Catalytically active membranes for decomposition of organic compounds in aqueous solutions

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Abstract. This work is devoted to the preparation of microfiltration ceramic tubular membranes based on α-Al2O3 with deposited catalytically active layers for use in wastewater treatment processes. Cobalt and manganese oxides were used as the material of the catalytically active layer; deposition was carried out using a mixture of aggregative stable aqueous dispersions of Co3O4 and MnO2 nanoparticles. According to the data of scanning electron microscopy, the thickness of the obtained deposited layers does not exceed 3 μm. X-ray fluorescence analysis confirmed the presence of Mn and Co on the surface of the samples. The resulting membranes with a mass of 10 mg of the deposited layer of the oxide mixture were tested in the methylene blue decomposition reaction in dilute aqueous solutions (1,2 mg/L). The reaction was carried out in a batch reactor at room temperature, complete discoloration of the solution was observed after 180-240 minutes.

Currently, much attention is paid to wastewater treatment. A large number of works are devoted to the development of new materials for purification, including the production of new membranes [1-3], sorbents [4-7], catalysts [8-11], etc. The development of new complex technological solutions is also an urgent way to increase the efficiency of waste and natural treatment [12-16]. One of them is the combination of the technology of membrane treatment from colloidal matter and/or during the separation of emulsions and catalytic post-treatment from organic compounds in dissolved form. The implementation of this process is possible by applying a catalytically active component to the surface of micro- or ultrafiltration membranes.

Tubular ceramic microfiltration membranes based on α-Al2O3, with an outer diameter of 10 mm and a wall thickness of 2 mm, were selected as objects of study in this work. The porosity of the membranes was 45 ± 3%. The most probable pore diameter, determined by the bubble method, lies in the range of 1.6-1.8 μm, while defects were observed in the samples, the diameter of which reached 6 μm. The specific surface area of the original membrane (substrate) was determined for the crushed membrane, fraction 1.0-2.0 mm, by the method of low-temperature nitrogen adsorption on a Gemini 2390t (Micromeritics, USA) specific surface area and porosity analyzer at the Center for Shared Use of the Dmitry Mendeleev University of Chemical Technology of Russia. The specific surface of the crushed substrate was 0.26-0.28 m²/g.
For the deposition of catalytically active layers, materials such as mixed cobalt oxide [8] and manganese dioxide [9] were chosen. It is known that these oxides are successfully used in the decomposition reaction not only in their individual form but also in the composition of one catalytic system [10, 11]. To apply these components, it was decided to use aggregative stable aqueous dispersions of nanoparticles of these oxides. Hereafter, for the sake of brevity, these dispersions will be referred to as “sols”. Sols of cobalt oxide and manganese dioxide were synthesized according to the techniques described in [11, 17].

To obtain manganese dioxide sols, two reagents were selected, which were added to the potassium permanganate solution with rapid mixing: sodium thiosulfate and sodium sulfite. To obtain the deposited layers, we used a sol obtained by mixing newly synthesized Co$_3$O$_4$ and MnO$_2$ sols synthesized by different techniques (hereinafter, the "T" index denotes that the layers were prepared using the MnO$_2$ sol synthesized over sodium thiosulfate, and the "S" index denotes that the layers were prepared using a MnO$_2$ sol synthesized over sodium sulfite). The volume ratio of sols was selected, at which the system retains its aggregate stability for several weeks. The resulting sols were dark brown opalescent liquids. The sol concentration did not exceed 0.01 wt-% in terms of the sum of oxides, the mass ratio [Co$_3$O$_4$]: [MnO$_2$] was 4:1.

It was found that the final pH of the dispersion medium of mixed sols is neutral, for the «Co$_3$O$_4$+MnO$_2$(T)» sols it was 6.4 ± 0.1, and for the «Co$_3$O$_4$+MnO$_2$(S)» sols - 7.3 ± 0.1 pH units. To determine the charge sign on the surface of nanoparticles and the surface of the substrate, the electrokinetic potential was determined on a Photocor Compact Z analyzer (Russia). The operation principle of the device is based on the method of dynamic light scattering in the flow velocity measurement mode (in the laser Doppler anemometer mode). The low concentration of sols made it possible to determine the electrokinetic potential without diluting the systems; in the case of a substrate, the membrane was crushed, pound with a pestle, and the highly dispersed fraction was elutriated. It was found that the sols particles are negatively charged (the magnitude of the electrokinetic potential modulous 30 mV), and in a dispersion medium with a pH of 5.5 to 7.5, the substrate particles are positively charged and the ζ-potential of α-Al$_2$O$_3$ is approximately 10 mV. According to the data of scanning electron microscopy, the average grain size of the substrate is about 15 μm, while according to the data of transmission electron microscopy, the most probable diameter of nanoparticles does not exceed 100 nm (0.1 μm).

The results obtained suggest that when the substrate is brought into contact with the sol, heteroaggregation of nanoparticles will be observed on the substrate surface. Therefore, to obtain functional layers on the surface of ceramic tubular membranes made of aluminum oxide, an analog of the filtration method described in detail in [17] was chosen. The volume of the sol passed through the substrate was selected based on theoretical calculations and then corrected based on the obtained experimental results. Membranes with deposited layers were dried at room temperature. The morphology of the substrates and deposited layers was assessed using microphotographs obtained using a JSM 6510 LV SSD X-MAX scanning microscope (JEOL Oxford Instruments, Great Britain) at the Center for Shared Use of the Dmitry Mendeleev University of Chemical Technology of Russia.

The analysis of the microphotographs showed that the particles of aluminum oxide, from which the carrying agent was formed, are covered with a uniform layer of the applied components with a thickness of about 3 μm; no cracks are observed on the surface. Examples of microphotographs are shown in Figure 1.

The obtained microphotographs show that a deposited layer with a thickness of 1-3 μm is formed on the surface of the substrate. X-ray fluorescence analysis of the membrane surface confirmed the presence of both manganese and cobalt in the deposited layer (see table 1). It should be noted that, for both samples, the cobalt content on the surface is very close, while the manganese content differs almost threefold. This is probably due to the different colloidal-chemical properties of the used manganese oxide sols, but additional studies are required to accurately reveal these regularities. The presence in the samples of aluminum and silicon (elements that make up the substrate) can be explained by the fact that the deposited layer is formed directly on the surface of the substrate grains.
without closing large pores and, accordingly, without changing the fundamentally porous characteristics of the initial membrane.

Figure 1. Microphotograph of the surface (left x100) and cleavage (right x5000) of the deposited \( \text{Co}_3\text{O}_4-\text{MnO}_2 \) layer: a) Sample "T"; b) Sample "S".

Table 1. Data from X-ray fluorescence (XRF) analysis results on the content of chemical elements on the membrane surface.

| Sample | Element, weight % |
|--------|-------------------|
|        | Mn   | Co   | Al  | Si   | O    | C    |
| T      | 6.28 | 26.03| 7.38| 2.38 | 45.30| 12.20|
| S      | 2.98 | 27.18| 7.00| 2.25 | 46.30| 13.68|

The obtained membranes with a mass of 10 mg of the deposited layer of the mixture of oxides were tested in the reaction of decomposition of organic dyes in a batch reactor with a working volume of 250 ml. A methylene blue solution with an initial concentration of 1.2 mg/l was chosen as a model system. The reaction was carried out over \( \text{H}_2\text{O}_2 \) with a concentration of 0.4 M at room temperature and atmospheric pressure. The optical density of the solution was chosen as a control. The results of the
experiments showed that when using the membrane sample "T" complete discoloration of the solution occurs after 180 minutes, and when using the sample "S" – after 240 minutes. By the method of atomic absorption spectroscopy "Quantum Z.ETA" in the Center for Shared Use of the Dmitry Mendeleev University of Chemical Technology of Russia showed that the content of each of the metals in the reaction mixture after the reaction for both experiments does not exceed 3.5 mg/l. The washout of cobalt from the deposited layer does not exceed 4-5 wt-%, and manganese – 7-9 wt%-.

The results obtained showed that these membranes can be used multiple times in a batch reactor or a continuous reactor, combining the stages of filtration and catalytic decomposition.

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