Optimizing the Treatment of Oil-Containing Wastewater with “Catan” Type Catalysts

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Abstract. This work studies the effects of “Catan” type heterogeneous metal complex catalysts on the treatment of oil-containing water with active sludge. Both studied catalysts, but primarily catalyst 525, were able to eliminate oil from standard and real wastewater even without active sludge. The catalyst 525 and catalyst 524 also reduced the chemical oxygen demand (COD) in the oil-containing wastewater. According to the COD indicator, catalyst 525 was also more effective than catalyst 524. However, the greatest decrease in COD was observed in systems where both active sludge and “Catan” type catalysts were used. Thus, the joint use of “Catan” type catalysts and activated sludge significantly increased the removal rate of petroleum products and improved the quality of oily wastewater.

1. Introduction

Raw oil, as well as numerous products of its processing, widely used in the sector of national economy as fuel, lubricants, crude materials for the petrochemical industry, etc. Therefore, they often penetrate in significant amounts in the industrial and domestic wastewater and together they enter into the water, soil, underground aquifers. The oily water effluents have become one of global environmental pollutants. Oil pollution disrupts the natural biochemical processes that cause the death of flora and fauna of lakes, rivers and seas, reduces the fertility of soil.

It is difficult to eliminate the pollutants found in wastewater from the petrochemical industry. The complexity of treating oil-containing wastewater is due to the extreme diversity of its impurities and the high resistance of some hydrocarbons and their derivatives to removal [1, 2, 7]. Therefore, the oil refining industry views optimization of its wastewater treatment as a very urgent problem. Currently, the activated sludge method is the most versatile and widely used method for all wastewater treatment, including oil-containing wastewater [3]. The literature chronicles developments in the processes and technologies available for purification of heavily polluted water from petrochemical plants through the usage of various catalysts [3, 4].
A search of patents related on the topic of catalytic wastewater treatment showed that over the last 20 years, during the period from 1995 to 2014 106 patents, with the theme of catalytic treatment of waste water and 54.7% of them were registered in Russia, 23.58% in USA, 13.2% in China. Most of the patents are dedicated to the improvement of carriers for catalytic components. Further, patents can be divided into the following subjects:

- The catalysts for purification of phenol-containing wastewater;
- The catalysts that accelerate the processes of de- and nitrification;
- The catalysts that accelerate the process of decomposition of sulfur compounds

Previously, the most widely used homogeneous catalysts. The positive features of homogeneous catalysts are the high selectivity and activity. However, they have a significant disadvantage. It is difficult or impossible to separate such catalysts from the environment in which the catalytic process was carried out. This leads to the fact that the catalyst is consumed irretrievably. In addition, homogeneous catalysts usually contain heavy metals and other chemically active substances, as well as toxic compounds. Owing to this, often there is secondary pollution of waste water after the reaction of catalytic oxidation. Heterogeneous catalysts are new and more promising generation of oxidation catalysts in liquid media.

Extensive researches on the development and improvement of heterogeneous catalysts constantly carry out in our country and abroad. As a carrier are used: activated carbon, ion exchange resins, various polymers. Different methods of immobilization of active components on the surface of the media are used as well.

Among the domestic heterogeneous catalysts, created in recent years, the most active, technologically advanced and relatively inexpensive catalysts, which have received industrial application, are the catalysts produced using organometallic complexes with variable valence as the active base and the polyethylene as the carrier. Employees of JSC “SPA Catalysis” have developed heterogeneous metal complex catalysts, and they produce these catalysts in large volumes [5], thus positioning these catalysts as an option for biocatalytic cleaning, i.e., the simultaneous treatment of wastewater with activated sludge and catalysts [5].

Biocatalytic cleaning technology has already been implemented at certain companies. However, until now, the number of publications devoted to this method has not been sufficient.

In connection with the above, the aim of the present study was to examine the ability of “Catan” type catalysts to intensify the process of biological treatment of oil-containing water.

2. Materials and equipment

The materials used included the “Catan” type multifunctional heterogeneous catalysts 524 and 525, which were produced by JSC "SPA Catalysis". The low molecular weight polymer was used as a complexing agent in the metal complex. The fixing of the metal complex on the polyethylene allows not only to slow the processes of their irreversible oxidation, but also to preserve the possibility of diffusion of oxygen to the fixed complex, which is located on the surface of non-porous particles of the carrier.

Catalysts of type “Catan” have a high catalytic activity in a wide range of pH and concentrations of oxidizable compounds. They are defined by the satisfactory mechanical strength, chemical and hydrolytic resistance. The polymeric catalysts based on polyethylene can be used in an alkaline medium at the temperatures up to 100 °C, at the pressure up to 7.0 kgf/cm² and also at the mode of intense bubbling process.

The synthesis of catalysts “Catan” for the biocatalytic process of purification was carried out by dint of the coordinating combination of catalytically active metal complexes that are insoluble in the reaction medium with the functional groups of the polymeric carrier. It played the role of polymer macroligand. The synthesized catalysts of type “Catan” that is used for biocatalytic wastewater treatment have such properties as high catalytic activity, selectivity in the processes of nitrification-
denitrification, hydrolysis resistance, and mechanical strength. The useful life of such catalysts is 3-5 years.

To research the capability of intensification of biocatalytic process of purification of oil refinery wastewater were used two types of heterogeneous catalyst: a multifunctional catalyst for the oxidation of organic substances and nitrification (catalyst 525) and selective catalyst for the reduction of nitrate and nitrite (catalyst 524).

The high-pressure polyethylene (State standard specification 16337-77) of brand 10803-020 produced at JSC Angarsk petrochemical company was used as a carrier for the preparation of heterogeneous catalysts. As catalytic active base were taken the oxides of metals of variable valence (CuO, MnO₂, Fe₂O₃, Cr₂O₃, ZnO, CuO, NiO, V₂O₅, marked as "analytical grade" or "reagent grade" and without preliminary purification). Also were used pyrite cinder, that are waste from sulphuric acid production of mining-chemical industrial complex in Stepnogorsk city TS 6-08-885-93, containing in its composition trace elements: Ba, Pb, Mn, Ni, Zn, La, V with mass percent from 0.1 to 0.007 (tab. 1). Iron ions are in the form of a spinel Fe₂O₃ and Fe₃O₄.

| Table 1. The chemical composition of the catalysts, mass % |
|-----------------|-----------------|-----------------|----------------|----------------|----------------|----------------|----------------|
| Fe₂O₃           | FeO             | CaO             | Al₂O₃          | SiO            | CuO            | MgO            | K₂O            | Na₂O           |
| 65,03           | 4,06            | 1,3             | 2,78           | 3,67           | 2,03           | 0,26           | 0,35           | 0,29           |

In the testing catalysts are used complexes of metals of the first transition row that are close to the natural carriers of oxygen: Mn (II); Fe (II); Co (II) Ni (II); Cu (I). They are capable of reversible oxygenation in aqueous solutions, have the composition of the inner coordination sphere, similar to the natural active centers. The coordination of the oxygen molecule in the internal sphere of the metal ion of the oxygenating complex is accompanied by a transfer of electron density from the central metal ion on the O₂. It leads to the intramolecular redox reaction, as a result of which coordinated particle O₂ acquires the properties of a superoxide- ion (O₂⁻) or peroxide-ion (O₂²⁻) [5].

The test samples of the catalysts were made by mixing the starting components in a homogenizer in two stages:

1) For the synthesis of the organometallic complex (OC) the mixture of metal oxides was blended in the homogenizer at a temperature of 130-135 °C with low molecular weight polymer in the ratio of 0.1:9,0 - 0.5:9,5 (catalysts 524 – 524, respectively). The mixing in the homogenizer lasted 15 minutes.

2) Then, to the resulting in a homogenizer OC was added the high-pressure polyethylene (PE) in a ratio of OC:PE equals to 1,4:2,5 – 1,2:2,5 (catalysts 524 – 524, respectively). After that the catalyst’s mass was intermingled for 30 minutes at the temperature of 130-135 °C. The synthesized catalyst mass was fed into a screw extruder KE-200, where the temperature about 200-2100 °C was maintained. The melt of catalyst mass from the extruder was supplied to the granulation device, where was done the modeling of the catalyst in the form of a grid with the rods 5 mm in diameter and the cell 10 mm×10 mm size.

Activated sludge was taken from the biological treatment plants in Irkutsk. The sludge flakes have a structure of average density, water above the settled sludge is transparent. There are the fauna with a large number of protozoa, the cytoplasm of which are digestive vacuoles. During micro-copying (60× и 100×) is observed the almost complete absence of free, not associated with sludge flakes bacteria.

Prior to the experiment, the sludge had been mixed for one day with a standard mixture of artificial wastewater (sodium carbonate, 50.0 mg/L; sodium acetic acid, 50.0 mg/L; potassium phosphoric acid monosubstituted, 25.0 mg/L; ammonium phosphoric acid disodium, 25.0 mg/L; calcium chloride, 7.5 mg/L; magnesium sulfure acid, 5.0 mg/L; and peptone, 100-150 mg/L) [8]. During this period of adaptation, as well as during the experiments, the temperature of the sludge was maintained at 20°C with aeration and a 1 to 8 ratio of air/water. Aeration was performed by means of laboratory microcompressors (Dezzie, model D-044), and 0.01% of oil was added to the standard wastewater
(Markov field, Irkutsk region). Emulsification of the oil occurred as a result of air bubbles during the aeration process.

To study industrial oily waste, wastewater samples were taken from oil storage tanks and from the petrochemical JSC Angarsk refinery (Angarsk petrochemical plant “Rosneft”). The waste water of oil storage tanks contains crude oil, heating oil, diesel, gasoline, and detergents that were used to clean the oil storage tank. The refinery was a petrochemical site that processes crude oil into EURO 5 standard gasoline.

In order to maximize contact between the surface of the catalyst and the reaction mixture, the catalyst was set up in the center of the model aeration tank (fig. 1). A tank with a cylinder and a capacity of one dm3 was used. The aeration system, which consisted of silicone and hollow glass tubes that were perforated at the bottom, was advanced into the cylinder [8].

![Figure 1. The scheme of the aeration tank model.](image)

The experiment continued for 24 hours. Before the experiments, the catalyst was activated for 12 hours with the water-air mixture. During the experiment the chemical oxygen demand was fixed [9]. For quantitative analysis of the oil, the fluorimetric method was used, and the determination was carried out on a “Fluorat-02-3M fluid analyzer” [10]. The investigated oil was extracted with hexane in a separating funnel. Then it was kept for phase separation. The upper layer was separated and transferred in the cuvette of the analyzer. The calibration of the analyzer was performed using solutions of a known mass of oil in n-hexane. Calibration solutions were prepared from certified mixtures obtained on the basis of the solution composition of the state standard sample oil products [10].

All experiments were repeated with at least 5 independent experiments consisting of 3 parallel measurements for each experiment. The Excel software package was used for statistical processing of the data. Conclusions are made assuming that the probability of a correct forecast was $R \geq 0.95$.

3. Results and discussions

The catalysts 524 and 525 increased the speed of cleaning in experiments without the presence of toxicants. After 8 hours of cultivation in the sample of standard wastewater + sludge + catalyst 525 was recorded significant decrease in NO$_3^-$ concentrations from 8.03±1.13 to 1.95±0.38 mg/l, i.e. the content of nitrates decreased by 75.6% (td=16.28 $P \geq 98\%$) (fig. 2).
The study of oil removal during standard wastewater treatment revealed the following. The concentration of oil in the environment was decreased by only 16% when the catalyst 524 was added without activated sludge. Even without the presence of activated sludge, the catalyst 525 mediated 84% of the reduction in the sample’s oil content during a 24-h incubation. Notice, that the decrease in the level of oil in this case was even stronger than in the experiment with activated sludge without the addition of catalysts. Under the influence of only activated sludge, the concentration of oil during the same period declined by only 51%.

The minimum content of oil hydrocarbons (12% of initial value) in standard wastewater after exposure to activated sludge and catalyst 525 was recorded at the end of the experiment (table 3).
Table 3. The concentration of oil in the standard wastewater before and after the 24-hour incubation.

| Sample                                                      | Oil (mg/dm³) |
|-------------------------------------------------------------|--------------|
| Initial value                                               | 1.00±0.15    |
| Standard wastewater                                         | 0.92±0.23    |
| Standard wastewater + active sludge                         | 0.49±0.07    |
| Standard wastewater + catalyst 524                          | 0.84±0.21    |
| Standard wastewater + catalyst 525                          | 0.23±0.08    |
| Standard wastewater + catalyst 524 + active sludge          | 0.35±0.12    |
| Standard wastewater + catalyst 525 + active sludge          | 0.12±0.04    |

Analysis of COD revealed that the greatest degree of standard wastewater purification, with the addition of 0.01 % oil, is observed in the presence of activated sludge and catalyst 525. By the end of the experiment, this indicator decreased by 82.7 % from its initial value. Activated sludge without catalysts reduced COD by only 47.8 %. In the experiments utilizing only the catalyst 524 in oil-containing standard wastewater, the COD fell 29.97 % during 24 hours. When the catalyst 524 was combined with sludge, the COD fell 54.95 % (tab. 4).

Table 4. Chemical oxygen demand (mg/dm³) in a standard wastewater in the presence of 0.01 % oil, before and after the 24-hour incubation.

| Sample                                                      | COD          |
|-------------------------------------------------------------|--------------|
| Initial value                                               | 116.1±14.5   |
| Standard wastewater + active sludge                         | 60.6±11.7    |
| Standard wastewater + catalyst 524                          | 81.3±12.6    |
| Standard wastewater + catalyst 525                          | 64.9±9.12    |
| Standard wastewater + catalyst 524 + active sludge          | 52.3±7.37    |
| Standard wastewater + catalyst 525 + active sludge          | 20±8.53      |

In the samples with the catalysts the transformation of the derivatives was much more intense. The nitrites was subjected to the greatest destruction. The of their concentration was about 86% for both catalysts. The same indicator in the control had decrease at 82.9 %. The concentration of ammonium ions in the presence of catalysts 524 and 525 reduced by 53.8 and 50.3 %, respectively. In the system standard wastewater + active sludge + oil 0.01 g/l decrease in the content of ammonium ions amounted to 23.5%. The change of concentration of nitrates was the lowest. In samples with catalysts 524 and 525 the decrease was 36.3 and 43.8 %, respectively. In monitoring this indicator decreased by 23.5 % (fig. 3).
The catalysts improved the wastewater treatment with activated sludge in a real petrochemical wastewater plant. The COD values in the wastewater from the Angarsk petrochemical refinery were not highly dependent on the presence of the 524 or 525 catalysts in addition to the active sludge (tab. 5).

**Table 5.** Chemical oxygen demand (mg/dm$^3$) after a 24-hour incubation in wastewater from the OJSC Angarsk Petrochemical Company.

| Sample | Catalyst | Initial value | After a 24-hour incubation |
|--------|----------|---------------|---------------------------|
| Wastewater from petrochemical site of OJSC Angarsk Petrochemical Company + activated sludge | 524 | 176.1±26.4 | 65.1±6.3 |
| | 525 | | 55.7±7.9 |
| Wastewater from oil storage of OJSC Angarsk Petrochemical Company + activated sludge | 524 | 168.3±25.2 | 43.8±5.1 |
| | 525 | | 17.1±1.8 |

However, in the experiments with wastewater from the oil storage tanks, the effect of the catalyst 525 was stronger than the catalyst 524, with the COD decline amounting to 89.8 and 73.9%, respectively. The “Catan” type catalysts intensified the activated sludge mediated degradation of petroleum products from the petrochemical industrial site complex (tab. 6).
Table 6. The elimination of active sludge and catalysts of oil products from petrochemical site wastewater of the OJSC Angarsk Petrochemical Company.

| Sample                                      | Catalyst | Concentration of oil (mg/dm$^3$) | Elimination degree % |
|---------------------------------------------|----------|----------------------------------|----------------------|
| Wastewater from petrochemical site + activated sludge | -        | 32.5±4.87                        | 68.6                 |
|                                              | 524      | 102.3±8.7                        | 80.6                 |
|                                              | 525      | 11.8±1.77                        | 88.4                 |
| Wastewater from oil storage of + activated sludge | -        | 3.5±0.52                         | 98.5                 |
|                                              | 524      | 237.1±35.56                      | 99.7                 |
|                                              | 525      | 1.2±0.18                         | 99.5                 |

The wastewater from the petrochemical platform of gasoline EURO5 contained more derivatives of nitrogen than the wastewater from oil storage tanks. However, the intensity of the transformations of the derivatives of nitrogen in the effluent from petrochemical site was much higher. The content of ammonium ions in presence of catalysts 524 and 525 in the wastewater as a petrochemical platform was decreased by 89.3 and 83.01 %, and on the runoff from oil storage tanks by 86.6 and 75.4 %. Without the presence of catalysts this indicator by types of wastewater was reduced by 68.2 and 22.7 %, respectively. The decrease of total mineral nitrogen in the samples of the catalysts is significantly lower than in controls. The catalyst 524 had the greatest influence on the transformation of ammonium compounds and catalyst 525 on nitrates (fig. 4).

![Figure 4](image-url)
Thus the use of the biocatalytic method and the oil-degrading isolates makes it possible to reduce the concentration of oil up to close to background values with low operating costs.

In summary, the “Catan” type catalysts eliminated oil from standard and real wastewater even without activated sludge. In addition, the treatment of wastewater in the presence of catalysts of the type "Catan" was faster than that in samples only with active sludge. Catalyst 525 had a stronger effect. The combined utilization of “Catan” type catalysts with activated sludge significantly increased the elimination of petroleum products. Catalysts 525 and 524 reduced the COD of oil-containing wastewater. This indicator also showed that catalyst 525 was more effective than catalyst 524. The largest decrease of COD was observed in systems where both active sludge and “Catan” type catalysts were present. Thus, the combined effects of “Catan” type catalysts and activated sludge significantly increased the removal rates of petroleum products and the quality of the cleaning of oil-contaminated standard and industrial wastewater.

The biocatalytic treatment of wastewater is a promising approach that has a number of advantages over conventional methods that use only sludge. Biocatalytic cleaning does not require large capital expenditures or operating costs because metal mesh containers with catalysts can be placed directly into existing treatment facilities. “Catan” type catalysts are high-tech, relatively inexpensive and have a certain selectivity, chemical stability and mechanical strength. These catalysts will be characterized by their stability over the next 3-5 years.

4. References
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