# ANALYSIS OF THE COMPOSITION OF ORGANIC COMPOUNDS OF RENDERED-SAFE WASTE WATERS RELEASED BY REFINERIES

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**ABSTRACT**

There has been examined the problem of pollution of water environment by waste waters released by refineries. Also, there has been carried out a study of the physicochemical composition of waste discharges by refineries, after mechanical treatment. To identify organic compounds in oil pollutions, an infrared spectroscopy method has been applied. It has been revealed that the studied discharges mainly contain saturated hydrocarbons. In addition, it has been proved that the application of the reagent method makes it possible to intensify the process of treatment of wastes discharged by refineries.

**Keywords:** waste waters, compounds, physicochemical, composition.

## I. INTRODUCTION

The environmental state, including the state of water resources, has tremendously worsened in many regions over the past years. The greater threat comes from oil pollution, which is severely detrimental to the sea flora and fauna; therefore, pollution control has become one of the principal challenges to the humanity.

From this viewpoint, the Caspian Sea is of particular importance, because of extreme pollution of its waters by crude oil, petroleum products and other toxic substances for many years. Oil-containing waste waters, released by the oil-refining industry, are one of the key pollutants of the Caspian Sea.

The waste waters, released by refineries, are presently treated in accordance with traditional methods, including mechanical and biological purification plants. However, the treatment is not yet effective to get the purified water with the required quality. Mechanical purification structures – sand catchers, oil removers and settling basins – are capable of catching the floating and, partly, emulsified oil, thereby reducing the concentration of emulsified oil in the waste water to an average rate of 100 to 150 mg/l. [1]. Subsequently, it is satisfactorily proceeded with the biological treatment of oil-containing waste waters, on the condition that the concentration of petroleum products, flowing into the treatment installation, doesn't exceed 25 mg/l. Anyway, even an extensive biological treatment fails to reach the required extent of removal of certain organic and inorganic admixtures (organic acids, spirits, aldehydes, cetones, esters, etc.) from the waste waters, released by refineries.[2].

## II. MAIN PART

Therefore, to improve the operation of waste disposal plants at refineries, a series of physicochemical methods have recently become worthy of application on a wider scale; however, treatment solutions also require regular analyses of chemical composition of waste waters, released by refineries. Of particular importance is the analysis of organic components of chemical compositions.

We have carried out extensive analyses of the chemical composition of waste waters, released by refineries; the obtained data are based on waste waters released – after treatment in settling basins – by one of the Baku-based refineries (See: table 1). These are waste discharges from the first sewer system. For the given example, the core pollutants of waste waters are petroleum products, coarsely-dispersed admixtures, petroleum acids, etc. Waster waters are characterized by sufficient ratio of chemical oxygen demand, as well as high concentration of substances, which are extractable by hexane and diethyl spirit.

The mineral composition of waste waters consists of bicarbonates, chlorides, sulfates, and magnesium-, calcium- and sodium ions, etc.

While analyzing the composition of oil pollutants – complex blend of unseparable admixtures of different organic compounds – it is impossible to get, through the application of general methods of chemical analysis, all properties of the studied waters.

Therefore, with the purpose of identifying organic compounds of oil pollutants, there has been applied infrared spectroscopy method, in order to study the composition of organic components of waste waters, released by refineries following mechanical treatment at oil removers and settling basins.

Table 1

Physicochemical composition of waste waters released by refineries

| № | Indicators | Properties of waste waters released by refineries | |
|---|---|---|---|
| | | After settling basins | Flowing into half-industrial plant |
| 1 | Color | Yellowish-greenish | Yellowish-greenish |
| 2 | Smell | Pungent oily | Pungent oily |
| 3 | pH | 7,7 -7,9 | 7,8 |
| 4 | Coarsely-dispersed admixtures, mg/l | 203,0 - 213,0 | 425,0 |
| 5 | Petroleum products, mg/l | 195,2 - 264,4 | 234,2 |
| 6 | Petroleum acids, mg/l | 11,0 - 16,8 | 23,8 |
| 7 | Hexane-extracted substances, mg/l | 219,8 - 255,6 | 328,4 |
| 8 | Diethyl ether extracted substances, mg/l | 312,4 - 332,4 | 393,2 |
| 9 | Chemical oxygen demand, mgO/l | 552,1 - 608,0 | 716 |
| 10 | Emulsifier S, mg/l | 1,0 | 3,2 |
| 11 | Solid residual, mg/l | 8908,0 | 10442,0 |
| 12 | Total hardness, mg-equiv/l | 53,0 | 54,4 |
| 13 | Carbonates ($CO_3^{-2}$), mg/l | non-existent | non-existent |
| 14 | Bicarbonates ($HCO_3^-$), mg/l | 244,0 | 195,2 |
| 15 | Chlorides (Cℓ), mg/l | 3210,6 | 3947,6 |
| 16 | Sulfates ($SO_4^{-2}$), mg/l | 1989,0 | 2607,9 |
| 17 | Magnesium ($Mg^{+2}$), mg/l | 492,0 | 499,2 |
| 18 | Calcium ($Ca^{+2}$), mg/l | 240,0 | 256,0 |
| 19 | Ion total ($Na^+ + K^+$), mg/l | 1904,4 | 2630,0 |
| 20 | Ion weight total, mg/l | 8080,0 | 10135,9 |

The study method implies the extraction of waste waters by hexane, as well as drying of the extracted material by sodium sulfate, removal of the dissolvent and, finally, the dilution of the buttend in $CC\ell_4$ and taking an infrared spectroscopy. It should be noted that infrared spectrums have been taken on SPECORD spectrometer, with the amplitude of measurement from 500 to 4000 $cm^{-1}$. The behavior of the taken infrared spectrums is given in Fig. 1. Their analysis has revealed that they are typical for the spectrums of saturated hydrocarbons, with the absorption band occupied by methyl (1380 $cm^{-1}$) and methane (1460 $см^{-1}$) groups.

In the studied examples of waste waters, the composition of organic distillate is basically characterized by sufficient concentration of emulsified oil – the factor that forms the behavior of the taken infrared spectrums. Therefore, waste waters – following their mechanical treatment in factory presets – still have high concentration of saturated hydrocarbons.

Oil catchers and settling basins, installed at refinery facilities, are noted by unsatisfactory performance. To raise the efficiency of operation of mechanical treatment installations, there must be installed and put into operation thin-layer clarifiers and flotators, capable of treating with reagents. This assertion has come true following a series of analyses of waste waters [3] and corresponding data, obtained on the basis of the application of gas-liquid chromatography method; there is convincing evidence that physicochemical treatment of waste waters, with reagents, reaches the highest rate of efficiency in case of treatment of macromolecule hydrocarbons, with biological treatment proving itse lf as most effective for low-molecular hydrocarbons (up to $C_{15}$ ). These data are important in making decision on the approval of effective technology for fine cleaning of waste waters released by refineries.

In this connection, there has been developed and commissioned a half-industrial plant with advanced technological scheme for fine cleaning of waste waters released by Baku-based refineries [4,5].

The plant is composed of best modified assembling parts, thereby intensifying the process of treatment of waste waters; the components of the plant operate as a united technological chain. The structure of the plant includes installations of chemical and physicochemical treatment – thin-layer clarifier, pressure flotator, with reagent treatment by locally produced coagulant and flocculent, and structure for biological treatment.

There has been carried out an extensive analysis to study in detail the chemical composition of waste waters flowing to the half-industrial plant. The waste contained the admixture of blended discharges from the first and second sewer systems and bleed waters (See: table 1). Also contained in the composition of discharges, flowing into the plant, was sufficient concentration of saturated hydrocarbons (See: Fig. 1).

For the disinfection of the waste water after mechanical treatment and for obtaining the increase in the result, a new method of reagent treatment using aluminum sulfate and the flocculant SAAB which is protected by the Azerbaijan Patent Office, is developed. The main goal of the study was decreasing the concentration of oil products in the waste water below the limit of 25mg/l, which is

allowed limit if water is considered for biological treatment.

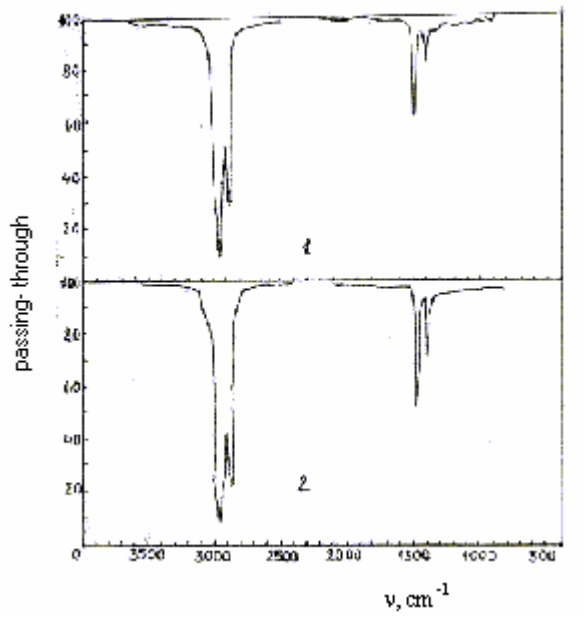


Fig. 1. Infrared spectrums of organic compounds ex tracted by hexane from waste waters released by refineries
1 – after factory presets of mechanical treatment (oil removers, settling basins)
2 – waste waters flowing into half-inindustrial plant

Removing formed floc after the reagent treatment is realized by the methods of both precipitation and flocculation. Realized laboratory experiments have shown that application of the coagulation results in reducing main oil products up to 98.8% and disperse matter up to 96% in waste water. For the treatment of the waste water under study aluminum sulfate dosage of 25-50 mg/l and the SAAB flocculant dosage of 1-2mg/l was sufficient.

For making the method of reagent treatment cheaper a new method of combining the local SAAB floculant with the high-quality bentonite is devised. It was found that using bentonite together with flocculant can completely replace the traditional coagulant-aluminum sulfate application. Bentonite dosage of 50 mg/l and SAAB flocculant dosage of 2 mg/l was sufficient. Application of the method of mass spectroscopy for determining oil component fraction of waste water has shown that there are oil-derived acids and negligible amount of oil products.

Experiments realized under industrial conditions have shown that using aluminum-sulfate coagulant (50 mg/l) or bentonite (100 mg/l) together with the SAAB flocculant (2 mg/l) treates oil refinery waste water up to the standards for being directed into biological treatment process.

Based on laboratory studies and industrial experiments, it can be concluded that method of coagulation using local coagulant and flocculants is effective for treating oil-refinery waste.

Combining coagulation and flocculation allows effective treatment of waste water during mechanical treatment stage which leads to effective biological treatment thereafter.

For the purpose of cleaning the traces of the reagents and for further treatment of waste water, at the end of the mechanical treatment plant, an adsorption reactor containing determined amount of natural zeolites exposed to the electrical gas discharge treatment is added. Studies have shown that electrical gas discharge treatment reasonable increases adsorption properties of the zeolites leading to the increased degree in the treatment of waste waters. Guided by the results of the given study, for physical and chemical treatment of waste waters of oil refinery using methods of coagulation and adsorption as a part of more general scheme of mechanical and biological treatment, recommendations are prepared and technical feasibility is evaluated.

## III. CONCLUSION

The application of reagent method has made it possible to intensify – and subsequently, improve – the entire process of pretreatment of waste waters by mechanical treatment installations, as well as ensure the required extent of neutralization of wastes flowing into biological treatment structures (provided that the concentration of petroleum products doesn't exceed 25 mg/l), and generally raise the efficiency of operation of the combined technological scheme for the treatment of waste waters released by refineries.

The recommended technology (know-how) provides the way of repeated use of purified run-off waters in the water supply for refineries, and is an effective solution to prevent water environment from pollution.

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