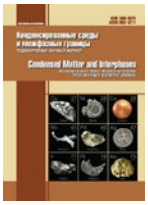

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New nanocomposites for deep water deoxygenation

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Abstract

New metal-polymer nanocomposites for deep water deoxygenation have been obtained and studied. A macro- and monoporous sulphocation exchanger with a nanometer pore size was used as the polymer matrix, and the metal was nanodispersed copper deposited in the pores of the matrix. A specific feature of the studied nanocomposites is their sodium ionic form, which eliminates the possibility of the formation of soluble copper oxidation products. The established linear dependence of the copper capacity on the number of cycles of ion-exchange saturation - chemical deposition shows that the process of metal deposition into the pores of the matrix does not have significant obstacles during 10 cycles and contributes to the production of high-capacity samples.

The high efficiency and duration of the life cycle of high-capacity copper ion exchanger nanocomposites have been shown. Experimental studies of water deoxygenation in column-type apparatus with a nanocomposite nozzle were confirmed by a theoretical analysis of the process dynamics. Experimental data and theoretical calculations showed the deep level of water deoxygenation had practically unchanged values of pH and electrical conductivity. Residual oxygen can be controlled and does not exceed 3 μg/l (ppb).

The hygienic and economic substantiation of the expediency of using the obtained nanocomposites is provided. The necessity of using modern nanocomposite metal-polymer materials for deep water deoxygenation circulating in technological systems was analysed. When using this innovation, the metal components of the distribution facilities will be protected from corrosion and, therefore, the hygienic requirements for the water quality of centralised drinking water supply systems will be ensured. Deep chemical water deoxygenation using copper ion-exchange polymer nanocomposites in sodium form allows solving the problem of the corrosion resistance of metals, ensuring that water meets hygienic requirements on a large scale.

The competitive advantage of the considered water deoxygenation system in comparison with the known systems is the rejection of the use of precious metals-catalysts (palladium, platinum), pure hydrogen, and complex design solutions. The proposed new nanocomposite installation for water deoxygenation is characterised by its ease of use and can be built into a filter system for water purification.

SWOT analysis of the advantages and disadvantages of the proposed method of water deoxygenation showed that its main advantages are the high oxygen capacity of the nanocomposite, low residual oxygen content (3 ppb (μg/l)) in the water, and ease of operation of the deoxygenator. Calculations of the economic efficiency of the nanocomposite have been carried out. The breakeven point is reached when producing only ~100 l of nanocomposite and a volume of sales ~1,600,000 roubles, above which a profit can be obtained. The payback period for an investment of ~15,000,000 roubles is rather short and will not exceed 2 years.

Keywords: Metal-polymer nanocomposites, Water deoxygenation, Hygiene requirements, Economic efficiency

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1. Introduction

The content of molecular oxygen in water to the level required for modern technological processes can be reduced, using traditional methods of deoxygenation: physical, chemical, electrochemical and sorption. It seems expedient to develop and introduce into the practice of water treatment an innovative method of deep water deoxygenation using new nanocomposite metal-polymer materials and evaluate their hygienic and economic efficiency. The proposed approach to water deoxygenation is based on the reduction of oxygen by nanoparticles of reactive metals deposited in porous ion-exchange matrices, with the retention of oxidation products in them.

Metal-polymer nanocomposites are three-dimensional polymer chains of highly porous materials, consisting of a polymer framework, metal nanoparticles, and, as a rule, fixed ionogenic groups and counterions. It is preferable to use macroporous structures with pore sizes up to 100 nm. In macropores, metal nanoparticles (about 10–30 nm) occupy separate areas, localizing near ionogenic groups on the walls and in the volume of macropores. Ion exchange is reversible, due to which multiple depositions of metal into nanopores is possible [1–4]. The size of the metal particles can be controlled [5]. Nanocomposite materials, the outer and inner surfaces of which are open to highly efficient sorption, chemical, and electrochemical processes are obtained [6–10]. The metal in the ion-exchange matrix can be in the form of highly dispersed particles (usually, nanoparticles) in a zero-valent state or be a part of oxides, poorly soluble hydroxides, simple and complex salts, fixed in a polymer matrix. Due to the fact that metal-ion exchanger nanocomposites are capable of simultaneously electron (redox) and ion exchange reactions, they are called electron ion exchangers and belong to the class of redoxites.

Nanocomposite materials based on polymer matrices and precious metals allow reducing the oxygen content in water to the level required for modern technological processes. The achieved high level of control over the properties of nanoparticles synthesised in various matrices clearly indicates good prospects for the use of nanocomposite materials in solving the problem of the deep removal of oxygen from water [11–15]. However, unlike noble metals and pure hydrogen used for these purposes, reactive metals (copper, iron, etc.) in ion-exchange matrices can be more widespread for water deoxygenation [16–18].

The aim of this study was the production of new copper-ion exchange nanocomposites (NC) and the investigation of these NCs for deep water deoxygenation, including the substantiation of the feasibility of their use from a hygienic and economic perspective.

2. Experimental

In order to achieve this aim, metal (Cu°) – sulphocation exchanger (Lewatit K2620) nanocomposites were used. The determination of the content of the metal component was carried out using complexometric titration, the size of metal particles was investigated using scanning electron microscopy (SEM) and X-ray diffraction analysis (XRD), and the composition of grains was determined using energy dispersive X-ray spectroscopy (EDS). The dynamics of water deoxygenation by granular layers of nanocomposites was studied.

The Lewatit K2620 (Germany) sulphocation exchanger, which is a strongly acidic macroporous resin based on cross-linked polystyrene with a spherical shape of granules, containing sulfonic acids, served as an ion-exchange matrix for the preparation of metal-containing NC [19]. It is characterised by its monoporosity. The pore size is strictly fixed (41 nm). The high ion exchange capacity (1.86 meq/cm^3) and the optimal grain radius (0.028 cm) promoted the deposition of metal nanoparticles and the conduction of target process. The high degree of crosslinking in combination with the compact structure of the

granule ensured the chemical and mechanical stability of this material. Metal-containing nanocomposites based on the Lewatit K2620 have a significant adjustable metal capacity.

The synthesis of NC containing dispersed copper can be considered as being the process of ion-exchange saturation of fixed polymer groups with copper from a solution followed by its chemical reduction [7]. A feature of the synthesis in comparison with [20] is the production of NC in the sodium form ensuring the formation of oxide products of copper oxidation with oxygen in the future

$$2[R-SO_3^-]H^+ + Cu^{2+} \rightarrow [R-SO_3^-]_2\,Cu^{2+} + 2H^+, \quad (1)$$

$$[R-SO_3^-]_2\,Cu^{2+} \xrightarrow{Red+OH^-} [R-SO_3^-\,Na^+]_2 \cdot Cu^0. \quad (2)$$

The number of processing cycles regulates the amount of metallic copper in the ion exchanger (from 1 to 10 and more meq/cm^3).

The capacities for metallic copper, the size of copper particles, and the elemental composition of NC were determined. Metal capacity is the main parameter determining the quantitative content of metal in a nanocomposite. In order to determine the amount of copper in NC, the metal was transferred to a soluble state and then its concentration in the solution was analysed.

The particle size of the dispersed metal was determined by X-ray phase analysis and using a JSM 6380LV scanning electron microscope (Japan). For X-ray analysis, copper-containing nanocomposite granules (1 cm^3) was placed in a metal cuvette. In the studied range of diffraction angles, the polymer matrix did not increase the background of X-ray patterns and did not produce its own peaks. X-ray diffraction patterns were obtained using a Thermo ARL X-TRA diffractometer (Switzerland) with MoK_α-radiation, in the range of angles 2θ = 15–40° in scan mode by points with a step of 0.05° and an accumulation time of 3 seconds. Copper powder was used as a reference.

Scanning electron microscopy (SEM) is one of the most widely used methods for the diagnostics of nanomaterials and nanostructures. SEM is a method for analysing the surface structure of micro-objects, based on the interaction of an electron beam with compound, designed for obtaining an image of the surface of an object with a high spatial resolution (several nanometers), providing information about the composition, structure and some other properties of near-surface layers.

The determination of the elemental composition of the sample was carried out using energy dispersive analysis. The method is based on the registration of characteristic X-ray radiation excited by an electron beam. The samples for the energy dispersive analysis were grain sections prepared for SEM. The spectra were recorded using an INCA Energy-250 scanning electron microscope attachment (Great Britain).

For the investigation of the dynamics of oxygen uptake, the installation was designed (Fig. 1), consisting of a direct-flow column *1* filled with a layer of granular nanocomposite *2,* through which water with an oxygen concentration equal to atmospheric concentration was passed. This was achieved by a long preliminary and simultaneous (during the experiment) aeration of the water layer at the inlet. The flow rate of a of the molecular oxygen solution in distilled water was controlled by a flow meter *6*.

The concentration of the oxidant was recorded with an AKPM-01 oxygen analyser (Russia), which was protected from external electromagnetic fields

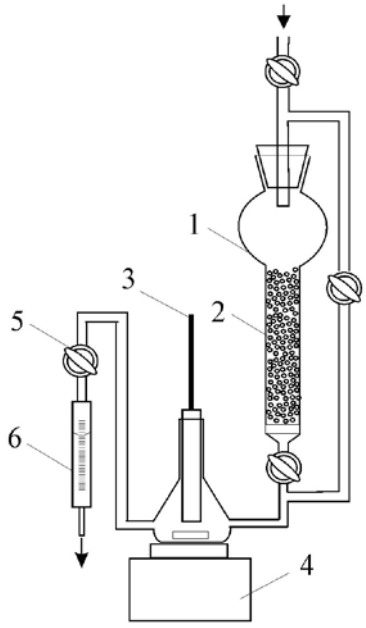

Fig. 1. Diagram of the installation for studying the dynamics of oxygen absorption by the NC layer: *1* - column, *2* – granular layer, *3* - oxygen meter, *4* - magnetic stirrer, *5* - adjustable tap, *6* - water flow meter

by a metal mesh. The maximum permissible error of the analyser in the concentration range of 0–2,000 μg/l and 2–20 mg/l, is ±(2.5+0.025*A) and ±0.025*A, respectively, where A is the readings of the oxygen meter in the selected unit of measurement. Oxygen meter sensor *3* was hermetically attached to a vessel, the water in which was stirred with a magnetic stirrer *4*, which allowed to consider it as an ideal mixing reactor. The individual elements of the installation were interconnected with polypropylene hoses, which minimised the passage of oxygen into the system. After the deoxygenating column, a mixed-bed polisher (MBP) was installed, which trapped impurity particles that could be washed out by passing water. All experiments were carried out at room temperature and under atmospheric pressure.

Simultaneously with the registration of the dynamic output curves of oxygen absorption, the pH and electrical conductivity of the filtered water were monitored. The pH value of water was determined using an ANION-4100 ionomer (Russia). An aqueous sample with a volume of 5 μL for spectral analysis was taken with a micropipette. The values of the electrical conductivity of water were recorded using a Cond 7110 conductometer (Germany). All solutions were prepared using distilled water with a specific electronic conductivity of $5 \cdot 10^{-4}$ S/m at 20 °C.

3. Results and discussion

3.1. Physical and chemical properties of synthesised Cu°·Lewatit K2620 nanocomposites

Cu°·Lewatit K2620(Na^+) nanocomposites with varying copper content were obtained. The dependence of the NC capacity for copper on the number of deposition cycles was obtained (Fig. 2). The capacity increased linearly with the number of fittings. From the linear dependence, it follows that the process of deposition of metallic copper into the pores of NC did not have significant obstacles during 10 deposition cycles.

The rather small particle sizes calculated from the XRD results allowed us to conclude that the globules revealed on SEM micrographs were associates with a size of 100-200 nm, consisting of smaller structures with a size of about 10-30 nm. According to the data of energy dispersive analysis, it was found that the obtained NC with a capacity for copper of 9.80±0.01 meq/cm³

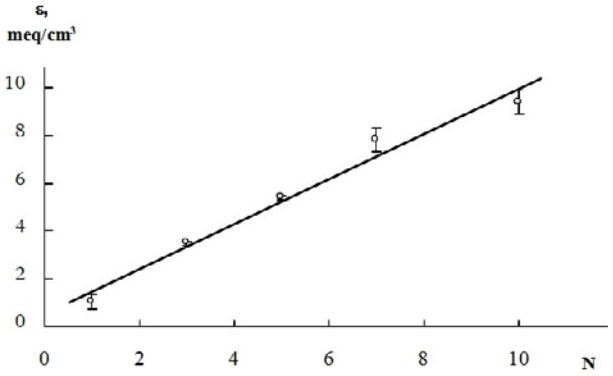

Fig. 2. Dependence of the capacity ε of the Cu°·Lewatit K2620 nanocomposite on the number of N deposition cycles

contained ~18 wt% of copper with predominant localization in the near-surface parts of the grain (Table 1).

Thus, Cu°·Lewatit K2620(Na^+) nanocomposites with a high capacity for the metal component were obtained and characterised.

3.2. Chemical water deoxygenation

The process of chemical water deoxygenation was investigated. The experiment was carried out in two column-type deoxygenators connected in series (Fig. 1) for 150 h. The dimensions of the first deoxygenator were determined by the need to fix the changing digital values on the oxygen sensor for recording of data over time. The height of the first column was $L = 42 \cdot 10^{-2}$ m, section $S = 1.2 \cdot 10^{-4}$ m², the capacity of the NC was $\varepsilon_{Cu^0} = 6.68 \pm 0.08$ meq/cm³ with the number of deposition cycles $N = 7$. Water saturated with atmospheric oxygen was supplied to the deoxygenating unit at a rate $u = 0.33$ cm/s, which was regulated by a pump. The volumetric flow rate

Table 1. The elemental composition of the nanocomposite Cu°·Lewatit K2620 (Na^+) with a capacity of 9.80±0.01 meq/cm³ depending on the radial distribution over the grain R/R_0, R_0 is the grain radius

Element	Weight %			Average weight %
	$R/R_0 = 0$	$R/R_0 = 0.5$	$R/R_0 = 1$	
Cu	5.13	13.97	34.09	17.73±16.79
C	38.06	35.57	37.87	37.17±1.57
O	17.55	14.46	11.69	14.63±3.32
Na	7.14	5.65	3.36	5.38±2.15
S	8.68	6.94	4.05	6.56±2.65

was accordingly u = 0.40 cm³/s (1.43·10⁻³ m³/h). The water passing through the first deoxygenator entered the second deoxygenator, which further purified the water at the outlet. The total height of this filter was L = 28.5·10⁻² m, filter section S = 6.83·10⁻⁴ m², water flow rate u = 0.058 cm/s, the volumetric flow rate, respectively, was u = 0.40 cm³/s (1.43·10⁻³ m³/h), the capacity of the nanocomposite was ε_{Cu^0} = 9.38±0.01 meq/cm³ with the number of deposition cycles N = 10.

The results are presented in Table 2. As can be seen, the oxygen concentration in the water at the outlet of the first deoxygenator significantly decreased from 4 - 6 mg/l to 0.1 - 0.3 mg/l and after the second filter reached 0.00 mg/l with practically unchanged pH and electrical conductivity of water. Fluctuations in concentration (Fig. 3) were most likely caused by periodic stoppages of the experiment and the associated suction of oxygen through the connecting hoses. The amount of absorbed oxygen naturally increased with time in both deoxygenators.

Table 2. Experimental data on the reduction of oxygen dissolved in water at the outlet of the first and second deoxygenators with granular layers of Cu^0Lewatit (Na^+) nanocomposite

Time, h	O_2 concentration in the water at the inlet C_0, mg/l	O_2 concentration in the water after the first layer C_1, mg/l	O_2 concentration in the water after the second layer C_2, mg/l	Water pH at outlet	Water conductivity at the outlet æ, mS/cm
0	4.22	3.22	4.60	6.9	1.9
5	4.66	0.08	0.12	7.1	2.2
10	4.70	0.08	0.06	7.7	2.3
15	4.70	0.17	0.00	7.6	1.7
20	4.82	0.08	0.00	7.4	1.8
30	4.88	0.30	0.01	7.0	2.2
40	4.78	0.09	0.03	7.4	1.9
50	4.68	0.19	0.08	7.1	1.7
60	4.80	0.34	0.03	6.8	1.7
70	5.19	0.23	0.03	6.7	1.8
80	5.43	0.43	0.00	7.0	2.0
90	5.53	0.17	0.01	7.1	2.1
100	5.55	0.05	0.03	6.9	2.0
110	5.31	0.47	0.00	7.1	2.5
120	5.76	0.09	0.00	7.3	2.3
130	5.77	0.67	0.00	7.2	2.2
140	5.80	0.66	0.00	7.0	2.0
150	5.75	0.51	0.00	7.1	2.1

The theoretical analysis of the dynamics of oxygen uptake on the first and second deoxygenators was carried out using a software product (Mathcad), based on a mathematical model of external and internal diffusion and a staged oxidation reaction [21]. The data used for the calculation are shown in Table 3. The theoretical dependence of the relative concentration of oxygen in water at the outlet of the 1st deoxygenator is shown in Fig. 4. The dependence shows after what time of the experiment the oxygen concentration will decrease from C_0 = 5.0 mg/l to C_1 = 0.3 mg/l and will reach $C_{lim} = C_1/C_0$ = 0.06. The service life of the first deoxygenator was 152 h, which is consistent with the experiment and allows theoretical estimates of a longer life cycle of the nanocomposite in the second deoxygenator.

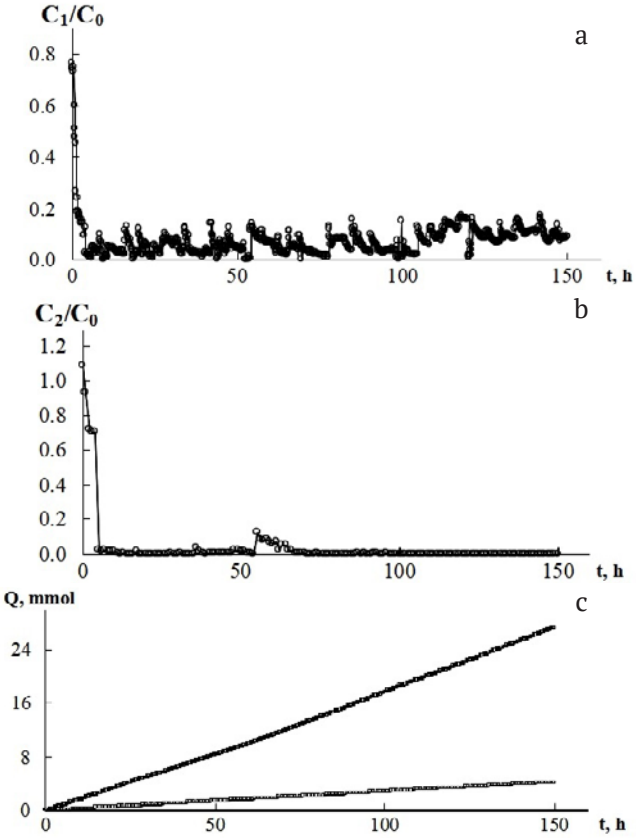

Fig. 3. Kinetic dependences of the relative oxygen concentration at the outlet after the first deoxygenator C_1/C_0 (*a*), after the second deoxygenator C_2/C_0 (*b*), the amount of Q (*c*) absorbed oxygen from the water after the first (*1*) and second (*2*) deoxygenators

Table 3. Technological characteristics of the water deoxygenation plant

Chemical deoxygenator No. 1	
1. Grain layer height L, m	0.42
2. Sectional area of the layer *S*, m^2	$1.2\cdot10^{-4}$
3. The radius of the nanocomposite grains R_0, m	$2.8\cdot10^{-4}$
4. Loading volume of nanocomposite in one column, m^3	$50.4\cdot10^{-6}$
5. Grain filling ratio of the column, χ	0.70
6. Ion-exchange capacity of NC for hydrogen per bulk volume, meq/cm^3	1.86
7. Capacity ε_{Cu^0} for copper per bulk volume, meq/cm^3 (mol/l)	6.68±0.08 (1.67)
8. Water flow rate l/h (cm/s)	1.43 (0.33)
9. Oxygen concentration in water at the inlet to the first deoxygenator C_0, mg/l (mol/l)	5.01±0.39 ($1.56\cdot10^{-4}$)
10. Oxygen concentration in water at the outlet of the first deoxygenator *C*(*L*), mg/l (mol/l)	0.30 ($0.9\cdot10^{-5}$)
11. Deoxygenator service life, theoretically calculated, h	126
Chemical deoxygenator No. 2	
1. Grain layer height L, m	0.285
2. Sectional area of the layer *S*, m^2	$6.83\cdot10^{-4}$
3. The radius of the nanocomposite grains R_0, m	$2.8\cdot10^{-4}$
4. Loading volume of nanocomposite in one column, m^3	$198\cdot10^{-6}$
5. Grain filling ratio of the column, χ	0.70
6. Ion-exchange capacity of NC for hydrogen per bulk volume, meq/cm^3	1.86
7. Capacity ε_{Cu^0} for copper per bulk volume, meq/cm^3 (mol/l)	1.43 (0.058)
8. Water flow rate l/h (cm/s)	9.38±0.01 (2.37)
9. Oxygen concentration in water at the inlet to the first deoxygenator C_0, mg/l (mol/l)	5.01±0.39 ($1.56\cdot10^{-4}$)
10. Oxygen concentration in water at the outlet of the first deoxygenator *C*(*L*), mg/l (mol/l)	0.003 ($0.9\cdot10^{-7}$)
11. Deoxygenator service life, theoretically calculated, h	1258

The theoretical dependence of the relative concentration of oxygen in water at the outlet from the second deoxygenator is shown in Fig. 5. The dependence shows after what time of the experiment the oxygen concentration will change from C_0 = 5.0 mg/l to C_1 = 0.003 mg/l and will reach $C_{lim} = C_2/C_0$ = 0.0006. Since the operating time of the first deoxygenator is relatively short, after 152 h only the second deoxygenator remained in operation. However, due to the different column

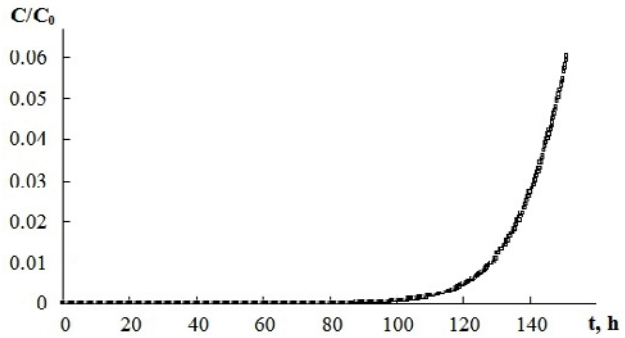

Fig. 4. Theoretical dependence on the time of the relative concentration C/C_0 of oxygen dissolved in water at the outlet of the 1st deoxygenator

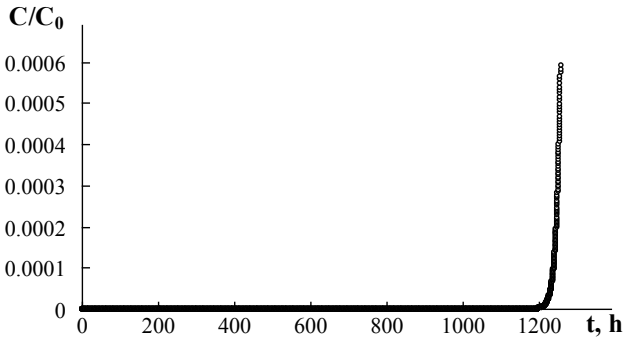

Fig. 5. Theoretical dependence on the time of the relative concentration C/C_0 of oxygen dissolved in water at the outlet of the 2nd deoxygenator

parameters, the water flow rate, and also the higher capacity of the NR for copper, the second deoxygenator gives a low oxygen concentration (up to 0.003 mg/l) for a significant period of operation (1,258 h).

The main result achieved (Table 4) indicates that the first deoxygenator deoxygenates water by 94% within 152 h. Then the concentration in it will increase and will soon reach the initial one, i.e. the first deoxygenator will stop deoxygenating the water, and the entire load will be on the second deoxygenator, the operating time of which will be ~ 1,260 h and can be adjusted by the size of the column commensurate with the wear of all filters in the purification system. The degree of deoxygenation will be 99.99%, residual oxygen will be 0.003 mg/l (3 ppb).

A copper-ion-exchange nanocomposite was used in the sodium ionic form, in which the process of oxygen absorption occurs to solid-phase oxides of mono- and bivalent copper, which is clearly recorded on the cuts of NC grains. The processes take place along sequential routes without the participation of sodium counterions

Table 4. Results of laboratory tests of the deoxygenators

Deoxygenator	O_2 concentration at the inlet C_0, mg/l	O_2 concentration at the outlet C, mg/l	C/C_0	Experiment time t_{exp}, h	Theoretically calculated time of continuous operation t, h	$\frac{C_0 - C}{C_0}$, %
1	5.01±0.39	0.30	0.06	150	152	94.01
2	5.01±0.39	0.003	0.0006	150	1258	99.99

$$4Cu + 4OH^- = 2Cu_2O + 2H_2O + 4e^-,$$
$$O_2 + 2H_2O + 4e^- = 4OH^- \quad (3)$$

and

$$2Cu_2O + 4OH^- = 4CuO + 2H_2O + 4e^-,$$
$$O_2 + 2H_2O + 4e^- = 4OH^-. \quad (4)$$

General scheme

$$Cu + O_2 \rightarrow Cu_2O \rightarrow CuO \quad (5)$$

shows the path of chemical water deoxygenation due to the oxidation of copper nanoparticles deposited in the pores of the ion-exchange matrix in the sodium form.

Thus, the deep removal of corrosive dissolved oxygen ensures that the water meets hygienic requirements (Appendix 1). The economic efficiency of the life cycle of a new nanocomposite material is considered in Appendix 2.

Appendix 1

Hygienic aspect

The quality of drinking water is an environmental factor that largely determines the health and standard of living of the population. Improving the quality of drinking water is a priority designated by the Decree of the President of the Russian Federation "On national objectives and strategic aims for the development of the Russian Federation until 2024". As part of the implementation of the federal project «Clean Water» Rospotrebnadzor in 2019 developed and approved Methodological Recommendations MR 2.1.4.0143-19 «Methodology for assessing the quality improvement of drinking water supplied to centralised water supply systems.»

According to reports [22, 23] on the state of the sanitary and epidemiological well-being of the population in the Russian Federation and, in particular, based on the example of the Voronezh region, positive dynamics in water quality from centralised water supply sources and distribution facilities were noted.

The share of centralised drinking water supply sources in Russia that do not meet sanitary and epidemiological requirements decreased in 2019 compared to 2012 (the growth rate is –5.27%) and amounted to 14.93%. In the Voronezh Region, all sources of centralised drinking water supply met sanitary and epidemiological requirements in 2019. The share of the population of Russia and the Voronezh Region provided with quality drinking water from centralised water supply systems was 85.5 and 88.3%, respectively.

According to data on the state of water from centralised water supply sources in Russia [22], the proportion of water samples that do not meet the requirements for sanitary and chemical indicators decreased during 2012–2019 from 28.63 to 25.71% (by 2.92%), for microbiological indicators it decreased from 5.47 to 4.12% (by 1.35%). The share of water samples from the distribution facilities that do not meet the standards for sanitary and chemical indicators decreased from 16.68 to 12.38% (by 4.3%), for microbiological ones it decreased from 4.45 to 2.68% (by 1.77%).

As part of the implementation of the federal project «Clean Water» within the territory of the Voronezh Region, there is a state program «Provision of high-quality housing and communal services for the population of the Voronezh Region» (for the period until 2025). Water supplied to the population for drinking needs must meet hygienic requirements, which are formulated in the Sanitary Rules and Norms "Drinking Water. Hygienic requirements for the quality of water from centralised drinking water supply systems. Quality control" (SanPiN 2.1.4.1074-01), introduced in 26.09.2001. A positive trend was revealed by the analysis of data on the quality of drinking water from centralised water supply sources in the Voronezh region [23]: the proportion of water samples that do not meet hygienic requirements for sanitary and chemical indicators decreased from 44.4 to 36.0%, in terms of microbiological indicators it decreased from 2.0 to 1.6% over the period 2012-2020. In the distribution facilities of the centralised water supply of the region, the proportion of drinking water samples that do not meet hygienic standards in terms of sanitary and chemical indicators decreased from 28.0 to 12.7%, in terms of microbiological indicators it decreased from 1.7 to 0.8%.

Despite the positive dynamics, in the Voronezh region there is water of low quality due to both natural (increased content of iron, manganese, boron, hardness salts) and man-made factors (anthropogenic pollution of groundwater; high deterioration of water supply networks). The solution to this problem requires environmentally oriented management methods; technical improvement, repair and replacement of treatment facilities, distribution facilities and, finally, introduction of more advanced innovative methods of water treatment, in particular, the use of nanocomposite metal-polymer materials for deep water deoxygenation. The latter is very important, since dissolved oxygen contained in water is an impurity competing and corrosive agent, damaging equipment and pipelines, causing significant damage to metals and alloys, and reducing the quality of water supplied to the population [24, 25]. As a result, heavy metals such as iron, zinc, copper, and others appear in drinking water, which have a toxic effect on the human body. Iron and manganese, found in high concentrations in drinking water, cause allergic reactions, skin and subcutaneous tissue diseases, and

increase the risk of blood diseases. In addition, the presence of molecular oxygen in water intended for the manufacture of pharmaceutical dosage forms is undesirable.

The result of deep deoxygenation of water achieved in this study using an innovative technology based on modern metal-ion-exchange nanocomposites provides a solution to these problems.

Appendix 2

Economic efficiency of the life cycle of a new nanocomposite material

For the calculation of the economic efficiency of a new nanocomposite material, SWOT analysis was used as an analysis of a business in the context of a market environment. It consisted of a study of the advantages and disadvantages to the business, in addition, it determines the possibilities for the successful functioning of the organization under current and forecast market conditions [26].

After analysing the advantages and disadvantages (Tables 5 and 6), we can conclude that the main competitive advantages are:

– high oxygen content;
– low residual oxygen content (3 ppb (μg/l));
– and ease of use of the filter.

It is also necessary to create such favourable conditions that would allow the further development of an innovative project and increase its competitiveness. It is necessary to cope with such risks as the lack of investors (to present the project in a way that it will interest potential consumers).

At the beginning of the development of the release of new products, the production process is characterised by high costs of labour, material, and other resources. As the number of manufactured products increases, the technological process is stabilised, technological and other shortcomings are eliminated, and production links are established. During this period, various technical and organizational measures are actively carried out, which reduce the destabilizing influence of factors in the process of the release of new products. As a result, the technically required values of resource consumption are established, the costs are gradually reduced and reach the required value at the level of technically justified norms.

We will calculate the cost of the material (Table 7). The laboratory will be able to produce 200 litres of the material per month. Therefore, 2,400 litres per year. The price also includes control of the properties of the obtained products and conditioning (preparation of an ion-exchange basis for the introduction of metal).

Property control involves the following analyses:

– analysis for the amount of copper in the sample; it should be performed 3 times, i.e. the total cost increases by 900 roubles;

– acidity analysis; it should be performed 12 times, i.e. the total cost will increase by 600 roubles;

– analysis for copper ions; one analysis costs 50 roubles; it should be performed 12 times, i.e. 600 roubles.

Table 5. Consumer advantages of the development in comparison with analogues

Property	Traps for removing oxygen from chromatographic columns (Cheminst) [27]	Catalysts containing palladium (Lanxess) [28)]	The proposed nanocomposite, containing copper
The use of additional reagents	No	Requires a constant hydrogen supply	No
Application area	For chromatography only	Wide range of applications	Wide range of applications
Regeneration	Not regenerated	Not required	Regeneration is only required after the entire filter has been used up
Deoxygenation depth	1 ppb (μg/l)	< 20 ppb (μg/l)	3 ppb (μg/l)
Lifetime without regeneration	–	5 years	5 years

Table 6. Strategic planning (SWOT analysis)

Strengths and weaknesses	Opportunities and threats
Strengths: – a material that can be used for water deoxygenation filters has been developed; – oxygen is removed using sorbents; – deep cleaning, product purity, simplicity; – high oxygen sorption capacity; – high service life (5 years); – ease of filter regeneration; – high motivation for the rapid achievement of commercial success; –application in many areas.	Opportunities: – is able to deeply deoxygenate water without precious metals and pure hydrogen; – it is able to retain its properties and characteristics for several years under a layer of water; – creation of favourable conditions for the development of an innovative project; – increasing competitiveness.
Weaknesses: – the need for regeneration of the sorbent; – lack of funds for promotion.	Threats: – financial instability (possible changes in taxation, inflation); – lack of investors; – inflexible response to the market situation; –immunity to innovations.

Table 7. Cost of reagents for 1 litre of NC

Reagent	Price + VAT (20%), Roubles/kg	Place of purchase	Required amount, kg	Cost of goods + customs duties (25%), rub.
Cation exchanger Lewatit K-2620	490	Lanxess	1	610
Cation exchanger KU-2*8	144	Vekton	0.5	79
Anionite AV-17-8	336	Vekton	0.5	185
Sulphuric acid, reagent grade	94	Vekton	1	113
Sodium hydroxide, reagent grade	180	Vekton	1,25	248
Copper sulphate pentahydrate, pure grade	580	Vekton	4	2552
Sodium dithionite, Germany	852	Vekton	3	2811
Total				6596

Reagents and work on treating the starting material for the synthesis of the filler is estimated at 550 roubles. The material production requires equipment - special columns made only to order. They can be made of clear plastic or glass. Two columns are required. The cost of one column is 9,000 roubles. Their useful life is 5 years.

The equipment is capable of producing 200 litres per month. In the linear method, accrual of depreciation is performed by equal instalments over the entire useful life of fixed assets. Depreciation rate (H_{dep}) is calculated as a percentage of the original (reinstatement) value of the property [29]:

$$H_{dep} = (1/n) \cdot 100\% \quad (6)$$

where n – useful life of the equipment (months or years).

Depreciation rate: 1/(5*12) * 100% = 1.66666 %/month.

The cost of two columns is 2 * 9,000 = 18,000 roubles.

Monthly depreciation: 18,000*1.66666%/100% = = 300 roubles/month.

Amount for the year of depreciation: 300 * 12 = = 3,600 roubles/year.

Linear method:

– at the end of the 1st year: 18,000 – 3,600 = 14,400 roubles;

– at the end of the 2nd year: 14400 – 3,600 = 10,800 roubles;

– at the end of the 3rd year: 10800 – 3,600 = 7,200 roubles;

– at the end of the 4th year: 7200 – 3,600 = 3,600 roubles;

– at the end of the 5th year: 3,600 – 3,600 = 0.

The rent of premises will be also required. Cost of 1 sq. meter is 400 roubles. The premises of 20 sq. meters is required. Therefore, 400 * 20 = 8,000 roubles. [30]. Two workers will be required. The salary of one worker is 20,000 roubles per month.

Social security contributions include [31)]:
– contributions to the Social Insurance Fund (2.9%) – 1,160 roubles;
– contributions to the Pension Fund (22%) – 8,800 roubles;
– contributions to the Federal Compulsory Medical Insurance Fund (5.1%) - 2,040 roubles.

Total deductions for the unified social tax (UST) amount to 11,000 roubles. Thus, the wages of production workers are 51,000 roubles (Table 8).

For technical and industrial goods sold to the population, a surcharge of no more than 25% is applied (12,403*25/100 = = 3,101 roubles). Thus, the price of material for 1 litre will be 15,504 roubles.

In order to sell the fillers, a small business enterprise in the form of IP should be registered. It will cost 3,500 roubles. The first batch will be a trial run. Possible risks in the implementation of the project are equipment stoppage, financial crisis, and lack of funding. Potential consumers are companies producing equipment for water and waste water treatment: GIDROTECH, Bayer, Creminst, National Water Resources, Kontur-Aqua, and others.

It is necessary to calculate the minimum volume of production at which the costs will be offset by income, and with the production and sale of each subsequent unit of production, the enterprise begins to make a profit. Therefore, you need to determine the breakeven point.

200 litres will be produced per month.

Fixed costs:
– depreciation (RUB 300);
– rental of premises (8,000 roubles);
– salary (51,000 roubles);
– VAT (RUB 396,400);
– commission (190,800 roubles).

Therefore, the planned fixed costs are 646,500 roubles per month.

Variable costs:
– raw materials and supplies (6,596 roubles);
– quality control (2,100 roubles);
– air conditioning (550 roubles).

Therefore, the planned variable costs will be 9,246 roubles per 1 litre (hence, 1,849,200 roubles per month).

The breakeven point in monetary terms is the minimum amount of income at which all costs are fully paid off [32]:

$$\text{BEP} = \frac{Zfix}{(B - Zvar)} * B, \quad (7)$$

where BEP – breakeven point; Z_{fix} – the amount of fixed costs per month; Z_{var} – the amount of variable costs per month; B – revenues from sales:

$$\text{BEP} = \frac{646500}{(3100800 - 1849200)} * 3100800 =$$

$$= \frac{646500}{1251600} * 3100800 = 1601683 \text{ roubles.}$$

This is the minimum amount of income at which all costs are fully paid off.

Table 8. Total cost of production for 1 litre of NC

Name of cost elements	Price in rub.
Depreciation	1.5
Material costs	6,596
Wages of production workers with accruals	255
Other expenses	
Premises for rent	40
Property control	2,100
Conditioning	550
Total	9,541
VAT 20%	1,982
Commission 10%	954
Total	12,477

Breakeven point in units of production:

$$\text{BEP} = \frac{TFC}{P - VC}, \quad (8)$$

where *TFC* - the amount of fixed costs; *VC* - the variable costs per unit of production; *R* - unit cost.

$$\text{BEP} = \frac{646500}{15504 - 9246} = \frac{646500}{6258} = 103 \text{ l.}$$

This is the minimum amount of products at which the income from the sale of this product will completely cover all the costs of its production (Fig. 6).

The breakeven point is reached at 103 litres of products and sales of 1,601,683 roubles.

We will calculate the planned volume of product sales and profit for the month:

Price × Volume = Variable unit costs × Volume + Fixed costs + + Profit:

15,504×200 = 9,246×200 + 646,500 + Profit

3,100,800 = 1,849,200 + 646,500 + Profit

Profit = RUB 605,500 per month.

Planned sales volume = 3,100,800 roubles

Payback period = Investment / (Annual net profit + Annual depreciation) = 14,539,200/(605,500×12 + 3600) = 2 years, i.e. it has a relatively short duration.

The fact that the used nanocomposite can be regenerated and reintroduced into production should be taken into account.

4. Conclusions

New copper-ion-exchange nanocomposites in the sodium ionic form were obtained by ion-exchange saturation and chemical deposition. These nanocomposites are characterised by a narrow range of sizes of base metal particles and capable of reducing oxygen dissolved in water with the formation of solid-phase oxidation products. The cyclic process of ion exchange saturation - chemical deposition leads to a linear

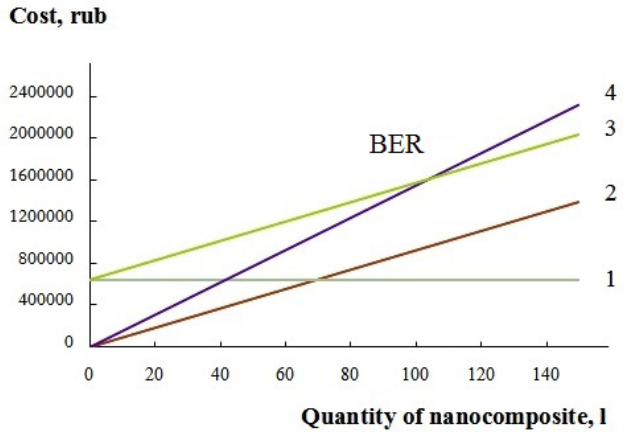

Fig. 6. The dependence of the cost on the amount of nanocomposite. *1* - fixed costs, *2* - variable costs, *3* - total costs, *4* - income, BEP - breakeven point

dependence of the copper capacity on the number of cycles and allows obtaining high-capacity samples.

Experimental data on the dynamics of oxygen absorption by granular layers of columnar nanocomposites have been obtained. The correspondence of the experimental output curves with curves theoretically calculated according to the previously proposed mathematical model of dynamics, based on external and internal diffusion and a sequential chemical oxidation reaction, has been established. The experiment and calculation show the attainability of a deep level of water deoxygenation with practically unchanged pH and electrical conductivity values. Residual oxygen can be controlled and does not exceed 3 μg/l (ppb).

The hygienic and economic substantiation of the expediency of using the obtained nanocomposites is provided. Deep chemical water deoxygenation using copper-ion-exchange nanocomposites in sodium form allow solving the problem of the corrosion resistance of metals, ensuring the compliance of water with hygienic requirements on a large scale.

The competitive advantage of the considered water deoxygenation system in comparison with the known systems is the rejection of the use of precious metals-catalysts (palladium, platinum), pure hydrogen, and complex design solutions. The proposed new nanocomposite installation for water deoxygenation is characterised by its ease of use and can be built into a filter system for water

purification. The breakeven point is achieved with the production of ~100 litres of nanocomposite and a sales volume of ~1,600,000 roubles, above which a profit can be obtained. The payback period for an investment of ~15,000,000 roubles is rather short and will not exceed 2 years.

Author contributions

All authors made an equivalent contribution to the preparation of the publication.

Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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