Catalytic decomposition of trilon B on the nickel-ferricyanide catalyst

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Abstract. The method of nickel-ferricyanide catalyst preparation is elaborated. The results of catalytic decomposition of trilon B on the prepared catalyst are presented. The developed method allows performing the efficient decomposition of trilon B (>99.9%) either in acid or in alkaline medium in temperature interval of 37-80°C. Technologically-fit dynamic conditions of the process, providing the intensity of a heterogeneous interaction, are selected and explored, and the nickel-ferricyanide catalyst resistance is achieved. The instrument flowchart of the developed method of catalytic decomposition is introduced for industrial application during the reprocessing of low- and medium-activity effluent, containing complexons.

1. Introduction
Organic complexons are widely used compounds in radiochemical technologies both during the decontamination processes and many other production activities.

In this case, huge amounts of radioactive waste (effluent), containing complexons such as ethylene diamine tetraacetate (EDTA), trilon B, oxalic and citric acids, surface-active substances, etc. are generated each year by radiochemical and nuclear power plants production. The problem is that such compounds form resistant complex compounds with radionuclides ($^{60}$Co, $^{137}$Cs, etc.) (fig. 1), impede and reduce the efficiency of radioactive effluent reprocessing by traditional physicochemical methods (sorption, ion-exchange, precipitation).

![Trilon B as the decontaminating agent](image-url)

Fig. 1. – Trilon B as the decontaminating agent
Therefore, localization, concentration and reprocessing of the radioactive waste (effluent) can be considerably simplified after the decomposition and removal of the mentioned organic complexons from it.

Preliminary purification of the radioactive waste from complexons and its impurities also allows to reprocess and store the effluent from radiochemical and nuclear power plants more efficiently and to reduce the initial cost of production.

The oxidation (using $\text{O}_3$, $\text{H}_2\text{O}_2$) and photooxidation decomposition (using ultraviolet treatment and $\text{H}_2\text{O}_2$) are among the most efficient methods of complexons destruction \[1,2\]. However, the catalytic decomposition of complexons is more preferable for radiochemical technology than mentioned methods of decomposition, because it allows minimizing the power inputs, resource consumption, and amounts of secondary waste and additional operations during the processes of complexons decomposition. The methods of oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$), trilon B ($\text{C}_{10}\text{H}_{14}\text{N}_2\text{Na}_2\text{O}_8$) and EDTA ($\text{C}_{10}\text{H}_{16}\text{N}_2\text{O}_8$) decomposition using the silica gel and anionite platinum-covered catalysts, activated carbons, fibrous activated carbon-base materials were explored by the authors of \[3,4,5,6\].

Nevertheless, it should be noted that platinoids are rather expensive metals, besides practically it is impossible to avoid metal loss during the decomposition process, and when using activated carbons the catalyst degradation was registered \[4\].

2. Experimental part

In present work the ferricyanide catalyst covering the “VP-1AP” anion-exchange resin surface was made (fig. 2). It was used as the heterogeneous solid catalyst for the catalytic decomposition of complexon trilon B. Ferricyanide was chosen because of its ability of catalytic decomposition of hydrogen peroxide with the formation of a hydroxyl radical (powerful oxidizing agent) and $\text{[Fe(CN)}_6^{3-}\text{]}$ anion resistance, ability of ferricyanide fixation on the anionite surface with the formation of sparingly soluble transition metal salts, and because of ferricyanide low-cost. The amount of the transition metals ferricyanide on the anionite “VP-1AP” surface was optimized by the determination of the sufficient contact time for the complete complexons decomposition using technologically-fit dynamic mode.

The catalyst preparation process included the following operations: the preparation of the ferricyanide solution ($\text{K}_3\text{[Fe(CN)}_6\text{]}$), the preliminary preparation of the “VP-1AP” surface by the alkaline treatment ($\text{NaOH}$ solution, 40 gram per liter), mixing and heating (80°C) of the ferricyanide solution with the anionite (resin), second alkaline treatment ($\text{NaOH}$ solution, 40 gram per liter). After prepared catalyst washing, the surface of the “VP-1AP”, covered with the ferricyanide, was treated by the $\text{Ni(NO}_3\text{)}_2$ solution in order to fix the formed ferricyanide composition (a sparingly soluble nickel ferricyanide) on the surface of “VP-1AP”.

Using a method of the nitrogen thermal desorption the determination of the complete specific surface of the prepared catalyst (5-7% R-$\text{Ni[Fe(CN)}_6\text{]}$, R – “VP-1AP” resin) was experimented and was $18,47\pm0,396\text{ m}^2$ per gram. Earlier, in the article \[6\] it was determined that the time of the complexons catalytic decomposition (EDTA) is influenced by the available for the adsorption process surface. For the prepared nickel-ferricyanide catalyst the effective area was evaluated as the 75-85% of the complete specific surface, because of the “VP-1AP” resin application as the catalyst support.

![Fig. 2. – “VP-1AP” anion-exchange resin (a) and nickel-ferricyanide catalyst (b)](image-url)
During the experiments the following standard test technological solutions were used: solution №1 – trilon B 1,2 g/l, NaNO₃ 5,0 g/l, Na₂C₂O₄ 5,0 g/l, pH 2; solution №2 – trilon B 1,2 g/l, NaNO₃ 5,0 g/l, Na₂C₂O₄ 5,0 g/l, pH 9.

The catalytic decomposition of the complexon trilon B was implemented in a dynamic mode in the temperature-controlled column. The solutions were passed through the static bed of the nickel-ferricyanide catalyst at the rate of 7-8 columnar amounts per hour. The solution and catalyst contact time was nearly 50-60 seconds.

The catalytic column characteristics were the following: height of the static bed of the nickel-ferricyanide catalyst – 16 centimeters, inner diameter of the column – 2,7 centimeters. The columnar amount was about 90 milliliters. The ratio between the diameter of the catalyst bed to its height – 1:5,9.

The base framework of the used laboratory facility is shown in figure 3.

![Laboratory facility for the heterogeneous catalytic decomposition of trilon B method research](image)

1 – Temperature-controlled column;
2 – Thermostat;
3 – Peristaltic pump;
4 – Stock solution capacitor;
5 – Receiver tank;
B-01 ÷ B-03 – needle valves.

Fig. 3. – Laboratory facility for the heterogeneous catalytic decomposition of trilon B method research

3. Results and discussion
Hydrogen peroxide, with optimal concentration of 6 gram per liter, was used as the oxidizing agent. The hydroxyl radical (•OH) with the oxidation potential of 2,8 V was formed during the interaction between hydrogen peroxide and the surface of the nickel-ferricyanide catalyst.
Table 1
Experimental results of the heterogeneous catalytic decomposition of trilon B on the nickel-ferricyanide catalyst in acid medium (solution №1)

| T, °C | pH  | [Trilon B], g/l | [Fe], mg/l | [Ni], mg/l | Decomposition degree of trilon B, % |
|-------|-----|-----------------|------------|------------|-------------------------------------|
| -     | 2,0 | 1,1             | -          | -          | -                                   |
| 37    | 1,7 | 0,056           | < 0,60     | 46         | 94,90                               |
| 45    | 1,8 | 0,017           | < 0,60     | 11         | 98,46                               |
| 52    | 1,8 | < 0,001         | < 0,58     | 1,7        | > 99,91                             |
| 60    | 1,9 | < 0,001         | < 0,56     | < 0,1      | > 99,91                             |
| 70    | 2,0 | < 0,001         | < 0,33     | < 0,1      | > 99,91                             |
| 80    | 2,0 | < 0,001         | < 0,30     | < 0,1      | > 99,91                             |

Table 2
Experimental results of the heterogeneous catalytic decomposition of trilon B on the nickel-ferricyanide catalyst in alkaline medium (solution №2)

| T, °C | pH  | [Trilon B], g/l | [Fe], mg/l | [Ni], mg/l | Decomposition degree of trilon B, % |
|-------|-----|-----------------|------------|------------|-------------------------------------|
| -     | 9,0 | 1,1             | -          | -          | -                                   |
| 37    | 8,7 | 0,093           | < 0,30     | < 0,1      | 91,54                               |
| 45    | 8,8 | 0,038           | < 0,30     | < 0,1      | 96,55                               |
| 52    | 8,9 | < 0,001         | < 0,30     | < 0,1      | > 99,91                             |
| 60    | 8,9 | < 0,001         | < 0,33     | < 0,1      | > 99,91                             |
| 70    | 9,0 | < 0,001         | < 0,30     | < 0,1      | > 99,91                             |
| 80    | 8,8 | < 0,001         | < 0,30     | < 0,1      | > 99,91                             |

Despite the fact that the process of trilon B decomposition flows during the whole temperature interval, though a rise of temperature more than 85-90°C can cause a destruction of the organic matrix of the catalyst support (“VP-1AP” resin). That’s why, the optimum condition of the heterogeneous catalytic decomposition of trilon B using the nickel-ferricyanide catalyst, concerning temperature factor, was determined as 50-60°C. Catalyst resistance was estimated relatively to the concentration of iron and nickel in the solution after the process of trilon B decomposition. The detected amounts of iron and nickel in the solution were below the detection limit of the used ICP-spectrometer. This fact confirmed the resistant stabilization of the nickel-ferricyanide catalyst on the “VP-1AP” resin surface.

Thereby, the prepared during the research nickel-ferricyanide catalyst (5-7% R-Ni[Fe(CN)6], R – “VP-1AP” resin) has demonstrated a high efficiency during the process of the thermal oxidation decomposition of the trilon B complexon in the interval of pH 2-9 and temperature interval 37-80°C. But, it must be admitted that during the process of catalytic decomposition, along with the complete destruction (mineralization) of trilon B, the formation of the most likely intermediate decomposition products, such as nitrilotriacetic (NTA) and hepato-iminodiacetic acid (HIDA), is possible, which can potentially effect the following sorption and precipitation processes of radionuclides (60Co) extraction by complex compounds formation. At present, the decomposition products chromatograms and infrared spectra, obtained during the oxidizing catalytic process, are being explored. Future tasks are connected with the identification of intermediate decomposition products after the catalytic decomposition of trilon B on the nickel-ferricyanide catalyst, its complexing properties investigation, assessment of its influence on the following radionuclides extraction, concentration determination of...
the referred above intermediate decomposition products provided that they will not effect the process of radionuclides ($^{60}$Co, etc.) extraction.

The installed productivity of the catalytic column indicates about the possibility of the technological application of the explored catalyst during the process of the complexons oxidation decomposition. For example, the developed method can be used during the recycling of the process liquors of radiochemical plants, when the intensification of the oxidation process is needed, in particular, during reprocessing of the radioactive effluent, containing $^{60}$Co in the form of complex compounds. As a consequence of the developed research, the invention application was processed and registered [7].

Also, the instrument flowchart of the developed catalytic process during the recycling of low- and medium-activity waste, containing complexons (trilon B), was introduced (fig. 4). The aggregative design engineering of the catalytic column for the developed process was made. Critical parameters of the column: height – 1900 millimeters, diameter – 100 millimeters; the volume of the piled catalyst bed – 3.9 liters; productivity – up to 1.5 m$^3$/day.

![Fig. 4. – Flowchart of the complexons catalytic decomposition process](image)

At present, the developed catalyst efficiency during the process of real radioactive effluent (containing $^{60}$Co, high content of trilon B, oxalic ion, surface-active substances) reprocessing is being experimented. Future tasks will be connected with technological approbation of the developed method in real radioactive effluent (containing complexing compounds) reprocessing technological framework.

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