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ABSTRACT

of the dissertation for the degree of Doctor of Philosophy

DEVELOPMENT OF THE METHOD OF ECOLOGICALLY EFFECTIVE TREATMENT OF OIL INDUSTRY WASTEWATER

Specialty: 2391.01-Ecological Chemistry

Field of science: Chemistry

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INTRODUCTION

Relevance of the topic and degree of elaboration. The increase in the number of various industrial facilities in the world has caused the volume of industrial wastewater (IW) to increase many times. As a result, it is known that despite the recent treatment of these waters in accordance with ecological standards, the ecological situation of the environment has worsened. Thus, the dumping of IW into water basins has caused environmental pollution of water resources and a significant decrease in their volume[1]

One of the main sources of pollution of the world's water resources, mainly surface and underground drinking water, is IW formed in the oil refining industry. As a result of the development of oil production and oil refining industries from the end of the 18th century to the middle of the 19th century, it played an important role in improving the lifestyle of mankind and in the creation and development of other industries. However, due to the fact that previously there were no ecological and sanitary standards in the production areas of those industries, and also the cleaning, processing, and disposal of various types of waste were not carried out, environmental problems that could negatively affect people's health and existed in the biosphere for a long time arose[2].

In addition to the mentioned, as a result of the evaporation of the oil product waste mixture (OPWM) and other organic and inorganic volatile compounds remaining in the purified part of those waters released into water bodies along with the IW formed mainly in the oil refining industry (OPI), the hydrosphere, atmosphere, serious pollution of the troposphere and eventually the biosphere also occurs. That is why, mainly the IW formed during technological processes in the oil

[1]Burenin, B.B. Protection of water bodies from pollution by oily wastewater// Ecology of production. Scientific and technical journal. M.: 2015. №2. p.54-62.

[2]Bukhalter, E.B.,et al. Ecology of the oil and gas complex: Study guide in 2 volumes. TOM1., M.: UPPrint. «Oil and gas» 2003.416 p.

production industry (OPI) during the purification of oil-rich reservoir water (ORW) and also in the production areas of the oil refining industry (ORI)

That is why, the IW formed during the technological processes of oil purification of the oil production industry (OPI) and also in the production areas of the oil refining industry (ORI) mainly consists of oil, OPWM, it is important that the ecological scientific research conducted in the direction of cleaning harmful organic compounds and suspended substances is economically and ecologically significant.

As it can be seen from the above, the scientific research work on the ecologically effective deep cleaning of the oil reservoir water received in the OPI and the IW formed in the ORI is one of the urgent topics that can be implemented in the direction of solving the environmental problems related to the pollution of water basins.

Dissertation work reflects the results of long-term scientific research conducted on deep cleaning of ORW samples taken from the treatment areas of oil extraction facilities of OPI and also IW samples taken from ORİ treatment plants in laboratory conditions, using many extractants, coagulants and flocculants.

In the course of the conducted scientific research, it became known that in the purification of water samples containing oil and OPWM, it is an effective extractant from "petroleum" ether with a boiling temperature of 40-70^{0}C, which is of great economic and ecological importance and is considered as a cheap raw material in the oil refining industry. It is possible to use that extractant initially in the purification process, and then use a defined solution of $Al_2(SO_4)_3$ salt as a coagulant and, if required, a low-percentage solution of H_2SO_4 acid as a flocculant (at the same time as a neutralizer when pH=10–11), at pH=4-6, the optimal conditions were determined using $NaHCO_3$ solution. As a result of the conducted research, a new method was developed for deep cleaning of ORRW samples obtained in OPI and also IW samples formed in ORI.

With the mentioned new method, the concentration of oil is 5 times lower than the sanitary norms of OPWM (0.05 mg/l), i.e. the concentration is ≤0.01 mg/l, as well as complete transparency of the color of those waters, ~100% purification from suspended substances

was achieved. This scientific research work was registered and approved as an invention patent by AR Intellectual Property Agency in the registry of that agency.

The object and subject of the research. The problem of developing a new method for environmentally effective cleaning of ORW samples obtained in OPI from oil and also from IW samples formed in ORI, directly in treatment plants is the main object of the research work. The main subject of the dissertation was the development of a method for the deep purification of oil and oil product waste mixture (OPWM), which are the main purification indicators of ORRW and IW, from those waters, not only in ecological norms, but even ten times compared to sanitary norms.

Research goals and objectives. The main goal of the scientific research work was to carry out a deep, fully ecologically effective cleaning of also IW formed during technological processes in ORI mainly from oil, OPWM, suspended substances.

For this purpose, the following task has been set:

Conducting complex research works on the selection of extractant, coagulant, flocculant, neutralizer, their concentrations, determination of technological parameters and optimal conditions in order to carry out the coagulation process, which is considered economically and ecologically important with the developed new method, in accordance with the requirements of modern environmental safety.

Research methods. Research methods such as extraction, coagulation and flocculation were used in the research work for the purification of ORW samples from OPI and also IW samples from ORI. During the research, the following devices were used along with chemical analytical methods to clean the ORW and IW samples and determine their quality indicators.

The main indicator of the purification of ORW and IW samples is the determination of the amount of oil or OPWM (petroleum hydrocarbons) remaining in the water after purification. For this purpose, the spectra of those ORW and IW samples purified in the research work were taken using the analyzer multi N/C device, QX-KS 6890-5975 brand gas chromatograph-mass spectrometer and NMR

BRUKER device, which are considered modern research methods.

The main provisions for the dissertation defense:

A new coagulation-chemical cleaning method was developed for cleaning the oil and oil product waste mixture, which are the main environmental indicators of ORW and IW samples cleaning, from those waters, not only in ecological norms, but even in comparison with sanitary norms. In this regard, the optimal technological conditions of the specified method have been determined.

The development and results of the method of environmentally effective cleaning of oil from oil reservoir water (ORW) formed obtained in the oil production industry.

Development and results of the environmentally effective treatment method of the oil product waste mixture (OPWM) contained in the industrial waste water (IW) of the oil refining industry.

Development and results of environmentally effective cleaning method of IW from OPWM and suspended substances in mechanical cleaning facilities of the oil refining industry.

Comparative environmental analyzes of cleaning of IW samples with existing methods and also with the developed new method were carried out.

Scientific novelty of the research. A new coagulation method method has been developed for oil purification from oil reservoir waters obtained in the OPI, as well as for deep complex purification of oil in the OPWM, which is part of the IW formed during technological processes at the NES and plays a major role in environmental pollution.

According to the developed new method, the scientific research work on the selection of extractant, coagulant, flocculant, neutralizing components and determination of special optimal technological conditions for their use in order to achieve ecologically effective cleaning of ORW obtained in OPI and also IW formed in ORI has been completed.

In the conducted scientific research work, a special technological regime (regulation) and technological scheme were developed for the ecologically effective cleaning of IW formed in the oil refining industry in accordance with the developed new method according to its quantity and composition.

With the developed new method, the IW formed in the oil refining industry and entering the purification facilities, regardless of the flow rate and volume of the IW, are removed from oil, OPWM and suspended substances to approximately 100% within 20 minutes at a temperature of 5-20 ^{o}C, by mixing with air and complete transparency of the color has been achieved.

It was determined that the components used in the developed new method meet the requirements of modern environmental safety.

Investigations based on technical literature and according to the ecological analysis, it was determined that until now no ecologically effective method like the proposed new method is known.

Therefore, it can be considered scientifically based to guarantee the application of the developed new method in the environmentally effective cleaning of the ORW and also the IW formed in the ORI.

Theoretical and practical significance of research. As a result of the conducted studies on deep ecological purification of ORW obtained from OPI, as well as IW formed at ORI, the content of oil, OPWM, suspended solids contained in these water samples and considered the main indicator of purification, purification of approximately 100% and complete transparency of the black color of these waters was achieved and it was proposed to apply this method in industrial production.

Thus, the possibility of using a new technological process-environmentally effective method for the purification of ORW obtained in OPI from oil and also from OPWM of IW formed in ORI using cheap reagents is substantiated. That is why it can be considered scientifically based that this developed method is of great practical, ecological and economic importance.

Approval and application. The results of the dissertation were presented at the following scientific conferences:

- "Actual problems of ecology and pedology sciences in the 21st century" conference dedicated to the 96th anniversary of the birth of national leader Heydar Aliyev at Baku State University (BSU), (2019).
- World integration and communication between sciences, in international scientific and practical internet conference (2020).

- At the VIII International scientific conference "Chemistry of coordination compounds" dedicated to the 85th anniversary of the "Analytical Chemistry" department at Baku State University (BSU) (2020).
- At Baku State University (BSU) at the conference "Ecology and soil science in the 21st century" dedicated to the 97th anniversary of the birth of national leader Heydar Aliyev (2020)
- At Baku State University (BSU) at the conference "Ecology and soil sciences in the 21st century" dedicated to the 98th anniversary of the birth of national leader Heydar Aliyev (2021).
- At the conference "Engineering and energy new concepts and technologies" at Azerbaijan Technical University (AzTu) (2021)
- "Modern views and researches" at the international scientific-practical conference (2022).
- "Technogenic systems and environmental risk" at the V International XVII Regional Scientific Conference (2022).
- It was presented and discussed at the "Modern problems of theoretical experimental chemistry" conference (2020) dedicated to the 90th anniversary of Academician Rafiga Aliyeva.

Publications. Based on the materials of the dissertation, 21 scientific works including 1 patent, 7 articles, 13 theses were published in local and foreign publications.

The name of the organization where the dissertation work was performed. The dissertation work was carried out at the Department of Ecological Chemistry and the Scientific Research Laboratory of Environmental Protection of BSU.

The total volume of the dissertation in characters, with a separate indication of the volume of the structural sections of the dissertation. The dissertation is written in Azerbaijani and consists of 167 pages, consisting of introduction, 5 chapters, conclusions, abbreviations, bibliography and appendixes. The list of used literature includes 115 sources, 108 of which were foreign publications. The dissertation consists of 201302 characters (introduction – 14146, chapter I – 76783, chapter II – 12862, chapter III – 18972, chapter IV – 42731, chapter V – 33691, results – 2117). The dissertation contains 18 figures and 18 tables.

In the introductory part, scientific explanations are given about the relevance of conducting research on the selected topic, the purpose of the work, scientific novelty, and practical importance, and the defense of the dissertation is justified.

In the first chapter, the analysis of literature data was carried out in accordance with the main goal of the dissertation on the topic "Development of the method of ecologically effective treatment of industrial waste water of the oil industry". Therefore, a literature review was prepared by analyzing the explanations and information given in the literature about the causes of the formation of the ORW obtained in the OPI and also the IW obtained in the ORI, the cleaning methods and the environmental problems.

In the second chapter, in accordance with the work plan, NLS samples were taken from the treatment areas of Azerbaijan's OPI, and also samples were taken from industrial waste water (IW) formed at different times in the treatment plants operated in ORI enterprises in accordance with certain rules. During the research conducted on ORW and also IW samples taken from the above mentioned industries, quantitative analyzes of the composition of the samples before and after cleaning were carried out in accordance with the methods indicated in the literature, and the results were given in Chapter II of the experimental part of the dissertation.

The third chapter presents the progress and results of studies on the primary environmentally efficient cleaning of ORW samples taken from oil producing enterprises, as well as IW from oil refineries' oil depots, mainly containing only oil, using substances with coagulant properties $FeCl_3$, $FeSO_4$, $Fe_2(SO_4)_3$, $KAl(SO_4)_2$, $Al_2(SO_4)_3$ and the 5% concentration of CCl_4 determined by us later.

In the fourth chapter, the progress and results of research on environmentally effective cleaning of formed in the oil refining industry IW containing oil and OPWM by the coagulation method are given.

In the fifth chapter, a comparative ecological analysis of the methods used in the modern methods of cleaning the ORW obtained in the OPI in the developed countries of the world and also the IW formed in the production areas of the ORI was carried out. During the conducted ecological analysis, it was determined that in the recently

conducted scientific research-projects and patent-awarded works on the treatment of ORW obtained in OPI and also IW formed in the production areas of ORI, mainly modern equipment, devices and technological processes-methods were used, despite the application of cleaning, the ecological results of the new method developed by us have a significant advantage over those methods. As can be seen from the tables given in the sections of that chapter, it can be considered scientifically justified that the developed new method is of great ecological and economic importance.

At the end of the dissertation work, the results of the performed research and the list of cited literature are given.

MAIN CONTENTS OF THE WORK
MATERIALS AND METHODS OF RESEARCH

Identification of reagents for the environmentally effective purification of ORW obtained from the OPI

Initially, $FeCl_3 \cdot 6H_2O$, $FeSO_4 \cdot 7H_2O$, $Fe_2(SO_4)_3$, $Al_2(SO_4)_3 \times$ $\times 18H_2O$, $KAl(SO_4)_2 \cdot 12H_2O$ substances were used as a coagulant for deep cleaning of ORW samples taken from the cleaning areas of oil production industries, and CCl_4 as a special reagent. and also different percentage solutions of NaOH substances as flocculants were used. It was determined that the results obtained when using these compounds as coagulants without the presence of extractants were not satisfactory. Graphs related to the results obtained in the research studies explained above are shown in figure 1-2.

Thus, according to the results of the analyzes of the conducted research works, it was achieved to clean up to ~100% of oil, suspension substances from the composition of ORW formed and obtained in the oil production industry with a new method developed by using extractant, coagulant and flocculant and making its color transparent. The results of the study are shown in Table 1. Using only 5% $Al_2(SO_4)_3$ solution before the extraction reagent or petroleum ether, up to ~100% (99.998%) of the ORW content was removed from oil and suspended solids. along with the removal of substances, the dark cloudy black color of the sample has become completely transparent.

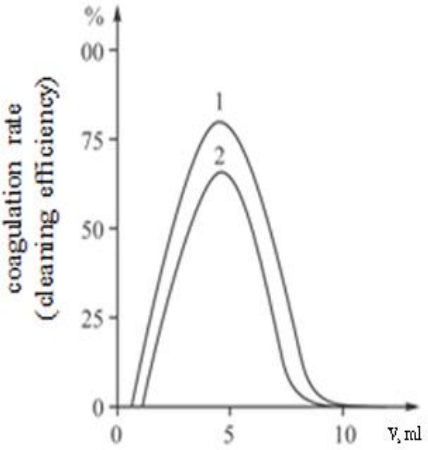

Figure 1.The effectiveness of cleaning the oil content of the oil industry's wastewater treatment plants depends on the coagulant concentration:1)using $Al_2(SO_4)_3$; 2)without using $KAl(SO_4)_2$ extractant for coagulation.

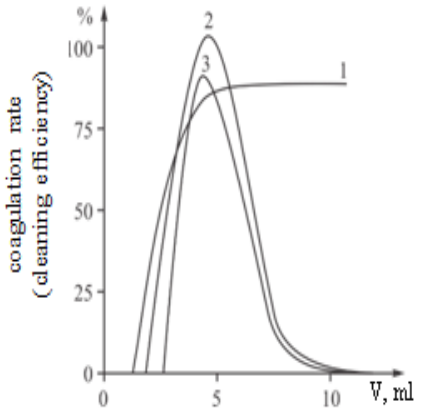

Figure 2. The degree of coagulation of the oil content of the oil industry's wastewater treatment plants with the participation of the extractant (dependence of cleaning efficiency on the coagulant concentration): 1) petroleum ether; 2) $Al_2(SO_4)_3$; 3) $KAl(SO_4)_2$.

When 5% $Al_2(SO_4)_3$ is used as a coagulant in the treatment of oil reservoir water samples, obtained in OPI, the pH of the medium drops from 7.2-7.5 to 2.5-4. The resulting strongly acidic environment is unacceptable. Therefore, 5% NaOH solution was added in the ratio of 1:6 to the 5% $Al_2(SO_4)_3$ solution used in the purification of ORW obtained from OPI. At this time, the acidic environment is neutralized, and the 5% NaOH used acts as both a flocculant and a neutralizing component. In this regard, a 5% $Al(OH)_3$ solution was used instead of a 5% $Al_2(SO_4)_3$ solution as a coagulant, and as a result, the ORW sample's purification indicators were the same, and the pH of the environment remained in the range of 7.1–7.5. Table 2 shows the results of research studies on the oil purification of ORW samples taken from the oil production industry and also on the purification of IW samples taken from the oil base of the oil refining industry using the above

coagulants used in the study.

Thus, deep cleaning of oily reservoir water (ORW) samples formed during oil removal from water in the tanks where oil raw materials are stored in OPI, and also environmentally effective deep cleaning of IW samples containing oil emulsion formed in ORI was achieved through a new chemical method.

At the same time, due to the fact that purified ORW and IW contain Na_2SO_4 and other impurities, mainly $Al(OH)_3$, instead of a coagulant in these waters, studies were conducted on the use of purified IW containing a coagulant as a coagulant. It was found that long-term use of purified IW as a coagulant at late stages is of great economic importance. At the same time, due to the fact that the EK-1 component initially used in the cleaning of the IW remains in the refined oil or OPWM, the possibility of providing the use of the conditionally named EK-2 mixture as an extractant substitute during the next IW cleaning process for a long time has been determined.

Based on the results of the research studies on the ecologically effective cleaning of ORW formed in the oil production industry, the application of the new method developed in the industry can be considered scientifically justified.

DEVELOPMENT OF A NEW ENVIRONMENTALLY EFFECTIVE CHEMICAL METHOD FOR DEEP CLEANING OF ORW FORMED-OBTAINED IN THE OIL PRODUCTION INDUSTRY

During the conducted researches, it was determined that in the oil production industry, ORW formed-obtained during the preparation of oil as a commodity raw material contains various oil emulsion (hydrophobic and hydrophilic), mainly sulfates and chlorides. The environment is neutral (pH ~6.85–7.25). The ORW formed-obtained in this way mainly refers to the oil extracted from the oil fields of the "Neft Daslari", "Surakhani" and "Ali Amirov" oil-and-gas production mines. That is why, during the preparation of oils extracted from different fields and different in terms of their composition as raw materials, ORW that differ from each other in composition are obtained. Due to the low demand for the cleaning speed of ORW obtained in oil production industry enterprises, a new chemical method for deep

Table 1.

Results of a study on deep ecologically effective chemical cleaning of IWWsamples in the oil production industry

Name of the source taken, volume	ITS sample											
	Composition before purification				Reagents used in purification		Composition after purification					
	The amount of oil in milli-grams per liter (mg/l)	The amount of suspended matter in milligrams per liter (mg/l)	pH	color	Attachment 1, milliliters	5% $Al_2(SO_4)_3$, milliliters	5% NaOH, milliliters	5% $Al(OH)_3$, milliliters	Oil, milligrams per liter (mg/l)	Suspended matter amount, grams per liter (g/l)	pH	color
1.Oil stones 1 liter	500-1000	250-350	7.2	Dark and opaque	2	3-5	18-30	3-5	0.02	0.02	7	Transparent
2.Surakhani oil extraction 1 liter	500-1000	250-350	7.1	Dark and opaque	2	3-5	18-30	3-5	0.01	0.01	7	Transparent
3.Nobel Oil Company 1 liter	500-1000	250-350	6. 9	Dark and opaque	2	3-5	18-30	3-5	0.01	0.01	7	Transparent
4.Heydar Aliyev Oil Refinery, 1 liter	500-1000	250-350	7.3	Dark and opaque	2	3-5	18-30	3-5	0.01	0.01	7	Transparent

Note: When using only 5% $Al(OH)_3$ as a coagulant, there is no need to use 5% NaOH and $Al_2(SO_4)_3$.

Table 2.

Results of experiments on the deep ecological chemical purification of IWW samples containing oil from the oil industry

Name of the source taken, volume in liters (l)	Composition before purification				Composition after purification									
	Amount of oil, mg/l	Sus-pen-ded mat-ter, mg/l	pH me-dium	Color	EK-1, m	K-1, ml	K-2, ml	EK-2, ml	KTS, ml	K-3, ml	Amount of oil, mg/l	Sus-pended matter, mg/l	pH me-dium (7-9)	Color (nor-mal light color)
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Oil base of Heydar Aliyev Oil Refinery 1 liter	500-1000	150-250	7.3	Dark cloudy	1-2	3-5	18-30				0.01	0.01-0.02	7.2	
								15-20	20-30		0.01-0.02	0.01-0.02	7.2	Transpa rent
					1-2					2-3	0.01-0.02	0.01-0.02	7.2	Transpa rent

Note: EX-1: Petroleum Ether; K-1: 5% $Al_2(SO_4)_3$; K-2: 5% NaOH; EX-2: Mixture of oil and petroleum ether; IWW: Chemically treated wastewater containing $Al(OH)_3$ and other compounds; K-3: 5% $Al(OH)_3$.

Cleaning of that ORW has been developed using special reagents of the highest economic and ecological importance during the preparation of oil as a commodity raw material. As can be seen from the results of previous and currently ongoing scientific research on the purification of ORW formed in the oil production industry, until now there has been no chemical method of purification that does not affect the quality of crude oil and can fully meet the requirements of environmental safety.

As in the developed countries of the world's oil production industry, in Azerbaijan, during the initial production of oil and its preparation as a commodity raw material, in some cases, it is heated to a certain extent, mainly by mechanical sedimentation in tanks, and mechanical purification from water is carried out with long-term intervals. At this time, it is not possible to deeply clean the ORW, which contains a stable oil emulsion (hydrophilic, hydrophobic type emulsions). Up to now, it has not been possible to clean these waters thoroughly, up to 100% of oil, despite passing through several stages of mechanical, physical-chemical, chemical, biological cleaning processes.

According to the explanations given in the technical literature, the amount of mechanical impurities in the oil prepared as commodity raw materials should be 0.05%, and the amount of water should be 0.1–0.5% in the maximum case, as well as have other quality indicators.

During the purification of ORW formed in the oil production industry with a new ecologically effective chemical method developed by us, the amount of oil in those waters was ~ 0.01-0.02 mg/l, the amount of suspended substances was ~ 0.01-0.02 mg/l, and the color became completely transparent. Purification of ORW with the developed new method was carried out in the temperature range of 5-20ºC.

According to the method of oil purification from ORW samples collected from oil producing facilities (except for the Balakhan oil producing complex), the following were used as an effective coagulant: a solution of $Al_2(SO_4)_3$ – (conventionally designated K-1), petroleum ether obtained from gasoline distillate

(from the 40-70°C fraction, conventionally designated EK-1), which are shown in Tables 1 and 2.

A special optimal mode was chosen when using the extractant conventionally marked as EK-1 and the coagulant reagents marked as K-1, besides, studies were repeatedly conducted with several different reagents.

The ecologically and economically important results mentioned below were obtained:

K-1 coagulant is then added to the purified water. Since the EK-1 component (petroleum ether) remaining in the organic-oil layer consists of mixtures of petroleum hydrocarbons, it does not have a negative effect on the quality of the oil.

Experimental work on the application of the same mixture containing oil and EK-1 solvent (extractant) component obtained during the cleaning of ORW samples formed in oil production with a new ecologically effective chemical method developed by us, to a certain extent, as a replacement for EK-1 extractant in the next ORW cleaning was conducted.

It can be noted that due to the presence of $Al(OH)_3$ in the salt mixture of purified ORW samples, research studies were also conducted on the use of those waters as a coagulant substitute in the subsequent purification of those types of waters. It was determined that the use of those mixtures for a long time in the later stages has a very high economic value.

DEVELOPMENT OF ENVIRONMENTALLY EFFECTIVE CLEANING METHOD IN MECHANICAL CLEANING INSTALLATIONS OF İNDUSTRİAL WASTEWATER (IW) OF OIL REFINING INDUSTRY (ORİ)

Coagulation method, one of the types of physico-chemical method, was applied for deep cleaning of industrial waste water (IW) samples taken from the mechanical cleaning facilities of the Oil Refinery named after Heydar Aliyev in laboratory conditions. $Al_2(SO_4)_3$ was used as a coagulant, petroleum ether as an extractant, and H_2SO_4 acid solutions of a certain concentration were used as a flocculant. Under particularly optimal conditions, a mixture

containing even 1,000–5,000 mg/l waste oil products (OPWM), as well as suspended solids, can be purified from IW up to ~100% (up to 99.998%). At the same time, complete transparency of the dark black color of the turbidity of IW samples was achieved. Based on the results of the conducted studies, spectra were taken with several devices to determine the presence of OPWM (organic compounds) in the purified water obtained from the ecologically effective treatment of IW with the optimal conditions determined. As can be seen from the spectrum of the treated IW sample in Figure 3, natural waters also contain very small amounts of some natural organic compounds. It was observed that these substances are in a very low amount compared to the standard substances used in the spectrum.

As can be seen from Table 3, the amount of the mixture of organic substances remaining in the purified water sample was ten times lower than the known ecological and even sanitary norms, and 500 times lower than the ecological norms of the oil refinery. In addition, the spectrum of the taken IW samples was taken on the NMR BRUKER device to determine the amount of organic compound mixture remaining in the same water sample purified by the new method.

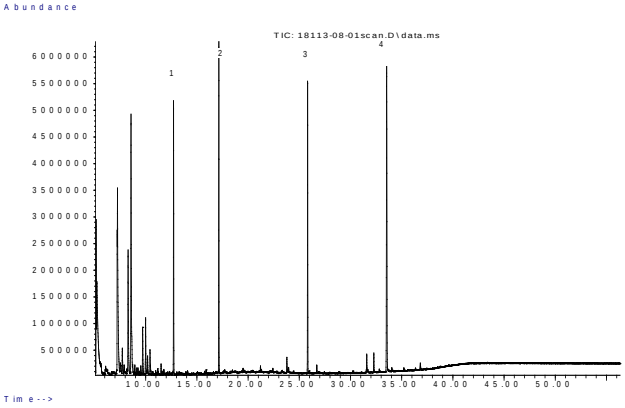

Figure 3. Peaks of the internal standard:
1. Heptamethylnonane; 2. Hexadecane; 3. Chloroctadecane; 4. Squalane.

Table 3.
The amount of individual CHACs obtained in the QX-KS 6890-5975 gas chromatograph mass spectrometer device of IW purified by the developed new method

Substances	T-VI mkg/l
Naphthalene	1.14
Acenatylene	0.11
Acenaphthene	0.12
Fluorene	0.41
Phenanthrene	0.82
Anthracene	0.19
Fluoranthrene	0.13
Pyrene	0.26
Benzo(a)anthracene	0.15
Chrysene	0.32
benzob(k)fluoranthene	0.30
benzo(a)pyrene	0.21
indeno(1,2,3- cd)pyrene	<0.01
benzo(ghi)preylene	0,07
Dibenzo(ah)anthracene	<0.01
EPA 16 CHAK	4.23

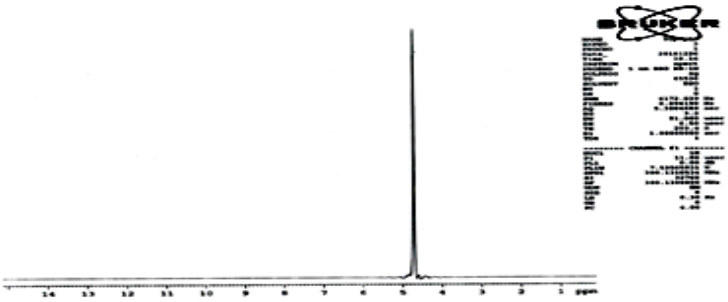

Figure 4. Spectra of purified IW water sample taken with NMR BRUKER device.

As can be seen from Figure 4, hydrogen atoms belonging to water were obtained with a high peak. However, the peaks of the groups of hydrocarbon compounds remaining in the water were

extremely small. This shows that the amount of organic compounds in the sample of IW purified by the new method is even ten times lower than the sanitary norm.

In the future, the cleaning of oil industry IW and also IW formed in other industrial enterprises and containing organic pollutants with a very simple, i.e., without additional installation work in existing treatment plants, with a new method developed by us will help to prevent the pollution of the world's vital water bodies, as well as non-returnable oil and OPWM will allow to achieve reuse of losses. The scientific justification of these listed issues is reflected in the dissertation work.

Thus, according to the results of the conducted research, the graphs of dependence of the coagulation process on the amount of reagents, temperature and time during the purification of oil industry IW samples with a new method are shown in figures 5-7.

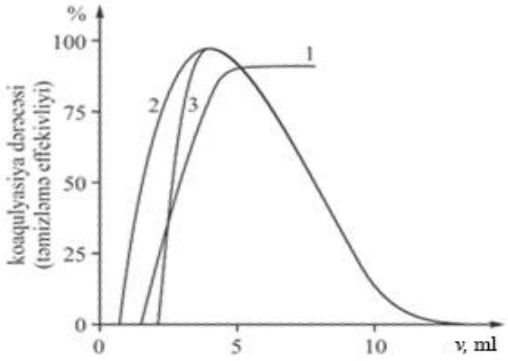

Figure 5. Dependence of the coagulation process (the efficiency of removal of OPWM from IW and suspension substances) on the amount of extractant (petroleum ether), coagulant (5% $Al_2(SO_4)_3$ solution) and flocculant (5% H_2SO_4 solution). 1) petroleum ether, 2) 5% $Al_2(SO_4)_3$ solution, 3) 5% H_2SO_4

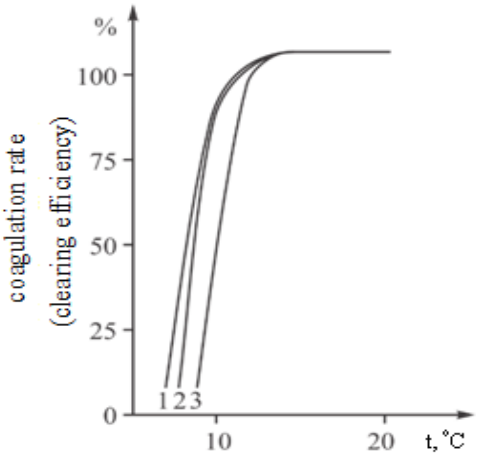

Figure 6. Dependence of the coagulation process on temperature: 1-extractant; 2-coagulant; 3-flocculant

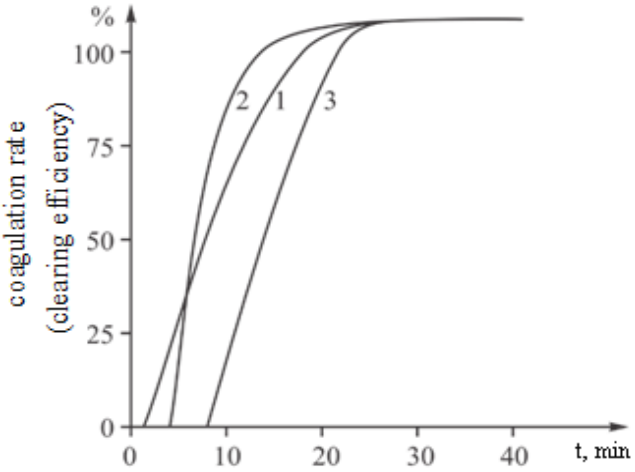

Figure 7. The dependence on time in the coagulation process is 1-extragent; 2-coagulant; 3-flocculant

The ecological indicators of the research results are presented in Table 4.

Rationale for effective purification of ORW samples obtained in OPI and IW samples formed in ORI by coagulation method

High results of the scientific research conducted on the implementation of the deep purification of oil from the ORW samples obtained in OPI and also the OPWM from the IW samples formed in ORI, the deep purification of suspended organic compounds by the coagulation method were obtained. Using the coagulant $Al_2(SO_4)_3$, petroleum ether extractant, acid flocculant H_2SO_4 (and NaOH as a flocculant-neutralizer during the purification of the IW-ORW sample), under determined optimal conditions, the purification of the ORW sample from oil, as well as the IW sample from OPWM, suspended organic compounds up to ~ 100%, as well as complete transparency of the color was achieved.

Table 4.

Ecological indicators of oil production and processing IWW samples purification by the developed new chemical-coagulation method

IWW sample			
Quantitativeanalysisindicator	The name of the source from which it was taken, the volume used in the purification, one lite		
	Oil Stones	The oil base name of Haydar Aliyev Refinery	Mechanical cleaning unit of Heydar Aliyev Refinery (introduction)
Before cleaning			
Oil or OPWM, mg/l	500-1000	500-1000	500-1000
Suspended matter mg/l	250-350	250-300	
pH medium	7.3-7.5	7,2	
BOD_5 mg O_2/l	350-450	300-350	
COD mg O_2/l	500-600	500-600	500-600
Phenol-type compound . mg/l	1.5-2.0	1.5-2.0	1.5-2.0
Chlorides mg/l	350-450	350-450	350-450
Sulfates	200-250	200-250	200-250
Dry residue	550-600	550-600	550-600
Color	Dark cloudy	Dark cloudy	Dark black
After cleaning			

Continuation of Table 4

Oil or OPWM, mg/l; MPC 0,05 mg/l	0.01-0.02	0.01-0.02	0.01-0.02
Suspended matter mg/l; MPC 5 mg/l	0.01- 0.02	0.01- 0.02	0.01- 0.02
pH medium	7.2	7.2	7.2
BOD_5 mg O_2/l ; MPC 5-6 mg/l	2.5-3.0	2.5-3.0	2.5-3.0
COD mg O_2/l MPC 35 mg/l	15-20	15-20	15-20
Phenol-type compound . mg/l MPC 0,001 mg/l	0.001	0.001	0.001
Chlorides mg/l	150-250	150-250	150-250
Sulfates	150-200	150-200	150-200
Dry residue MPC 1000 mg/l	250-300	250-300	250-300
Color	Transparent	Transparent	Transparent

Compared to the ORW obtained from the OPI, the IW formed in the ORI is a very complex liquid mixture due to its volume, flow rate, harmful substances and physicochemical properties. Thus, despite the treatment of the IW formed in the oil refining industry in accordance with the requirements of environmental norms, the flora and fauna of the waters are exposed to destructive ecological effects as a result of the disposal of a part of those waters in the volume of hundreds of millions of cubic meters per year. This causes long-term ecological problems in the hydrosphere, despite the dilution of industrial waste water in water bodies.

The coagulation method, which is one of the types of physico-chemical method, was used for the deep purification of industrial waste water (IW) samples taken from the facilities of the Heydar Aliyev Oil Refinery in laboratory conditions. With that developed new method, petroleum ether was used as extractant, $Al_2(SO_4)_3$ salt as coagulant, and H_2SO_4 acid as flocculant. In this regard, the determination of the optimal conditions played an important role in the development of the new method.

According to the researches conducted by us, it was

determined that during the several stages of purification of the IW formed not only in the above-mentioned enterprises, but also in the oil refining industry of the world countries, it was not possible to purify those waters from OPWM and suspended substances up to 100%. It is scientifically proven that the developed coagulation method is of great ecological and economic importance.

Taking into account the above explanations and the conducted analyses, scientific research work on the purification of IW samples taken from the purification facilities of the Heydar Aliyev Refinery in laboratory conditions has been carried out in several directions.

Taking into account the types of physico-chemical methods known during the research work, a new method of IW purification was developed. As mentioned, the composition and characteristics of IW formed in the oil refining industry are very complex. That is why it is very difficult to treat such wastewater. In this regard, all types of physico-chemical methods are used during the treatment of this type of wastewater. At this time, a large amount of electricity and other energy carriers, as well as valuable reagents, are used.

During the long-term research work carried out in laboratory conditions, it was determined that it is possible to completely clean IW from OPWM, suspending substances and make its color transparent using coagulant, extractant and flocculant under optimal conditions. This method can be comprehensively evaluated as a new method that is ecologically and economically effective and efficient.

With the new method developed, it was possible to clean up to 100% of suspended substances of IW, which cannot be cleaned by biochemical method.

During the research, the dependence of $Al_2(SO_4)_3$ as the most effective coagulant on the specially prepared solution, the amount of that solution and the volume of the cleaned IW was determined.

In addition to the above explanations, the following changes occur after the coagulant is added to the IW sample.

During the research, it was determined that the degree of mixing of the coagulant with water greatly affects the degree of purification of the IW sample. Complete coagulation is achieved by

rapid mixing for 10–15 min. As mentioned in the dissertation, according to the explanations given in the technical literature, this indicator depends on the collision frequency of particles in the orthokinetic phase during rapid mixing.

The solid phase particle growth phase mainly involves the time of crystallization center growth after the incubation period. The kinetics of crystallization depends on the growth rate of the crystallization center - the aggregation phase. As a result, as this center grows and the number of centers increases, the physical state of particle aggregation changes, and water polluting mixtures also settle together with the coagulant. Thus, the process of separation of the solid phase formed by the coagulant from water is considered its "aging" process. As a result of this, that is, during the aging period, the solid phase formation process ends and separates from the liquid phase.

During the research, the above-mentioned cases were observed at the use of IW with $Al_2(SO_4)_3$ coagulant and H_2SO_4 as a flocculant to accelerate, complete and create a neutral environment and petroleum ether as an extractant. The results of the process can be explained by the following chemical changes: After extraction, mixing is done by adding $Al_2(SO_4)_3$ – coagulant from the prepared solution to the IW sample. At this time, $Al(OH)_3$ formed from the hydrolysis of the coagulant turns into a colloid.

$$Al_2(SO_4)_3 + 6H_2O = 2Al(OH)_3 + 3H_2SO_4$$

Anions of separated sulfuric acid and hydrocarbonates of sodium, calcium and magnesium contained in the IW sample, etc. compounds react to form water-soluble salts. When the pH environment of IW is between 9–10, 5% H_2SO_4 acid used as a flocculant neutralizes the alkaline environment to pH=7.3–7.5. At the same time, a solution of low percentage H_2SO_4 acid is used to accelerate the coagulation process. At this time, the pH of the environment is brought to 7.4.

As a result of initial hydrolysis of $Al_2(SO_4)_3$ coagulant, $Al(OH)_3$ colloid is positively charged at a certain pH level and coagulates the charged colloids contained in the IW sample. When $Al(OH)_3$ settles due to its own weight, it settles suspended clay, soil

and other mechanical mixtures with it. Organic suspending substances are coagulated with an extractant and collected in the organic layer.

As can be seen from the above explanations, using a solution of H_2SO_4 to increase the intensity of purification of the coagulant $Al_2(SO_4)_3$, petroleum ether as an extractant, the method we developed succeeded in purifying the IW obtained in ORI from OPWM (organic mixtures) and making these waters transparent.

Thus, it can be considered scientifically justified to guarantee the full deep cleaning of the IW formed in the oil refinery with the developed method.

One of the main directions of the aim of the dissertation work is to develop a method of deep purification of IW formed in the oil refining industry, along with the deep purification of ORW formed in the oil production industry.

Based on that method, the technological scheme of ecologically effective cleaning of IW in the primary mechanical cleaning facilities of Heydar Aliyev Refinery is given in the dissertation work. As can be seen from the above-mentioned explanations, it is possible to purify samples from oil up to ~100% by the new method developed, and it is also proved that the IW samples formed in ORI can be purified up to ~100% by the new method developed from the mixture of oil and petroleum products waste and suspending substances has been done.

As indicated in the explanations given in the dissertation work, in general, the following indicators are considered for the deep purification of IWW formed in both production areas of the oil industry in modern times:

1. Achieving purification of the oil and oil product emulsion mixture in IWW to ~100%, i.e., even below sanitary standards (from 0.05 mg/l);
2. Minimizing the amount of phenols in the composition of IWW;
3. Purifying suspended solids in IWW up to ~100%;

4. Approaching (reaching) the levels of zero in the concentration of oil, grease, and organic substances (COD and BOD) in the purified IWW;
5. Ensuring the pH of IWW in the basic neutral interval of 6.5–7.5 (maintaining);
6. Clarifying the color of IWW.

For this reason, analytical chemical methods have been employed for the analysis to ensure more accurate and reliable results of the purification of IWW samples from the oil emulsion industry using our method.

The remaining amount of oil and oil product emulsion mixture and suspended solids in the cleaned IWW sample have been determined according to the methods and regulations shown in the literature information.

The results of research work on the new chemical coagulation method for the purification of IWW in the oil production and oil emulsion industries are presented in Chapters III and IV of the dissertation. In Chapter V, the comparative ecological analysis of the newly developed method with the methods currently used in the oil industry in developed countries has been discussed.

RESULTS

1. A new chemical-coagulation method was developed for the deep cleaning of oily reservoir water (ORW) samples obtained in the oil production industry (OPI) of Azerbaijan, as well as production waste water (IW) samples formed in the oil refining industry (ORI).
2. Purification of oil up to ~100% from the ORW samples taken in OPI by that method (the amount of oil from 500-1000 mg/l to 0.01-0.02 mg/l) and also from the ORI IW samples the amount of oil, OPWM from 500-1000 mg/l to 0.01-0.02 mg/l and the amount of suspending substances from 350-400 mg/l to 0.01-0.02 mg/l up to ~100% purification, translucency of dark black color of ORW and also IW samples was achieved [2, 3, 18].
3. It was determined that the reagents used in the purification of ORW and ORI IW samples by a new method meet all the requirements of modern environmental safety before and after the coagulation process [4, 18].
4. It has been determined that if the IW is cleaned by a new coagulation method in the oil refining industry, it is possible to prevent the loss of approximately ten thousand tons of crude oil, OPWM and pollution of water bodies with the same amount of crude oil and OPWM within a year [12, 13].
5. An optimal technological scheme for ecologically effective cleaning of the IW formed in the ORI with a new method was developed. Purification of IW in ORI by a newly developed coagulation method - the dependence of the degree of the coagulation process on the initial use of the extractant and the concentration-amount of the coagulant was determined [14].
6. Depending on the content of the next purified IW as an extractant substitute for oil containing petroleum ether and also OPWM containing petroleum ether obtained from the purification of ORW samples obtained in OPI and also IW samples formed in ORI by a new method developed. The possibility of using up to 1-2% has been determined [12, 18].
7. In the oil (production and processing) industry, as a substitute for coagulant from purified water containing $Al(OH)_3$, various metal-

containing sulfate compounds and other salts, obtained from the purification of IW by a new method, depending on the composition of the next purified IW, these purified waters. It has been determined that up to 5-10% are used [16, 17, 18].

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1. Hajiyeva, S.R., Shamilov, N.T., Bayramov, G.İ., Rakida, N.M. "Ecologically effective purification of production drainage waters with oil emulsion" //Conference dedicated to the 96th anniversary of the birth of the national leader Heydar Aliyev "Actual problems of Ecology and Soil Science in the XXI century", –Baku: –3-4 May, – 2019.– p.81.
2. Rakida, N.M. "Development of the method of deep ecological effective chemical treatment of industrial wastewater generated in the oil industry" //International journal of scientific & Engineering research.– USA:–6 June, – 2020, V. 11,– p.880-885.
3. Hajiyeva, S.R. "Development of an Ecologically Friendly method for the chemical treatment of industrial wastewater generated in the oil industry" /Sevindj Hajiyeva, Nazim Shamilov, Giyas Bayramov, Naila Jafarova, Narmin Rakida //Journal of Ecology and Natural Resources.– USA:– 2020. V.2,– p.1-3.
4. Rakida, N.M. "Effective purification of production drainage waters formed in the oil industry with the coagulation method" //International internet conference on integration with the world and interdisciplinary relations, –Baku: – 2020. – p.34.
5. Hajıyeva, S.R., Shamilov, N.T., Bayramov, G.İ., Rakida, N.M. "Application of the coagulation method for ecologically efficient purification of production drainage waters in the oil production industry" //International internet conference on integration with the world and interdisciplinary relations, –Baku:– 2020.– p.35.
6. Hajıyeva, S.R., Shamilov, N.T., Bayramov, G.İ., Rakida, N.M. "Application of the new method for efficient purification of oil industry drainage waters" //Materials of the VIII International scientific conference on "Coordination Compounds Chemistry" dedicated to the 85th anniversary of the Analytical Chemistry Department, –Baku: –22-23 December,– 2020. – p.148.

7. Hajiyeva, S.R., Shamilov, N.T., Bayramov, G.İ., Rakida, N.M. "Application of the method for ecologically efficient purification of production drainage waters in the oil industry" // Materials of the VIII International scientific conference on "Coordination Compounds Chemistry" dedicated to the 85th anniversary of the Analytical Chemistry Department, –Baku: –22-23 December, – 2020. – p.152.

8. Shamilov, N.T., Bayramov, G.İ., Rakida, N.M. "Application of ecologically effective chemical treatment of drainage waters" //Materials of the Republican scientific conference of young researchers on the topic "Ecology and Soil Science in the XXI century" dedicated to the 97th anniversary of the birth of the national leader Heydar Aliyev,–Baku: –16-17 June, – 2020.– p.87.

9. Shamilov, N.T., Bayramov, G.İ., Rakida, N.M. "Research on the method of ecological effective treatment of production drainage waters in the oil industry" //Materials of the Republican scientific conference of young researchers on the topic "Ecology and Soil Science in the XXI century" dedicated to the 97th anniversary of the birth of the national leader Heydar Aliyev,–Baku: –16-17 June, – 2020.– p.88.

10. Hajıyeva, S.R., Shamilov, N.T., Bayramov, G.İ., Huseynov, F.E., Abdullayeva U.N., Rakida, N.M. "Ecological efficient treatment of emulsified oil drainage waters" //Materials of the Republican scientific conference of young researchers on the topic "Ecology and Soil Science in the XXI century" dedicated to the 98th anniversary of the birth of the national leader Heydar Aliyev, –Baku: –5-6 May,– 2021.– p.87.

11. Hajıyeva, S.R., Shamilov, N.T., Bayramov, G.İ., Rakida, N.M. "Application of the new coagulation method for ecologically efficient purification of production drainage waters in the oil industry" //Materials of the Republican scientific conference of young researchers on the topic "Ecology and Soil Science in the XXI century" dedicated to the 98th anniversary of the birth of the national leader Heydar Aliyev, –Baku: –5-6 May, – 2021.– p.127.

12. Hajiyeva, S.R. "Ecological effective treatment of industrial wastewater formed in the oil-producing industry by coagulation

method" /Sevindj Hajiyeva, Nazim Shamilov, Giyas Bayramov, Narmin Rakida //Azerbaijan Chemistry Journal, –Baku: – 2021. №3, – p.63-67.

13. Rakida, N.M. "Ecological efficient purification of production drainage waters" //Azerbaijan Technical University, Fundamental Sciences, Scientific Works. –Baku: – 2021. №1,– p.120-125.

14. Rakida, N.M. "New method of treatment of wastewater from oil refining industry" //Azerbaijan Technical University, Fundamental Sciences, Scientific Works. –Baku: – 2021. №1,– p.179-184.

15. Shamilov, N.T., Bayramov, G.İ., Rakida, N.M. "The new chemical method for wastewater treatment in oil refining industry" //Azerbaijan Technical University, November, – 2021, – p.247-249.

16. Rakida, N.M. "Effective method of industrial waste treatment" //Khazar Journal of Science and Technology (KJSAT), – Baku:– 2022. №1, – p.58-62.

17. Rakida, N.M.. "Development of a new chemical purification method for oil containing industrial waste water" //Natural and Technical Sciences. –Moscow:– 2022. №8, –p.152-155.

18. Hajıyeva, S.R., Shamilov N.T., Bayramov, G.İ., Huseynov F.E., Valiyeva Z.T., Rakida N.M., Mammadov R.Y. "Purification method for production drain a gewaters. Invention patent. I2022 0011, 01.03.2022. Azerbaijan Intellectual Property Agency /

19. Rakida, N.M. "Environmental and economic significance of industrial wastewater treatment" //Modern Views and Research (International scientific and practical conference, –England:– 2022.– p.71-72.

20. Rakida, N.M. "Chemical treatment of industrial wastewater" //Technogenic Systems and Environmental Risk (V International XVII regional scientific conference).–21-22 April, – 2022. – p.211-213.

21. Shamilov, N.T., Rakida, N.M. "Cleaning of oil industry wastewater with environmentally effective chemical method" //Devoted to the 90th Anniversary of Academician Rafiga Aliyeva Modern Problems of Theoretical Experimental Chemistry. –Baku:– 29 September, – 2022.– p.200-201.

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