 0,17$ – the probability that pollutants will make a slip from mesopores;

$P_c = \frac{P_3\widetilde{P_3}}{P} = \frac{0,005}{0,054} = 0,09$ – the probability that pollutants will make a slip from micropores.

Then, the total probability will be equal to the sum: $P_\Sigma = P_a + P_b + P_c = 0,74 + 0,17 + 0,09 = 1,0$

That's why sorbents for wastewater treatment and discoloration tend to be manufactured with highly developed meso- and microporosity. Macroporous sorbents, which do not provide significant resistance to the flow, are produced mainly for cleaning gases from dust and particles suspended in them.

Conclusion

The use of carbon sorbent makes it possible to achieve high results in the treatment of wastewater and recycled water from various pollutants represented by various microorganisms and their nutrient media, which makes it possible to reuse purified and discolored water in everyday life and the national economy. Sorbents based on carbon materials are highly efficient and environmentally friendly systems for disinfection and demineralization of wastewater. The consequence of their use is a successful fight against microorganisms and their nutrient media, increasing the level of environmental safety to the maximum possible. The sorbent itself is not an expensive substance and, if necessary, can be easily replaced and regenerated.

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Conflict of Interest

None declared.

Review

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