THE ALTERNATIVE METHOD OF CONDITIONING INDUSTRIAL WASTEWATER CONTAINING HEAVY METALS BASED ON THE HYDROTHERMODYNAMIC CAVITATION TECHNOLOGY

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Abstract. This article provides the results of studies of modifying the physicochemical properties of industrial wastewater when treated in a cavitation reactor. The authors performed an analysis of physicochemical changes in the makeup of industrial effluent and defined the efficiency of reducing the content of heavy metal ions under various modes of hydrothermodynamic action. The article also proposes the methods of mathematical modelling for determining the optimal parameters of cavitation treatment of wastewater and reveals the advantages of upgrading the wastewater process equipment with the inclusion of a unit of SC-reactors.

Keywords: industrial wastewater, heavy metals in effluents, cavitation, cavitation technology, recirculating water management, industrial wastewater treatment.

1. Introduction.
Currently, the environmental legislation, both of the Russian Federation and other countries of the world, imposes strict requirements on the methods of treatment and disposal of industrial wastewater. These requirements aim at reducing the negative environmental impact of industrial effluents on water bodies. Modern wastewater treatment technologies, both domestic and foreign, make it possible to achieve almost any degree of purification, however, the use of chemicals and the large volume of purification by-products (precipitates) make it impossible to consider the available technologies as environmentally friendly and economically feasible. In most countries, industrial enterprises are required to introduce recirculating water use, and, respectively, enterprises are revising low-efficient standard methods for conditioning industrial effluent and searching for alternative methods for wastewater treatment. The issue of the greatest relevance is treatment of effluents containing heavy metal ions. As a rule, such wastewater is typical for industrial enterprises of instrument engineering, mechanical engineering, metallurgy, chemical and pulp and paper industries. Heavy metals pose a serious environmental and toxicological threat, their negative impact on human physiology has been repeatedly noted.

At local wastewater treatment facilities, the above enterprises prevalently apply the chemical methods for purifying their effluents. Unfortunately, these methods do not allow reaching the efficiency of treatment which will comply with the standards permitting to discharge the treated effluent into fishery water bodies, or into centralised public sewers, but, moreover, the residual concentrations are too high to use this effluent as treated process water and form recirculating water use systems. It is important that the presence of heavy metal ions can affect pH and electrical conductivity of the solution, and chemical compounds negatively affect the work of the utility systems: undergoing hydrolysis, they can act as strong acids, intensify frothing of the effluent, and participate in scaling [1]. In this regard, it is expedient to develop and introduce into production alternative
nonchemical innovative and highly effective methods of treatment of wastewater containing heavy metal ions. Such methods can include effluent treatment based on the effects of hydrothermodynamic cavitation.

The research objective is to identify the patterns of modifying the physicochemical parameters of water when exposed to hydrothermodynamic cavitation, to scientifically justify and develop a nonchemical technology for treating wastewater containing heavy metal ions using the methods of cavitation impact that occur on the phase boundaries in the medium being studied and to select optimal modes of cavitation treatment of wastewater in order to purify it effectively.

Method and methodology of work. The methodological base is the experimental methods of thermodynamic, kinetic and production research. Laboratory and bench semi-industrial cavitation installations have been used as an empirical base of research. When studying the effluent treatment efficiency, we used standard water quality assessment methods based on Russian state standards GOST 25150-82 and GOST 17.1.1.01-77, Natural Conservation Federal Statutory Document (CFSD) 1412.16.1-10, 14.1:2.105-97, and 14.1:2.4.214-06, as well as the methods of VBA-mathematical modelling and interpretation of the research results.

2. Results and discussions.

The change in the physicochemical properties of a liquid during hydrothermodynamic cavitation is based on high concentration (accumulation) of energy in a very small volume of a gaseous or liquid medium, followed by its release in a critically short period. The physical characteristics of a liquid have a different effect on the intensity of cavitation impact, increasing or decreasing the velocity of cumulative jets near solid boundaries of the flow. This effect especially strongly recoils upon the last stage of the collapse of the bubbles, when their sizes are very small. A rise in viscosity and density reduces the intensity of cavitation action — surface tension forces accelerate the collapse of bubbles, while dissolved and undisolved gases in the liquid slow down this process, damping the collision of the walls of the bubble. Therefore, degassing of the liquid is one of the ways to intensify cavitation. Changing the conditions of technological processes can also significantly affect the intensity of cavitation impact, and therefore the corresponding process rate. For example, lowering the temperature and pressure of saturated vapours increases the intensity of cavitation impact. A rise in pressure increases the velocity of the cumulative jet when the bubble collapses, however, with a significant increase in static pressure, it is difficult to obtain the modes of a developed cavitation.

The time of cavitation treatment also ambiguously affects the final result. Not always an increase in treatment time leads to an increase in the operational benefit. Therefore, applying hydrodynamic cavitation, it is necessary to take into account both the physical properties of liquids and the conditions of a specific technological process: pressure, temperature, treatment time, stream turbulence, solid particles, etc. The object of the research was industrial wastewater, the core physical and chemical indicators of which were obtained on the basis of quantitative chemical analysis of wastewater from the workshops of an instrument-making plant. Initial concentrations of pollutants and the requirements for residual concentrations of treated effluent for the purpose of its reuse are shown in Table 1.

| Index | Initial concentration mg/dm³ | Requirements for circulating process water of instrument-making enterprises |
|-------|-----------------------------|----------------------------------------------------------------------------|
|       |                             | IST 11.029.003-80 TYPES | ASTM D-5127-90 TYPES |
|       |                             | A | B | B | E-1 | E-2 | E-3 | E-4 |
| Cu    | 3.94                        | 0.002 | 0.002 | 0.003 | 0.001 | 0.001 | 0.002 | 0.5 |
| Fe    | 13.7                        | 0.015 | 0.02 | 0.03 | - | - | - | - |
| Ni    | 408.5                      | 0.1 | 1 | 2 | 500 |
| Mn    | 0.032                      | - | - | - | - | - | - | - |
As it has been mentioned above, hydrothermodynamic cavitation has been proposed as an alternative method of purifying water from heavy metal ions. At the same time, we used two independent research lines at different types of supercavitation reactors (SC-reactors). This formulation of the research problem concerning the effect of hydrothermodynamic cavitation on wastewater enabled obtaining the most adequate results on the reproducibility of the experimental conditions, and also made it possible to measure physical parameters in the cavitation area. Note, that the physicochemical effects are identical regardless of the method of excitation of cavitation, which is undoubtedly important when choosing SC-reactors for certain technological solutions.

It has been proved by [1–5] that complex physicochemical processes run under the conditions of hydrothermodynamic cavitation. These processes are divided into:
- oxidation-reduction reactions involving organic and inorganic substances present in the aquatic medium due to the formation H2O2, O2, O3, O and OH- in the solution;
- chain reactions in the solution, which are initiated by the products of cleavage of impurities present in the solution;
- destruction of macromolecules and initiation of depolymerization of polymer compounds;
- reactions between dissolved gases inside cavitation bubbles.

So, to substantiate the direction of purification from heavy metals, we performed an analysis aimed at obtaining the dependences of changes in the physicochemical parameters of an aqueous solution (effluent) under certain cavitation treatment modes. These dependencies are given in Table 2, and pictorially shown in Figure 1.

### Table 2. Change in physicochemical parameters of wastewater containing heavy metal ions under various modes of cavitation treatment and subsequent relaxation of the aqueous solution (effluent).

| Experimental data | Cavitation mode at a constant treatment time of 10 minutes |
|-------------------|----------------------------------------------------------|
|                   | untreated wastewater | 3000 | 5000 | 7000 | 10000 | 11000 | 12000 |
| indicators of wastewater containing heavy metal ions | rpm | rpm | rpm | rpm | rpm | rpm |
| t°C               | 19 | 25 | 30 | 38 | 43 | 42 | 50 |
| t_rel °C          | 21.5 | 24.5 | 26 | 28.5 | 32 | 30 | 34 |
| pH                | 3.91 | 4.24 | 4.46 | 4.62 | 4.71 | 4.77 | 4.93 |
| pH_rel            | 3.83 | 4.26 | 4.49 | 4.68 | 4.68 | 4.86 | 4.97 |
| REDOX             | 402 | 383 | 365 | 292 | 270 | 244 | 249 |
| REDOX_rel         | 330 | 342 | 334 | 331 | 316 | 282 | 265 |
| O2                | 7.64 | 8.56 | 8.89 | 9.95 | 10.37 | 9.89 | 8.57 |
| O2_rel            | 7.75 | 8.23 | 7.93 | 8.02 | 8.06 | 8.06 | 7.12 |

Change in the temperature of wastewater containing heavy metal ions under c

![Graph showing change in temperature](image-url)
Change in pH of wastewater containing heavy metal ions under different cavitation modes

![Graph showing changes in pH under different cavitation modes.](image)

Change in the redox potential of wastewater containing heavy metal ions under different cavitation modes and subsequent relaxation

![Graph showing changes in redox potential under different cavitation modes.](image)
Change in the oxygen saturation of wastewater containing heavy metal ions and cavitation modes with subsequent relaxation

Fig. 1. The diagrams of the dependences of change in the physicochemical parameters of wastewater containing heavy metal ions and the cavitation mode.

In order to justify the environmental friendliness of the method and the economic feasibility of applying cavitation reactors while improving the process flows for industrial wastewater treatment, we performed a comparative analysis on the efficiency and energy consumption of the conventional chemical method for purifying wastewater from heavy metal ions and the proposed method of hydrothermal cavitation treatment. The results of comparing the purification efficiency using different methods of treatment using chemicals or hydrothermodynamic cavitation are given in Table 3.

| Ion | Initial concentration mg/dm³ | Concentration of ions after different methods of the effluent treatment | Cavitation at 10000 rpm |
|-----|-------------------------------|-----------------------------------------------------------------------|------------------------|
|     |                               | 10 min | 15 min | 30 min | Effect, % | 10 min | 15 min | Effect, % |
| Cu  | 3.94                          | 3.75   | 3.75   | 3.55   | 9.8      | 2.75   | 1.15   | 70.8     |
| Fe  | 13.7                          | 12.66  | 10.7   | 5.6    | 59.12    | 2.66   | 0.64   | 95.3     |
| Ni  | 408.5                         | 334.9  | 288.07 | 96.9   | 76.27    | 37.25  | 16.25  | 94.54    |
| Mn  | 0.032                         | 0.022  | 0.022  | 0.022  | 31.25    | 0.017  | 0.017  | 46.8     |
The efficiency of industrial wastewater purification from heavy metal ions using different methods

Apart from the obvious advantage of cavitation technology for removing heavy metals from wastewater, it is worth noting that the chemical method of removing a complex of heavy metals requires bringing pH of the medium to 10.5-12.0, which surely entails an excessive use of chemicals. The insoluble precipitates which form in this process (as a rule, metal hydroxides) are subject to prolonged sedimentation and their water content is 60-75%, as a result, the technology of removing and treating such sediments of wastewater is becoming more complicated.

Analysing the obtained experimental data, we chose mathematical modelling with a set of VBA techniques, combined with the Excel computational capabilities (fig. 3) in order to determine the optimal mode of cavitation treatment of the industrial effluent.

Based on the matrices of change of the concentration of heavy metal ions in the wastewater being treated and of the obtained dependences on such factors as revolution speed of the cavitational impeller, treatment time, pH and temperature of the medium, second-order regression equations were obtained. These regression equations were used to build graphical interpretations in the form of surfaces (fig. 3), which allows to regulate the process of chemical-free conditioning of wastewater containing heavy metals and take into account technological and economic indicators later on. When calculating the data, we applied an algorithm for estimating the coefficients of a nonlinear regression model using the least-squares method. The evaluation criterion y1-2 is presented in the factor space of x1; x2; x3. Figure 3 shows an adjustment diagram of effluent treatment using copper ion as an example.

Fig. 2 Efficiency of purification of industrial wastewater from heavy metal ions using different methods of treatment.
Fig. 3. The adjustment diagram of the treatment process for wastewater containing heavy metal ions (the case of Cu2+ ion) using cavitation treatment.

Interpreting the results of mathematical modelling and comparing them with the actual changes in the concentrations of heavy metal ions in various modes of hydrothermodynamic treatment of the wastewater model, we can conclude that the optimal mode for removing a complex of heavy metal ions is processing at 10,000 rpm for 60 seconds. Under a more intense cavitation mode, we observed the formation of intermediate products of metal oxidation and recombination of active ions in an aqueous medium with the formation of coagulated structures in the form of metal hydroxides, for example, Fe(OH)3, or hydroxo-aqua complexes such as [Cu(OH)2](OH)2]0, [Zn(OH)2](OH)2]0, [Ni(OH)2](OH)2]0, [Ni(OH)2](OH)2]0, [Fe(OH)2](OH)3]0, [Fe(OH)3](OH)3]0. These substances, in turn, having electrostatic attraction due to a change in the charge of the complexion, from positive to negative (at pH above 10.0), act as coagulants. The resulting coagulated precipitate was also analyzed in the framework of this research, with determining the sizes of precipitate particles using the turbidimetric and sedimentation methods of the analysis. And the size of the precipitate flakes coagulated on the hydroxo-aqua complexes of Ni, Cu, Zn reaches 130-140 nm, while the precipitate flakes formed and sedimented on the Fe3+ ion complexes vary from 24 to 50 µm.

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Scope of application of the results. The results of this research can be applied in the upgrading of industrial local treatment facilities of enterprises with the introduction of a cavitation treatment unit in order to intensify the purification of wastewater from heavy metal ions.
Conclusion. These technical solutions allow achieving the water quality required for reuse. The main advantages of the proposed chemical-free method based on the effects of hydrothermodynamic cavitation are:

1. the opportunity to clean various effluents with significant fluctuation in the quantitative content of pollutants;
2. the opportunity of using the proposed technology when upgrading the existing equipment, as SC-reactors are easily integrated into the existing structures, for example, storage tanks, without significant alteration of their construction;
3. the opportunity to automate the purification process;
4. reduction of operational and economic costs;
5. reduction of negative impact on water bodies to which industrial wastewater is discharged.

The introduction of a cavitation treatment unit to intensify the purification of industrial effluent and to condition process water will permit forming a closed-loop water use cycle and significantly increasing the environmental sustainability of the region where industrial complexes are present.

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