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Research Article

Special Issue

THE TREATMENT OF WASTEWATER FROM DYES, USING MODIFIED MICROFILTRATION MEMBRANES

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ABSTRACT

The urgent task is the issues of wastewater treatment from dyes, formed as a result of textile, chemical, leather, painting and other types of activities. In these days, the method of membrane separation is widely used for the purification of wastewater from dyes. The methods of water purification from dyes, by means of initial and modified microfiltration membranes, based on a nylon substrate, with a surface layer of polyaniline and gelatin, prepared by the methods of polymerization, suspension and dynamic coating, are considered in the work. It was found, that the degree of water purification from the model dye "methylene blue" with the initial membrane was no more than 47%, and after modification of the membrane, depending on the method, the degree of purification from the dye increased to 94%. At the same time, the specific productivity of membranes decreased after chemical treatment, depending on the processing method, from 3 to 12%. The particle size of the dye model solution is in the range 82 - 7100 nm, that corresponds to the working range of microfiltration membranes. After membrane separation, there is the reduction of dye particles size in the suspension, but after the separation of suspension with the nylon-polyaniline membrane, it is observed an increase of particle sizes up to 10 μm.

Keywords: dyes, nylon membrane, chemical modification, polyaniline, gelatin.

1. INTRODUCTION

One of the most acute environmental problems of our time is the contamination of environmental objects with dyes, contained in industrial sewage waters of textile, chemical,

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leather, painting and other enterprises [1, 2].

There are more than one hundred thousand of commercially available dyes, with a production volume of over one million tons per year [3]. Due to its chemical structure, the dyes are resistant to discolouring, when exposed to light, water and many chemicals. Also many dyes are difficult to decolorize and they decompose by biological methods. There are many types of paint structures, such as acid, primary, dispersed, azo, diazo, anthroquinone and complex dyes. These dyes are very stable and can decompose only at temperatures above 1000°C. For this reason, synthetic dyes often receive special attention from researchers in the processes of wastewater treatment.

The main problem of stained wastewater purification is discoloration. Various methods and devices for wastewater treatment are currently used for solving this problem. For the purification of water from dyes, there are the following categories of purification methods: chemical, physical and biological. At present, the main methods of wastewater purification from dyes are physical and chemical methods. The significant part of them has a high cost, is focused on imported equipment, scarce reagents and required high energy consumption.

In recent times, the method of membrane separation is widely used. This separation is one of the most effective and qualitative methods of wastewater treatment. Membrane separation is the most productive and is carried out without phase transformations. Energy is used, mainly, on the creation of the initial solution pressure, its movement in the apparatus and squeezing through the membrane [4,5].

The methods of textile wastewater purification with various combinations of physicochemical and membrane processes are described in the work [6]. At first, wastewater, containing dyes, was subjected to coagulation and flocculation. Purification efficiency was evaluated according to the index of chemical oxygen consumption. Due to the low efficiency of these methods, post-treatment was carried out with microfiltration (MF) or ultrafiltration (UF), purification efficiency was 42% and more than 80%, respectively.

However, membranes also have a disadvantage: the productivity decreases during the separation process. An urgent task is the improvement of membrane properties such as strength, selectivity, purity and productivity.

One of the ways to improve membrane functions is to modify their surface, to increase selective and ion-exchange properties. This method is the fastest and the most cost-effective. It allows to use modern, highly effective modification techniques, which, due to their chemical, physicochemical or physical effects on the working surface of membranes, give already finished products new properties, useful in separation processes [7].

A great interest of researchers is attracted by the chemical synthesis of polyaniline (PANI). This is due to the possibility of obtaining the latter, with a complex of physico-chemical properties, varying over a wide range, while changing the chemical structure of polyacid, used as a matrix [8].

2. METHODS

The methods of water purification from dyes by means of initial and modified microfiltration membranes, based on nylon substrate, with a surface layer of polyaniline and gelatin, prepared by the methods of polymerization, suspension and dynamic coating, are considered in the work.

The purpose of the work is to increase the degree of purification of water-soluble dyes with microfiltration membranes, by modification of standard nylon membranes.

The way for obtaining nylon-gelatin dynamic membrane. The microfiltration polymer membrane, made of nylon (manufacturer - "Phenex Filter Membranes", 0.45 μm pore size) was used as the initial substrate, on which the dynamic layer was coated [9]. 1% gelatin solution was used as the applied dynamic layer. Dynamic layer was obtained by forming a porous nylon base on the surface, when filtering gelatin solution. After drying, the modified membrane was washed with distilled water. The percentage of gelatin in the dynamic membrane was determined by the gravimetric method, by the weight of the membrane before and after the modification.

To form the nylon-polyaniline membrane (nylon-PANI), initial nylon membranes were processed, using ammonium persulfate and aniline hydrochloride as reagents. Synthesis of membranes with a surface distribution of PANI was carried out by polymerization of aniline directly in the matrix of membranes, which were previously soaked for 2 hours in a solution of aniline hydrochloride. Then one of the membrane surfaces was treated with a solution of ammonium persulfate. At the same time, polyaniline particles were formed directly in the membrane matrix, as evidenced by the change of polymer color to dark green. The processing time of the membrane with ammonium persulfate was 5 minutes. The concentration of solutions of ammonium persulfate and aniline hydrochloride was 1 mol/dm^3. Obtained composite membranes were soaked in atmospheric air with a humidity of 90% for 96 hours [10, 11].

The particle size of the dispersed phase of emulsions and suspensions was determined by the method of dynamic light scattering (DLS), and the ζ potential was determined by the light scattering method with phase analysis (PALS) using the analyzer “NanoBrook Omni”.

The change in the membranes surface structure was recorded with a scanning electron microscope "Jeol JSM-6390 LA".

To detect the presence of silver in modified membranes, the elemental composition of the surface was investigated by X-ray fluorescence analysis, using the scanning electron microscope "Jeol JSM-6390 LA" with an energy-dispersive system "EX-230 ** BU".

Model colored solution of methylene blue dye was used in the work. The concentration of the model solution was 301 mg/dm^3. Methylene blue - (N, N, N', N'-tetramethylthionine chloride trihydrate $C_{16}H_{18}ClN_3S$) is s an organic thiazine dye. The structural formula is shown in Figure 1.

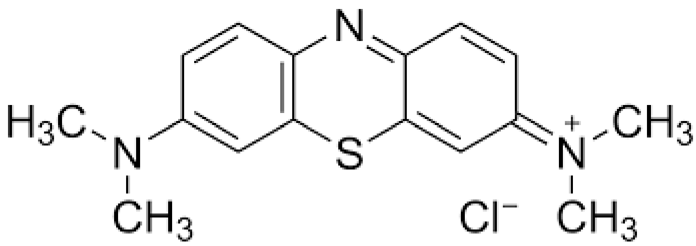

Fig.1. Structural formula of the dye "Methylene blue"

Specific productivity and separation degree of the dye model solution were considered as the main indicators of emulsion membrane separation. Separation degree of the dye model solution was calculated as the ratio of the dye content in solution before and after separation, determined using the spectrophotometer "UNICO 2800", at a wavelength of 585 nm and cell thickness of 10 mm,

The degree of purification from the dyes by the membrane was calculated by the formula:

$$\varphi = (Cf - Cp) / Cf , \quad (1)$$

Where Cf is the concentration of the dissolved substance in the initial solution, and Cp is the concentration of the solute in the filtrate.

The productivity of modified membranes (cm^3/cm^2*min) was determined by passing through them a certain volume of distilled water.

Separation experiments were carried out on a laboratory membrane unit, the scheme of which is shown in Figure 2. The initial solution of the dye is fed to the membrane module (1) with microfiltration membrane. Separation to filtrate and concentrate were made under the influence of pressure, generated by the compressor (5) and registered by the pressure gauge (6). The filtrate is collected in the receiving tank (4), water is collected in the working chamber of the membrane module (1) in the process of separation.

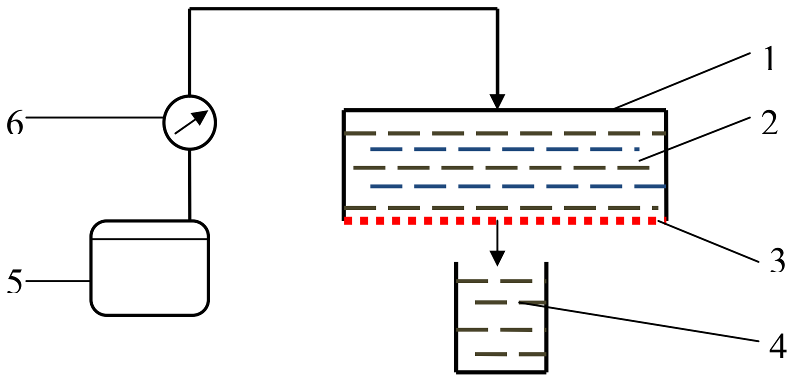

Fig.2. The diagram of laboratory unit for membrane separation: 1 - membrane module, 2 - model dye solution, 3 - microfiltration membrane, 4 - receiving capacity of filtrate, 5 - compressor, 6 – manometer.

In the process of separation of distilled water and model solution of the dye, the working pressure was 0.1 MPa, the temperature of the liquid was 25°C. The type of filtration is a dead end.

3. RESULTS AND DISCUSSION

The surfaces of the original and modified nylon-PANI membranes are enlarged 2500 times and are shown in Figure 3.

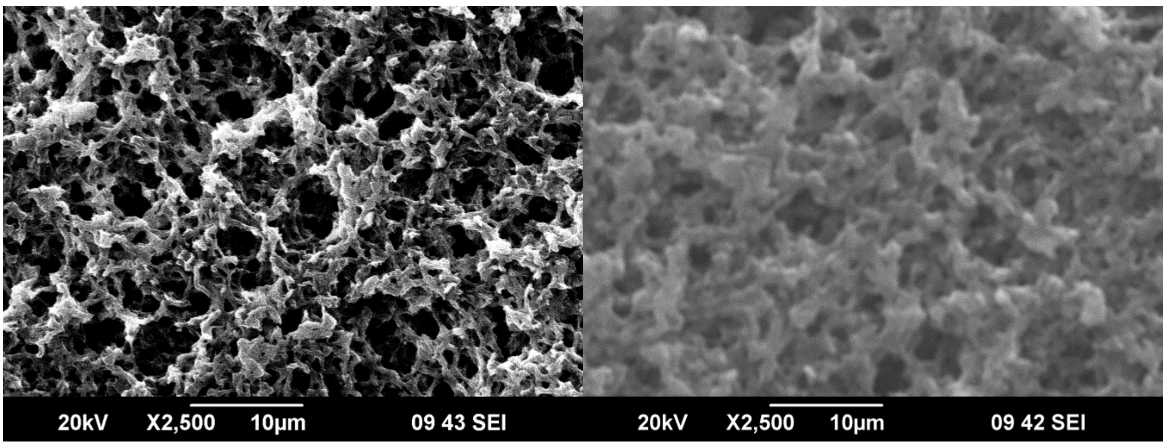

Fig.3. Morphology of surface of the original nylon membrane in an increase of 2500 times (left) and modified nylon-PANI membrane in an increase of 2500 times (right).

As follows from the photographs, the morphology of the original membrane surface has some changes after the treatment. If the initial membrane (Figure 3, left) has many pores, then after modification, the surface of the membrane is covered with a layer of polyaniline. It is also obvious, that the pore size after modification has decreased.

The specific productivity of the initial and modified membranes by distilled water and by the model solution of the methylene blue dye is shown in Table 1.

Table 1. Specific productivity of membranes

Type of membrane	Modifier content, % (by weight)	Specific productivity of membranes, $cm^3/cm^2 \cdot min$	
		by distilled water	by the model solution of dye
Nylon	-	9,3	7,6
Nylon-gelatin	3,2	9,0	7,1
Nylon-gelatin	5,1	8,2	6,8
Nylon- polyaniline	2,5	8,7	7,0

After surface treatment of the original nylon membrane, the specific productivity of the latter is reduced from 3 to 12%, due to the intensive accumulation of gelatin and polyaniline particles in the pores and on the surface of membrane. An increase of gelatin content in the membrane results in a decrease of the specific membrane productivity. The maximum productivity of the initial and dynamic membranes is observed when passing distilled water.

To restore the initial productivity of membranes after filtration of 1 dm^3 model solution of methylene blue dye, the membranes were washed with a 5% solution of sodium dodecyl sulfate and then with distilled water.

The results of water purification from the dye by the initial and modified membranes are presented in Table 2.

Table 2. Degree of purification of the model solution of methylene blue dye

Type of membrane	Modifier content, % (by weight)	Dye concentration in the solution, mg/dm^3		Degree of purification, %
		Initial	After purification	
Nylon	-	301±30,1	160±16,0	46,6
Nylon- polyaniline	2,5		90,0±13,5	70,0
Nylon-gelatin	3,2		27,0±4,05	91,0
Nylon-gelatin	5,1		18,3±2,75	93,8

According to the data in Table 2, modification of nylon membrane results in a detection of dye separation degree. The degree of water purification from the model dye "methylene blue" with the initial membrane is not more than 47%, and after modification of the membrane, depending on the method, the degree of purification from the dye increases to 94%. The maximum degree of purification from the methylene blue dye is achieved with a gelatin modified membrane; with an increase of gelatin content on the surface of membrane, the degree of purification increases.

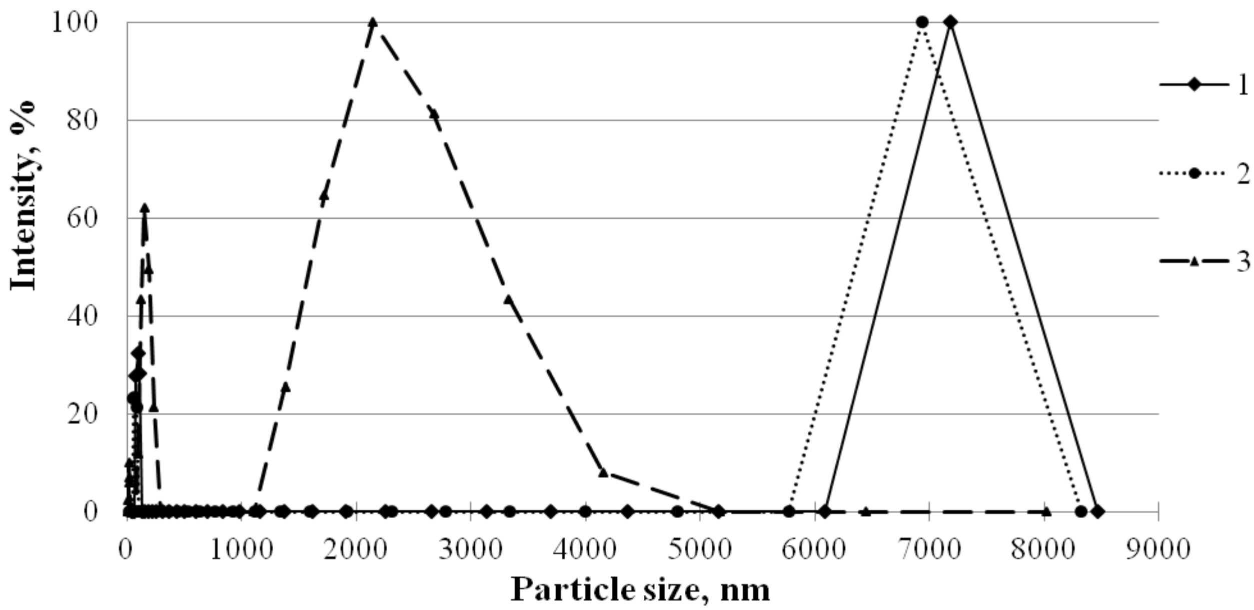

Fig.4. The graph of the distribution of the particle size of the dispersed phase of the initial phase and the filtrates of the "methylene blue" model solution (1-model dye solution, nylon membrane filtrate, nylon-gelatin membrane filtrate).

Table 3. The size of the particles and the ζ-potential of the disperse phase of the "methylene blue" model solution

	Particle size, nm	ζ- potential, mV
Initial dye solution	82-114, 7180	-16,16±1,6
Membrane filtrate - nylon	59-85, 6934	-15,36±1,5
Membrane filtrate - nylon-gelatin	13-26, 99-238, 1384-4153	-17,37±1,7
Membrane filtrate - nylon-polyaniline	9979	-14,7±1,5

According to the data, presented in Figure 4 and Table 3, the particle size of the model dye solution lies in the range 82 - 7100 nm, that corresponds to the working range of microfiltration membranes. After membrane separation, there is the reduction of dye particles size in the suspension, but after the separation of suspension with the nylon-polyaniline membrane, it is observed an increase of particle sizes up to 10 μm. This is due to the ion-exchange properties of polyaniline, the surface of this membrane is positively charged, while the charge of the double electrical layer between the dispersed phase and the dispersion medium is negative. In the process of passage through the pores, the particles acquire a positive charge, and that is confirmed by a decrease in the absolute value of ζ potential, that leads to aggregation of the dye particles and an increase in the particle size of the dye greater than 9,979 nm.

4. CONCLUSIONS

It was determined, that the degree of water purification from the dye "methylene blue" with the initial nylon membrane was not more than 47%, and after modification of the membrane, depending on the method, the degree of purification from the dye increased to 94%. The maximum degree of purification from the methylene blue dye is achieved with gelatin modified membrane. With an increase in gelatin content on the surface of membrane, the degree of purification of the dye increases.

The specific productivity of membranes after chemical treatment has decreased, depending on the processing method, not insignificantly, from 3 to 12%. The particle size of the dye model solution lies in the range 82 - 7100 nm, that corresponds to the working range of microfiltration membranes; for the original membrane - 450 nm. There is a decrease in the size of dye particles in the suspension after membrane separation with nylon and nylon-gelatin membranes; and after separation of the suspension with nylon-polyaniline membrane, there is an increase in particle sizes, up to 10 μm. This is due to the ion-exchange properties of polyaniline. The surface of this membrane has a positive charge. During passage through the pores, the particles acquire a positive charge, which leads to aggregation of the dye particles.

5. ACKNOWLEDGEMENTS

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