Study of the oxidation process of divalent iron in aqueous solutions during aeration through ceramic membranes modified by layered double hydroxides

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Abstract. The work considers the issues of intensification of the process of purification of natural waters from compounds of bivalent iron, namely the stage of its oxidation. In the experiments, corundum-based ceramic membranes with a deposited layer of aluminum oxide and the same membranes, but modified with layered double hydroxide (LDH) based on the trivalent iron ion, were used as the aerator material. Experiments were carried out to compare the aeration modes for both types of membranes; an aquarium aerator was taken as a comparison. The contribution of the selective layer with LDH to the oxidation rate of bivalent iron by atmospheric oxygen is shown, which confirms its catalytic activity. The process flow diagram of the aerator is proposed.

Today, the use of drinking quality water, as well as process water, provides for several requirements and restrictions on the content of various impurities in it. This led to the emergence of a variety of water purification systems, as well as the development of a specialized constantly growing field in science and industry [1-4]. Thus, various membrane technologies have found wide application: micro-, ultra-, nanofiltration, reverse osmosis, membrane degassing, method of electric deionization, etc. [5, 6]. There are a series of contributions [7-9] in which various inorganic, organic, hybrid materials are used to increase the efficiency of membranes, for example, single-layer graphene, cellulose nanofibers, etc. Although these methods show fairly high efficiency in laboratory settings have a serious drawback in terms of the economic component, as well as the complexity of obtaining such materials, the possibility of scaling up to pilot or industrial production. Layered double hydroxides can become one of the promising materials that can find their application due to their catalytic properties. Layered double hydroxides are known as minerals of the hydrotalcite-manasseite family (kaolin, bentonite, montmorillonite, etc.), therefore, like natural clays, LDH contains simultaneously cationic (hydroxide layers [M₁⁺₂Mₓ³⁺(OH)₂]) and anionic exchange groups, due to the electrostatic interaction
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It is known that for the oxidation of bivalent iron with atmospheric oxygen, to proceed with the following reaction (1):

$$4\text{Fe}^{2+} + \text{O}_2 + 10\text{H}_2\text{O} = 4\text{Fe(OH)}_3 + 8\text{H}^+ \tag{1}$$

and the formation of insoluble trivalent iron hydroxides in [12-14] described a method of forced aeration under pressure using ceramic membranes as a dispersing material for the aeration process. These membranes consist of corundum and have a selective alumina layer. In this work, it is proposed to deposit an additional selective layer of layered double hydroxides.

The selective layer, due to its deposition on an already prepared substrate, depending on the size of the obtained particles, can be used to fill the pores of a macroporous substrate based on alumina. In this case, it is necessary to ensure sufficient filling so that during the purging or regeneration of the membrane, this layer is not washed out of the pores, and the service life of such a membrane is at least a year. The second option for deposition is to obtain a thin film of LDH on the surface. In both cases, the decisive factor is the adhesion of the resulting material to the substrate. Inorganic LDHs are hydrophilic substances, which can, in part, promote the uniform distribution and sufficient coating on the substrate. It is also worth using materials that have an affinity for ceramics, by analogy with oxides, cations of iron, aluminum, magnesium, zinc, chromium can be promising. It is also possible to use nickel, copper, and gallium, but from an economic point of view, the choice of these metals will lead to a significant increase in the price of the final product, therefore, for typical experiments, including with modification, Mg$^{2+}$ is primarily considered as a bivalent metal, and Al$^{3+}$ and Fe$^{3+}$ are considered as a trivalent.

The authors used an approach to create composite membranes with separation into three main components: a porous substrate (mainly from the alpha form of aluminum oxide, which is a macroporous material with open pores), an intermediate layer (also aluminum oxide already with a smaller size of deposited particles and pores, reduces the membrane permeability to microporous), a selective layer (determines the basic filtration properties of the membrane, pores of the smallest size, in particular, due to nanoparticles on the surface, nanofiltration and reverse osmosis membranes can be obtained).

Since the presence of Fe (III) hydroxide can contribute to the full oxidation of Fe$^{2+}$ in the composition of water and its deferrization, being a catalyst for this process [15-20], in this work we used Mg$_2$Fe(OH)$_8$[(CO$_3$)$_{1/2}$mH$_2$O]. The size and shape of the resulting particles were determined by scanning electron microscopy, the particles are «flakes» with an average diameter of 200 nm and a thickness of 15 nm.

Membranes with selective layers with LDH were prepared as follows: at the first stage, suspensions of LDH were prepared in a 10% PVA solution, then the substrate with a deposited intermediate layer (about 5 μm thick) was immersed in the solution for 1 min, dried at room temperature for 24 h, and then at a temperature of 100 °C (6 h). The resulting membrane with a deposited layer of nanoparticles was fired at 200 °C for 6 h in a muffle furnace (heating rate 5 °C/min) until full annealing of PVA and partial annealing of oleate from modified LDHs from the resulting selective layer.

Next, we investigated the effect of an additional selective layer of LDH with Fe$^{3+}$ on the oxidation rate of Fe$^{2+}$ ions. The experiments were aimed at studying the influence of the contribution of the specific surface interface between the phases «water-air» and the factor «surface-water» on the oxidation rate of bivalent iron ions (Figure 1).

As a result of experiments on the oxidation of iron dissolved in water by bubbling air through ceramic membranes modified with Fe$^{3+}$ LDH, it was found that at constant concentrations of bivalent iron and oxygen, the rate of iron oxidation increases.

Based on this, it was assumed that the oxidation of Fe (II) to Fe (III) occurs not only in the volume and at the interface between the gaseous and liquid phases, but also the interface between the solid surface and the liquid phase, and when LDH is deposited to the surface an extended surface with
catalytic properties is formed on the ceramic membrane [13, 20, 21]. At the same time, when compared with similar dependencies for ceramic membranes without a selective LDH layer, in this work, the oxidation rate is significantly higher.

Further, an aerator-bubbler was designed for inclusion in the process flow diagrams of water purification (Figure 2).

**Figure 1.** Dependence of the loss of bivalent iron concentration on time for different aeration devices, with a specific contact area of the «water-air» phases of 350m²/m³ and an initial concentration of bivalent iron of 5 mg/l: 1 - bubbling through ceramic membranes with a selective layer of LDH, 2 - bubbling through ceramic membranes without LDH, 3 - bubbling through the aquarium aerator.

**Figure 2.** Drawing of the developed bubbler.
Hydrogen sulfide removal and additional oxygenation are carried out by fine bubbling of compressed air coming from the compressor receiver with a filter and an oil trap. Figure 2 shows a specially designed bubbler that is used for aeration. It includes 6 aeration elements in the form of 800 mm long porous ceramic tubes each with an outer diameter of 10 mm and a wall thickness of 2 mm, placed in holder pipes with a face seal and slots for the passage of air bubbles. The aeration elements are connected radially in the form of an «asterisk» and descend into the lower part of the tank on a rod, through which compressed air is supplied. The working surface area is 0.15 m$^2$. Compressed air consumption is monitored by the pressure indicated by a manometer. The aerator is supplied with oil and dust-free air. After turning on the aerator, the operating pressure is set to ensure the specified air flow rate. The aerated water is then directed to the storage settling tank, and from it to the supply tank. In these tanks, bivalent iron ions are oxidized by atmospheric oxygen and form molecules of oxides and hydroxides, which form colloidal nanoparticles that aggregate into microparticles. The largest particles sediment to the bottom of the tanks. To remove small particles, microorganisms and reduce the content of other harmful components, water can be directed to the ultrafiltration unit.

The effect of an additional selective layer of LDH with Fe$^{3+}$ on the oxidation rate of Fe$^{2+}$ ions is shown.

It has been suggested that the oxidation of bivalent iron into trivalent iron occurs not only in the volume and at the interface between the gaseous and liquid phases, but also the solid surface - liquid phase interface, and when LDH is deposited to the surface of the ceramic membrane, an extended surface with catalytic properties is formed.

The aerator-bubbler based on tubular ceramic membranes has been designed for the implementation of the aeration process in the water purification process flow diagrams.

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