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THERMOCHEMICAL LUMINESCENCE AND CHEMICAL TRANSFORMATION MECHANISMS IN HEAVY CRUDE OIL RESIDUES

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ABSTRACT

This study investigates the thermochemical luminescence (TCL) behavior of heavy residues derived from Karabakh, Absheron, and Naftalan crude oils to examine their chemical transformations and implications for quality. Crude oil is a complex mixture of hydrocarbons, dissolved gases, water, salts, and impurities, with its composition varying significantly. Advanced spectroscopic techniques, including UV, NMR, IR, and luminescence analysis, were utilized to explore the structural-group composition and physicochemical properties of these oils. TCL analysis revealed consistent characteristics among the heavy oil residues, marked by hybrid molecular structures and weakly bonded C–H linkages. The residues, after undergoing de-resinification and deasphalting, exhibited a notable uniformity, making them promising candidates for use as biologically active substances. Photoirradiation experiments demonstrated that the TCL maxima for heavy residues appear in lower-temperature spectral regions compared to many distillate fractions. The visible light emission was attributed to the decomposition of endoperoxides during the recombination of peroxide radicals. This observation opens the possibility of utilizing hydrocarbons as alternative light sources, including applications involving solar energy. These results have implications for improving refining processes, optimizing the transportation and storage of crude oil, and broadening the industrial applications of petroleum and its by-products.

1. **Introduction**

Since crude oil is a natural source for obtaining valuable hydrocarbons, its study has attracted the attention of scientists for many years. The study of crude oil and its products, composed of various hydrocarbons, their physical-chemical properties, structural-group composition, changes in its characteristics after photo- and thermal effects, including chemical transformations, is a pressing issue that requires resolution. This is of significant scientific and practical interest. In the investigation of the composition of crude oil, the examination of the structures of initial biological compounds and their transformation products plays an essential role. The study of the hydrocarbon composition of crude oils greatly aids in classifying them into different types.

The saturated hydrocarbons in crude oil determine the initial biomolecules during geochemical processes, as well as the chemical transformations occurring within them [8, 9]. On the other hand, studying the chemical group composition of these substances is crucial in selecting a more efficient method during the crude oil refining process, as well as in solving the issues related to the transportation and storage of crude oil. Moreover, it is essential for the utilization of crude oil and its products in various industries (such as petrochemicals, heavy machinery manufacturing, etc.), medicine, and other fields [1-3]. This is because the properties of crude oils and natural gases affect their application. By studying the thermal properties of crude oil and the oils derived from it, the impact of temperature changes on their physical-chemical properties over time can be determined. After removing asphaltene from well oil, the separation of its fraction composition and the analysis of hydrocarbons with a low boiling point are among the critical aspects [10].

It should be noted that the composition of crude oil includes not only various hydrocarbons but also dissolved gases, water, mineral salts, and mechanical impurities. Due to the presence of numerous different organic substances in crude oil, it is characterized not by a single boiling point but by a boiling range (which, depending on density, varies between 28-360°C) and by its fraction composition. The density of crude oil ranges from 750 to 1050 kg/m^3, and its freezing point is from minus 60°C to plus 30°C (this temperature increases with a higher content of paraffins in the oil and decreases with an increase in lighter fractions). The flash point, in a closed cup, varies between minus 40°C and plus 30°C, depending on the fraction composition [6, 7]. Crude oil dissolves in organic substances, does not dissolve in water, and forms a stable emulsion with it.

In earlier studies on Azerbaijani crude oils, the primary focus was directed towards obtaining narrow fractions of the oil (such as gasoline, ligroin, diesel, etc.) and examining their physical-chemical properties and composition. This approach did not allow for a comprehensive study of the characteristics specific to crude oils, accurate determination of relevant parameters, and identification of structural changes resulting from various external influences (such as radioactive rays, temperature, ultrasound, etc.). However, modern methods and methodologies applied to the study of the composition of crude oil and oil products allow for a complete investigation both individually and in a complex manner. The analysis of crude oil samples can be divided into three parts:

1) Investigation of the structural-group composition of crude oils using UV, NMR, EPR, IR, and chromato-mass spectroscopies, as well as luminescence methods; 2) Determination of the physical-chemical indicators of crude oil using standard methods; 3) General evaluation of crude oils based on their composition and properties.

One of the main methods in studying the hydrocarbon composition of crude oil and oil products is the highly sensitive luminescence method. This is because mono-, bi-, tri-, etc. cyclic aromatic hydrocarbons present in crude oil have the ability to luminesce. These types of compounds also affect the physical-chemical and optical properties of crude oil. In [14-16], the luminescence spectra of crude oil were obtained by excitation with xenon lamps of 400 W power.

In [17, 18], to investigate the effect of the side chain length on the fluorescence properties of solid substances, anthracenes with n-alkyl chains of different lengths were used. Based on the obtained results, it was found that as the length of the side chain increases, the luminescence of solid substances increases, and conversely, it decreases when the chain length decreases. Depending on the chain length, the luminescence shifts towards the red or blue side.

The aim of this study is to investigate the thermochemical luminescence (TCL) of the heavy residues of crude Karabakh, Absheron, and Naftalan oils as the research object, to study the chemical transformation processes occurring within them, to explore their mechanisms, and to determine the impact of these transformations on their quality.

2. Methodology Section

During the photo- and thermal-oxidation of crude oil and oil products, their properties deteriorate, resulting in a decline in quality and making them unsuitable for use. Therefore, as with other substances, one of their main characteristics is thermo-oxidative stability. In all standards, especially for oils and fuels, this value is taken into account. As a rule, this value is determined according to GOST 23175, GOST 305-82, and GOST 10227-86. These methods are labor-intensive, multi-stage, less efficient, not sufficiently accurate, and only applicable in the initial stages of oxidation. They are time-consuming and, consequently, inconvenient for conducting series analyses. However, unlike these methods, the TCL method is more precise and rapid [19].

The photoelectric apparatus used in the study of Karabakh oil and its components for TCL includes: a diffuse reflection base with an elliptical mirror, where the sample is placed at one focal point and the cathode of the photoelectron collector (FET-39A or FET-100) is positioned at the other focal point; a direct current amplifier; a heated cryostat; and an electronic potentiometer KSP-4. In the research process, the samples are placed at the center of a special spherical cuvette with a thickness of 0.1–1 mm and a diameter of 20 mm, and they are positioned parallel to the base of the photoelectron collector on a non-vacuum cryostat. This cryostat allows measurements in the temperature range of 196–300°C.

3. Results and Discussion

The TCL (Thermo-Chemiluminescence) of 50°C fractions of Karabakh crude oil with a boiling temperature range of 100–700°C was investigated. As shown in Figure 1, no TCL maximum was observed in the temperature range of 20–200°C for the 400–450°C fraction, similar to the lower boiling fractions of this oil, without any specific irradiation (only under laboratory light conditions). However, in the hydrocarbon residue (>500°C) of the mentioned oil, intense maxima at 75°C and 110°C were recorded due to the effect of irradiation (Figure 1, curves 2-4).

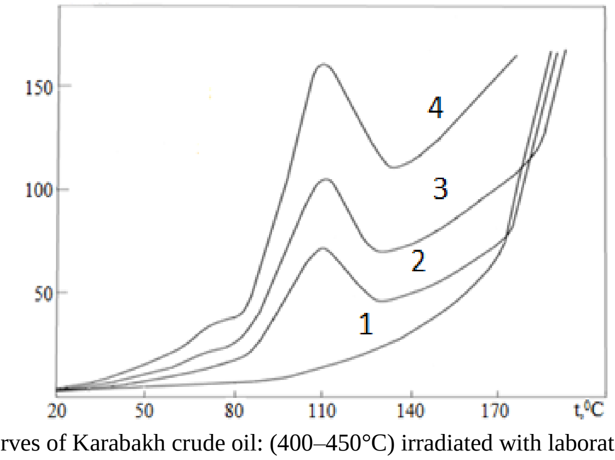

Fig 1. TCL curves of Karabakh crude oil: (400–450°C) irradiated with laboratory light (curve 1), and residuals (>500°C): 2 - irradiated with laboratory light (3 minutes), 3 - irradiated with daylight (3 minutes), 4 - irradiated with a mercury lamp (10 seconds).

It is known that, in the presence of weak hydrogen bonds and molecular oxygen in the oil's composition, radicals such as $H^{\bullet}$, $R^{\bullet}$, $HO_2^{\bullet}$ and $RO_2^{\bullet}$, are formed as a result of weak energetic effects according to the following scheme.

$$RH \longrightarrow R^{\bullet} + H^{\bullet}$$

$$RH + {}^3O_2 \longrightarrow R^{\bullet} + HO_2^{\bullet} \quad (1)$$

$$R^{\bullet} + {}^3O_2 \longrightarrow RO_2^{\bullet}$$

When the concentration of oxygen is high, the concentration of peroxide radicals slightly exceeds that of alkyl radicals $R^{\bullet}$, and a recombination process occurs, forming tetraoxides [20-24]. These tetraoxides decompose continuously when heated, resulting in luminescence, which is recorded as a thermochemical luminescence curve: (2)

$$RO_2^{\bullet} + RO_2^{\bullet} \longrightarrow ROOOOR \longrightarrow {>}C = O^{*} + ROH + {}^1O_2 \longrightarrow {>}C = O + ROH + {}^3O_2 + h\nu_1$$

In the TCL process, aromatic hydrocarbons (AHs) in oil act as both activators and photosensitizers, participating in a two-photon mechanism that leads to the decomposition of hydrocarbons and the formation of radicals:

$AH(S) + h\nu_2 \rightarrow AH(S^*) \rightarrow AH\ (T)$ (3)

$AH(T) + h\nu_3 \rightarrow AH(T^*)$

$AH(T^*) + RH(S) \rightarrow AH(S) + RH(S^*) \rightarrow AH(S) + RH(T) \rightarrow AH(S) + R_f^{\bullet} + H_f^{\bullet}$

Here, S, S*, T, and T*- represent the ground singlet, triplet, and excited singlet and triplet states of AHs, respectively. $R_f^{\bullet}$ və $H_f^{\bullet}$ · represents radicals formed during the photoluminescence process.

When the sample is exposed to photoirradiation in an oxygen atmosphere, new peaks appear in the TL (Thermoluminescence) curve [25, 26]. The photodecomposition of photooxidized compounds formed under irradiation leads to the release of light quanta. This process is termed photothermochemical luminescence (FTCL). However, it should be noted that AHs, in an oxygen environment, oxidize through a single-quantum mechanism to form cyclic peroxides. Linear AHs (such as acenes) oxidize through a molecular mechanism, resulting in the formation of endoperoxides:

(4)

$AH(S) + {}^1O_2$

$AH(S^*) + {}^3O_2$ endoperoxide AH + $AH(S) + {}^3O_2 + h\nu_4$ $\longrightarrow$

$AH^{+\cdot} + O_2^{-\cdot}$

This reaction is reversible, where light energy is stored as chemical energy. When the system is heated, the stored energy is released as light. Phenols, on the other hand, form cyclic peroxides that do not emit light upon decomposition, and this process is irreversible.

The dependence of the intensity of the TCL maxima of the Karabakh oil residue on laboratory light led to the idea that under the influence of this light, $R_f^{\bullet}$ radicals and AH endoperoxides are formed. To clarify the role of irradiation, additional FTCL studies were conducted on samples of Karabakh oil irradiated with a mercury lamp and sunlight (Figure 1, curves 1-4). It was found that the intensity of the 75°C and 110°C TCL maxima generally increases compared to the case with only laboratory light irradiation.

Considering that the light from the indicated source mainly excites only the AHs of the studied oil samples, it can be assumed that the increase in the intensity of the TCL maxima occurs solely due to the photoxidation process and the reactions associated with the accumulation of light energy.

To compare with Karabakh oil, similar studies were conducted on Naftalan oil. It was previously shown that the distillate fractions of Naftalan oil (NN) exhibit lower temperature TCL related to free radicals and their recombination, unlike the analogous fractions of other well oils. The hydrocarbon residue (>500°C) of Karabakh oil shows intense TCL maxima at 65°C and 105°C, with an additional TCL peak observed at 175°C (Figure 2, curves 1-3).

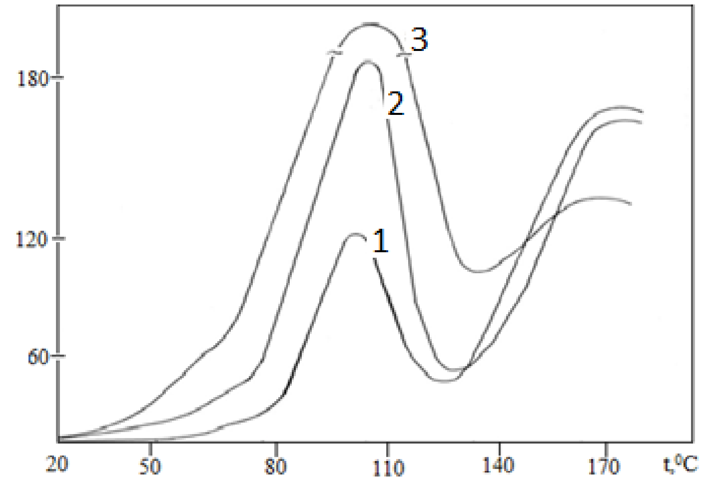

Fig 2. TCL curves of the hydrocarbon residue (>500°C) of Naftalan oil: 1 – after exposure to laboratory light (3 min.); 2 – after exposure to daylight (3 min.); 3 – after exposure to a mercury lamp (10 sec.).

The last peak was also observed in photoirradiated distillate fractions of Naftalan oil with a boiling point range of 200–500°C. This fact suggests a possible link with the biological activity (BA) of the given oil.

An increase in the intensity of the lower-temperature maxima after 3 minutes of solar irradiation in the hydrocarbon residue of Karabakh oil is also observed in the hydrocarbon residue of Naftalan oil (Figure 1, curve 3). After 10 seconds of irradiation with a mercury lamp, the intensity of the TCL maxima of the hydrocarbon residue of Naftalan oil significantly increases. The intensity of the TCL maximum at 175°C decreases, suggesting that the BA of the photoirradiated Naftalan oil is associated with lower-temperature TCL maxima at 65 and 105°C.

Another heavy oil taken for comparison with Karabakh oil is the heavy Absheron oil. During the study of TCL in the hydrocarbon residue (>500°C) of this oil under laboratory light conditions, three weak maxima were observed at 55, 90, and 103°C (Figure 3, curves 1-3).

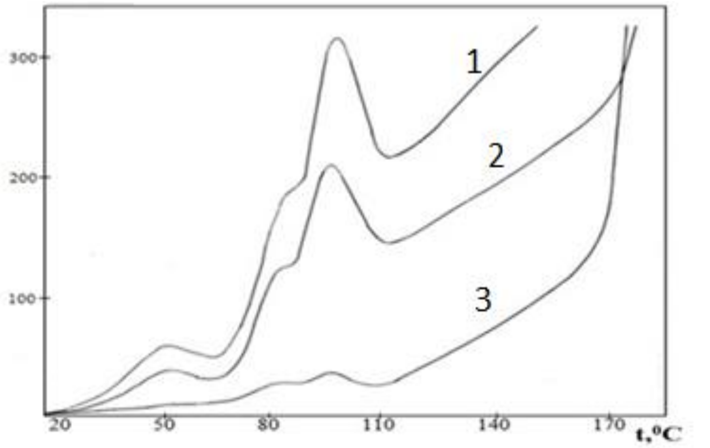

Fig 3. TCL curves of the hydrocarbon residue (>500°C fraction) of Absheron oil: 1 – after exposure to laboratory light (3 min.); 2 – after exposure to daylight (3 min.); 3 – after exposure to a mercury lamp (10 sec.).

The shift of the maxima towards the lower-temperature spectral region in the heavy hydrocarbon residue of Absheron oil, unlike Karabakh and Naftalan oils, can likely be attributed to the higher molecular weight of the hydrocarbons in this oil, which leads to the decomposition of the maxima at 105 and 110°C. The intensity of the indicated maxima increases after irradiation with a mercury lamp and daylight, with the most significant increase observed at 103°C. The TCL maxima observed under laboratory lighting conditions for the residue of Absheron oil were also recorded in the residue of Karabakh oil. This indicates that during the preparation of the studied oil residues for the experiment, they absorbed light energy under laboratory lighting conditions, which is sufficient for the appearance of TCL maxima.

To confirm the aforementioned findings, specific experiments were conducted in isolation from laboratory lighting. For this, the TCL of the Absheron oil residue was recorded twice in succession, before and after irradiation: after heating, the sample was cooled without removing it from the cuvette and kept in an oxygen atmosphere. In the first case, three TCL maxima were observed, while in the second case, two TCL maxima were recorded. These experiments confirm the idea that peroxide radicals generated during thermal exposure with oxygen play a key role in forming the relatively lower-temperature TCL maximum (55°C).

4.Conclusion

The experiments conducted on the TCL (thermochemical luminescence) of heavy residues of Karabakh, Absheron, and Naftalan oils (before and after irradiation) show many similarities in their TCL based on temperature maxima and intensity ratios. These hydrocarbon residues have a hybrid structure, with their main component consisting of compounds with weakly bonded C–H connections that are close in composition and structure. Considering that after the processes of de-resinification and deasphalting, the composition and structure of the oil hydrocarbons become more similar, they can also be used as biologically active substances. The conducted experiments demonstrate that all hydrocarbon residues of the studied oils have the same mechanism of thermochemical luminescence.

The study of the effect of photoirradiation on the petroleum hydrocarbons in the heavy residues of the oils indicates that, unlike many distillate fractions of the studied oils, their TCL maxima are in a relatively lower-temperature spectral region. During excitation in the spectral region related to electron absorption, a quantum of light corresponding to the visible spectral region is emitted as a result of the decomposition of AK endoperoxides formed during the recombination of peroxide radicals. Thus, by utilizing many oil hydrocarbons, this provides the potential to create alternative light sources based on accumulated light, including solar energy.

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ECOLOGICAL ANALYSIS OF ECOTOXIC INORGANIC VOLATILES IN INDUSTRIAL EFFLUENTS OF A RECYCLING STEEL SMELTING PLANT

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ABSTRACT

As it is known, the recycled steel smelting industry is considered as one of the economically and ecologically very important fields. In this industry, the reprocessing of obsolete steel waste, which is dangerous for the environment, is of great economic importance as well as environmentally beneficial. the processes of ore extraction and its subsequent stages of processing save on the use of natural resources. steel smelting is important. During the research carried out by us, it was determined that a large amount of water is also used in the recycling processes of out-of-service steel technological equipment in the recycled steel smelting industry. The object of the study was the Baku Steel Smelting Enterprise. For the first time, in-depth environmental analyzes of the composition of the industrial streams-wastewater received during the technological process of that production were carried out by us. It was determined by us the emissions of ecotoxicant substances - H_2S, SO_2, NH_3, SO_3, NO_2 Cl_2, *HCl, HCN,* PH_3 *which are contained in the industrial streams formed in the main production areas of that enterprise and evaporate in a short period of time.*

INTRODUCTION

The following explanations can be given based on the information given in many technical literatures [1-13] and the results of scientific research conducted in scientific and technical journals:

- A significant amount of water is used in ore extraction production areas, which are the primary raw materials of the metal industry and large production areas. At this time, industrial streams are also formed in the same volume. During the extraction of ore, the metal compounds contained in the ore enter the environment in the form of complex dust-aerosol, mainly metal oxides and salts, along with the change of the land relief. At the same time, it can be noted that during the process of extracting ore from underground, grinding ore, enrichment and preparation of ores as commodity raw materials for smelting according to the required indicators, industrial streams containing a certain amount of heavy metal compounds are formed in the environment.

- Along with the preparation of the raw materials required for the metallurgical industry, industrial effluents - waste waters, which differ from each other and have very complex characteristics due to their composition, are constantly generated in the ferrous and non-ferrous metal smelting industrial enterprise for its purpose.

- Discharge of metal oxides, S, SO_3, dust, soot waste mixture into the atmosphere in the form of aerosols, combined with compounds with ecotoxic inorganic substances (H_2S, SO_2, NH_3, PH_3 etc.) is happening. At the same time, inorganic and organic ecotoxicant aldehydes, benzopyrene, etc., which are dissolved in the industrial effluents formed in the above-mentioned production area. evaporation of compounds also occurs. As a result of the generation of waste gases, industrial effluents, and also received solid wastes, both in the ore extraction industry and in the steel smelting industry, environmental pollution is caused. That is why we purposefully carried out an in-depth environmental monitoring research study at the "Baku Steel Company" enterprise, which is one of the recycling steel smelting industrial enterprises. During the research, it was determined that coke, limestone, ferromanganese, ferrosilicomanganese, as well as many inorganic substances contained in unusable steel equipment at high temperature (~15000C temperature) of the reagents used in the melting of recycled steel, ecotoxic substances obtained as a result of various chemical transformations are used in cooling goes into the composition of the waters.

- For the first time, we have also determined the concentrations of inorganic substances with ecotoxic properties that evaporate quickly in the waste water of the above-mentioned industrial enterprise. Environmental analyzes of all harmful substances in the form of gases and aerosols formed in that enterprise, as well as concentrations of ecotoxic substances in the air, were carried out with Drager Tubes LLG gas detector and UQ-2 gas analyzer special devices. At the same time, samples were taken to determine the in-depth analytical analysis of industrial streams and solid wastes formed in that industry and research work was carried out in laboratory conditions. For this purpose, samples were taken from the waste water received at the above-mentioned institution, and the composition of the samples was determined using known analytical methods shown in the literature [1-12].

EXPERIMENTAL PART

Baku Steel Company, which is located in the Nizami district of Baku city and is considered one of the main industries, is considered as one of the enterprises that use a large amount of water. During the research, it was determined that gaseous harmful substances, waste water and solid waste with different composition and characteristics are constantly formed during technological processes in the enterprise. By us, the distribution and composition of gas wastes actually formed in that enterprise was determined by means of special devices. As we mentioned earlier, one of the directions of the main research work was the determination of the composition of the industrial streams formed and received in that enterprise. For this purpose, water samples were taken by us from the industrial streams formed in the above-mentioned main production areas and directed to the treatment areas. Qualitative and quantitative analyzes of the composition of the water samples were carried out. The composition of samples taken from the inlet and outlet of the industrial effluents used before the cooling system of the Electric Arc Steel Melting Furnace (EASMF) of the main production area of the mentioned enterprise and discharged to the treatment area was determined by means of the ICP-OES GBC Quantima device. Table 1 shows the analysis results of the composition of water samples taken from the (EASMF) production area of the Baku Steel Smelting Enterprise.

Table 1. Analysis results of the composition of water samples

The Name of Components	Unit of Measure	Water re-entered into the cooling system of the EASMF	Recycled effluent water from the cooling system of EASMF
SO_4^{2-}	mg/l	28.6	228.8
Cl^-	mg/l	96.9	95.5
H_2S^-	mg/l	0.02	1.5
Cl	mg/l	0.02	2.0
SiO_2^-	mg/l	14.12	14.96
Na^+	mg/l	137.8	222.5
K^+	mg/l	3.2	3.1
Al^{3+}	mg/l	9.49	41.4
Fe	mg/l	79.5	225.2
Mn	mg/l	0.372	7.98
Cu	mg/l	54.4	93.6
Mo	mg/l	23.7	25.0
Zn	mg/l	0.525	1.8
Pb	mg/l	0.162	0.673
Ni	mg/l	2.08	2.1
Cr	mg/l	3.44	4.68
B	mg/l	0.241	0.245
As	mg/l	<4	<4
Ba	mg/l	<0.6	<0.6
Hg	mg/l	<0.002	<0.02
Se	mg/l	<0.1	<0.1

As can be seen from Table 1, there are dissolved ecotoxic substances in those water samples. During the research, it was determined that the ecologically analyzed water samples also contain volatile, quickly evaporating inorganic ecotoxic compounds. This, in turn, can be considered as one of the sources of atmospheric air pollution. The distribution of volatile ecotoxicant inorganic substances contained in the mentioned water samples in the atmosphere regardless of temperature and their actual concentrations in the air were determined using a mobile gas analyzer, Drager Tubes LLG gas detector detector and UQ-2 gas analyzer devices. Environmental analyzes of concentrations of ecotoxic substances released into the atmosphere in waste water treatment areas were also carried out with the same devices.

The industrial streams formed in the recycled steel smelting plant are precipitated and purified in several stages and repeatedly used in the cooling cooling system. During the cooling process of the hot steel alloys of those industrial streams, they are repeatedly used in the cooling process until their volume decreases. In the area where the samples of the industrial streams taken for the study are the sources, a mixture of gas and aerosol wastes of extremely different characteristics is created mainly in the air environment around the Electric Arc Steel Melting Furnace (EASMF). That is why it is not possible to accurately determine the concentrations of volatile substances emitted into the atmosphere from the sources that form industrial streams with gas analyzer devices. In this regard, 5-20 minutes of each of the above-mentioned ecotoxicant inorganic substances dissolved in the samples of industrial streams taken from the production area mentioned by us. In laboratory conditions, evaporation concentrations in air were determined using Drager Tubes LLG gas detector and UQ-2 gas analyzer devices. Table 2 shows the results of the study on the determination of the air dispersion concentrations of each of the inorganic toxic CO, H_2S, SO_2, SO_3, NO_x, PH_3, HCl, Cl_2 gases evaporated from water samples of industrial streams in laboratory conditions.

Table 2. Analysis results of recycled industrial streams and the final stage treatment area of the enterprise

The Name of Components	Unit of Measure	Examples of recycled industrial streams in EASMF	Samples of industrial effluents of the final stage treatment area of the enterprise
H_2S	ppm	6.5	4.2
SO_2	ppm	4.2	3.1
SO_3	ppm	3.5	2.6
CO	ppm	18.5	16.7
NH_3	ppm	4.5	3.4
HCN	ppm	1.0	0.8
PH_3	ppm	0.7	0.4
HCL	ppm	0.9	0.63
Cl_2	ppm	1.5	0.8

Note: As a result of the entry of other dirty waters into the cleaning area of the enterprise at the final stage, dilution of industrial streams containing ecotoxic inorganic compounds occurs.

As can be seen from Table 2, the concentrations of inorganic ecotoxic substances in the air that are contained in samples of industrial streams and quickly evaporate, decrease several times depending on the time and the distance from the source, that is, by diluting, they approach the sanitary norms. So, since the indicated production area is in a covered area, despite the use of artificial ventilation system with a very high power in that area, the dilution of harmful substances in the air does not occur in a short period of time. The concentration of inorganic ecotoxic substances in wastewater samples obtained from the use of reused, cooled, not fully purified industrial streams in the subsequent stages of cooling of the molten recycled steel alloy released from EASMF is high. Tables 2 and 3 show the results of the environmental analysis of volatile inorganic ecotoxicants in air concentrations of samples of industrial effluents taken from that production area and also from the final stage treatment area of the enterprise.

After the waste water formed in the mentioned enterprise is collected in the common treatment area, mechanical sedimentation is carried out. In that area, concentrations of ecotoxicant inorganic compounds contained in the cleaning of industrial streams and quickly evaporating were determined in the air at different distances (10, 50, 100, 200 m) in the territory of the enterprise and outside the territory. Meteorological conditions were taken into account during the measurements. The concentrations of each of the fast-evaporating inorganic ecotoxic compounds released into the atmosphere from the cleaning area of the enterprise separately in the air from a distance and 5 min. The results of the study on the determination of time dependence are given in Table 3.

Table 3. The results of the study on the determination of time dependence

The Name of Components	Unit of Measure	Initial concentrations of inorganic ecotoxic substances in the air from industrial effluents in the cleaning area of the enterprise	Concentrations of inorganic ecotoxic substances in the air depending on the distance		
			20 m	60 m	100 m
H_2S	ppm	4.2	2.1	1.0	0.5
SO_2	ppm	3.1	1.5	0.8	0.4
SO_3	ppm	2.5	1.7	1.0	0.3
CO	ppm	16.7	10.1	2.5	0.8
NH_3	ppm	3.4	1.8	0.7	0.2
HCN	ppm	0.8	0.3	0.1	-
PH_3	ppm	0.4	0.2	0.06	-
HCl	ppm	0.6	0.4	0.1	-
Cl_2	ppm	0.8	0.6	0.2	-

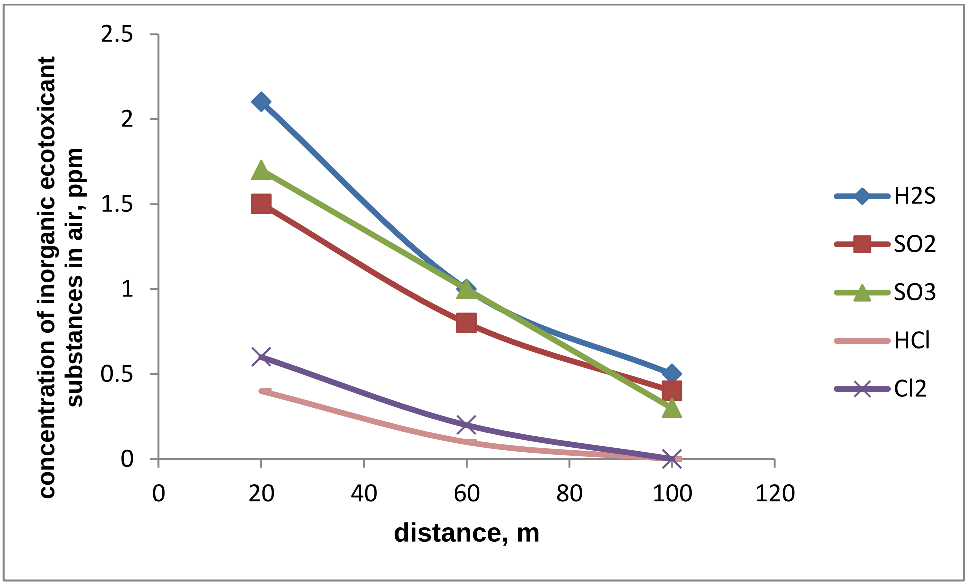

Figure 1. Graph of air concentrations of each of the inorganic ecotoxic substances in the treatment area for a period of 5 minutes depending on the distance.

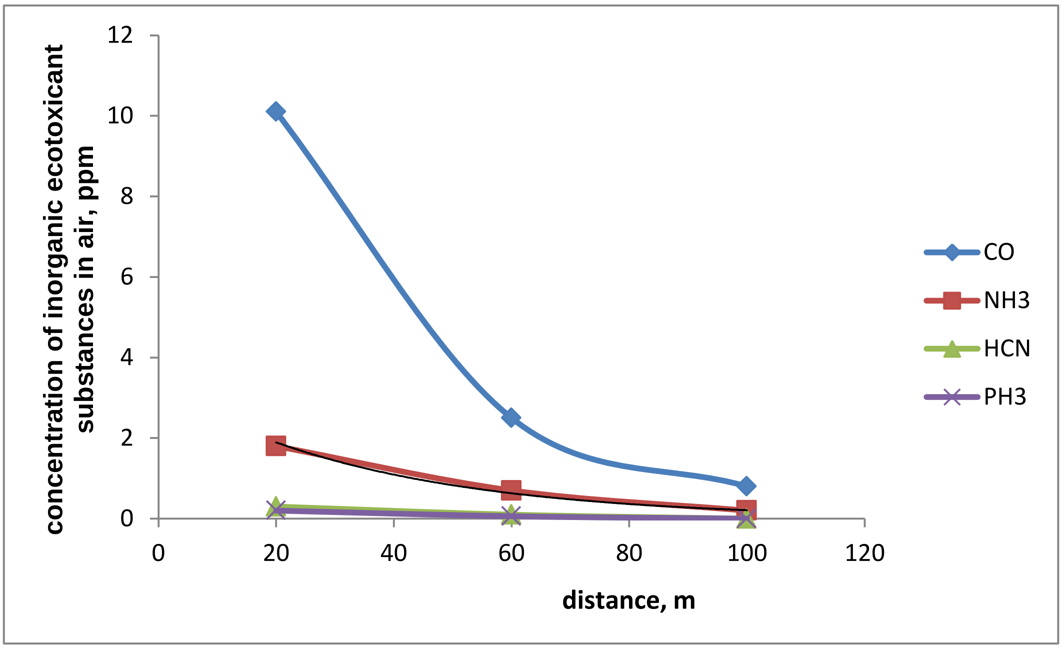

Figure 2. Graph of air concentrations of each of the inorganic ecotoxic substances in the cleaning area in a 5-minute period depending on the distance.

As can be seen from Figure 1-2 and Table 2-3, despite the fact that the concentrations of ecotoxic substances in the air that are dissolved and quickly evaporate in the industrial streams formed in the main production area of that enterprise are diluted close to sanitary norms depending on time and distance, each of them remains in the air for a long time. it is continuous. That is why it can be noted that ecotoxic substances that evaporate in solid and liquid waste formed in every industry are one of the factors that cause ecological pollution of the environment. At the same time, it can be considered reasonable to take into account the sources of atmospheric air pollution in the areas of storage and treatment of waste formed in the main production area of that enterprise.

Taking into account the above mentioned and the results of our environmental research, conducting scientific research in various directions on the development of new methods of deep cleaning, neutralization and purposeful disposal of all types of waste in the recycled steel smelting industry, as in other industries, can be considered as very important ecological issues of the time. At present, qualitative and quantitative analyzes of organic substances with ecotoxicity characteristics and quickly evaporating in the industrial effluents formed at the Baku Steel Company enterprise are being carried out. At the same time, environmental scientific research work is being carried out to determine the causes and composition of waste in the mentioned enterprise. A comprehensive scientific explanation of the causes of the formation of all harmful and ecotoxic substances in the wastes formed in the recycled steel smelting industry is also prepared based on the results of the research conducted by us.

During the research carried out by us, it was proven for the first time that the industrial flows formed in the above-mentioned enterprise lead to the pollution of the atmosphere with dangerous ecotoxic substances both in the working zone and outside the enterprise. At certain distances from those industrial streams, depending on the meteorological conditions, it was determined that the concentrations of these ecotoxic substances in the air are diluted and reach the permissible concentration limit.

In order to determine the concentrations of rapidly evaporating ecotoxicants contained in samples of industrial streams taken from the main production areas and purification facilities of Baku Steel Smelting Enterprise, those water samples were poured into special glass containers in laboratory conditions and the rate of evaporation of the samples was measured in the suction cabinet. During the research, it was determined that the rates of spreading of ecotoxic substances into the air environment in samples of industrial streams taken at different times are close to each other.

CONCLUSION

As can be seen in many technical literatures and the explanations given above, one of the most important issues is the collection of general information about the composition of raw materials and auxiliary reagents taken when carrying out environmental research work at an industrial enterprise, as well as the implementation of ecological analyzes about the composition, classification, characteristics of the products and all types of waste. is one. Therefore, along with the determination of the composition of the raw materials and auxiliary reagents used in the above-mentioned enterprise, we conducted an ecological research on the composition and characteristics of all types of waste received in the production process. A part of that research work was carried out on the determination of the causes, composition and characteristics of the negative impact on the environment of the industrial streams-wastewater formed at the Baku Steel Smelting Enterprise, which is considered one of the heavy industrial enterprises in Baku. As can be seen from the results of the conducted research, it was determined by us for the first time that one of the sources of atmospheric air pollution by the enterprise is the industrial flows formed in the production areas of that enterprise. The mentioned industrial streams and the directly mentioned industrial enterprise can be considered as one of the sources that pollute the atmosphere due to the evaporation, spreading, and change of concentrations in the air of the inorganic ecotoxic substances dissolved in those waters in a short period of time regardless of the temperature.

Despite the fact that each of the harmful substances given in the literature is within the permissible concentration limit in the working and sanitary zones, it causes the pollution of the biosphere in the end along with the pollution of all spheres. As a result, it was determined that it is possible to evaluate the environment as a source of negative environmental impact on human health. Taking into account the above results, it can be noted that the continuous determination of the composition of the industrial streams formed in the enterprise can be considered as an ecologically very important research work. As can be seen from the previous explanations, as a result of the use of auxiliary reagents with different composition and properties in the Baku Steel Smelting Enterprise, harmful and ecotoxic substances of various properties are released into the atmosphere. The industrial flows formed in that enterprise cause atmospheric pollution. That is why it can be considered reasonable that the cleaning of harmful substances with ecotoxic properties contained in industrial streams by the maximum possible physico-chemical method plays an important role in the fulfillment of environmental safety requirements in the modern era.

Thus, we consider it appropriate to conduct ecological studies on the application of a new purification technology for the purification of heavy metal compounds shown in table 1 along with the purification of volatile inorganic ecotoxic substances contained in the industrial streams formed in the enterprise where ecological research is conducted. In this regard, it can be noted that as one of the main results of the conducted ecological research work, the research work on the treatment of those waters is continued in order to reduce the possibility of the inorganic ecotoxic substances contained in the industrial streams having a negative effect on the health of the workers in the working zone and also in the sanitary protection zones of the enterprise. In this field, it can be considered scientifically based to evaluate the environmental research works in several directions as one of the ecological requirements of the time.

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INVESTIGATION OF DIETHYLAMINE, DIPROPYLAMINE, DIBUTYLAMINE COMPLEXES OF ALKYLARYLSULFONIC ACID SYNTHESIZED ON THE BASIS OF GAS OIL FRACTION AS BACTERICIDE

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ABSTRACT

In the research work, diethylamine, dipropylamine, dibutylamine complexes of the mixture of alkylarylsulfonic acids obtained on the basis of the light gas oil fraction obtained from the secondary oil refining process - the catalytic cracking process were synthesized, solutions of the samples were prepared in water, water + ethyl alcohol, water + isopropyl alcohol. Some physico-chemical properties of the samples were studied, bactericidal properties were studied by keeping them in a thermostat at a temperature of 32ºC for 15 days and calculating the amount of H_2S *produced at the end. It was determined that the aqueous solution of the diethylamine complex of the mixture of alkylarylsulfonic acids showed a high bactericidal effect (99%) at the concentration of 50 mg/l. Solutions of diethylamine and dipropylamine complexes in water at the concentration of 75 mg/l showed 100% bactericidal effect and reduced the number of bacteria to zero. Solutions of dibutylamine complex in water + ethyl alcohol, water + isopropyl alcohol at the relatively high concentration (150 mg/l) showed 100% bactericidal effect and stopped the life activity of bacteria.*

Introduction

Microbiological corrosion is a type of corrosion that occurs as a result of biological damage to metals. The effect of microorganisms on metals occurs in different ways. Among the main factors that cause corrosion are metabolic products with aggressive properties - acids, bases, enzymes, etc. takes the main place. They create a favorable environment for the initiation of the corrosion process according to the laws of electrochemistry [1].

Corrosion damages the economy of developed countries in the amount of 3-3.5% of the national product value. Most of the economic losses in the marine industry are caused by microbiological corrosion. According to statistics, it is about 20% of total economic losses due to corrosion of various equipment. The total global cost of biological damage and marine pollution is estimated at approximately 50 billion dollars annually [2-3].

Sulfate-reducing bacteria play an important role in the occurrence of microbiological corrosion. Sulfate-reducing bacteria are the most studied group of bacteria that cause microbiological corrosion and consist of 220 species and belong to bacteria that use sulfate as an electron acceptor [4,5]. Sulfate-reducing bacteria are anaerobic bacteria, which means they don't require oxygen for growth and activity. This allows sulfate-reducing bacteria not to be destroyed in extreme conditions. These bacteria reduce the sulfate fragment to sulfide. The electrochemical reaction takes place inside the biofilm where the metal interacts with water and sulfate-reducing bacteria. As a result, hydroxyl groups are formed, which facilitate the reaction. Sulfate-reducing bacteria are active in the pH range of 4 to 9.5 and can withstand pressures up to 500 atm [6,8]. The corrosion mechanism caused by sulfate-reducing bacteria can be described using the cathodic depolarization theory. However, other theories describing this process are currently known to science. According to the cathodic depolarization theory, the electrochemical reaction occurs in two sections: anodic and cathodic. In the anodic zone, iron changes into ionic form (Fe^{2+}). Fe^{2+} ions are released from the surface by losing electrons that go to the cathode area. Due to the release of iron ions, pits are formed in the anode. Then the iron ions react with the sulfide (S^{2-}) to form the by-product iron sulfide (FeS). In the cathode zone, electrons move to the surface and react with hydrogen ions (H^+) to form hydrogen gas (H_2). Due to the nature of the biofilm, water molecules ionize into hydroxide (OH^-) and hydrogen ions. Hydrogen ions cause the pH level in the biofilm to become acidic. And hydroxide reacts with iron ions to form iron hydroxide ($Fe(OH)_2$) or rust [9-10].

Anode: $4Fe \rightarrow 4Fe^{2+} + 8e$;

Dissociation/ionization of water: $8H_2O \rightarrow 8H^+ + 8OH^-$;

Cathode: $8H^+ + 8e \rightarrow 8H$;

Cathodic depolarization caused by sulfate-reducing bacteria:

$+ 8H \rightarrow SO_4^{2-} + 8H \rightarrow S^{2-} + 4H_2O$;

Corrosion product: $Fe^{2+} + S^{2-} \rightarrow FeS$; $3Fe^{2+} + 6OH^- \rightarrow 3Fe(OH)_2$;

General reaction: $4Fe + 4H_2O + SO_4^{2-} \rightarrow 3Fe(OH)_2 + FeS + 2OH^-$.

In order to prevent the damage caused by microbiological corrosion to industrial and service areas, bactericides with different compositions are used in industry.

As a result of the studies, it was determined that various alkaline and amine complexes of alkylarylsulfonic and oligoalkylarylsulfonic acids synthesized on the basis of light phlegm of catalytic cracking have a high bactericidal effect compared to industrially applied standart bactericidal-inhibitors (AMDOR-IK-7 and AMDOR-IK-10) [11-14].

Experimental Part

The presented research work is devoted to the synthesis and research of new bactericides against sulfate-reducing bacteria for corrosion protection of metals. At the initial stage, a mixture of alkylarylsulfonic acids was obtained based on the light gas oil fraction obtained from the secondary oil refining process – catalytic cracking process. Some physico-chemical parameters of alkylarylsulfonic acids are mentioned below. Density: 1.32 g/cm^3, freezing temperature: -8 °C, refraction coefficient: 1.48. In the next stage, diethylamine, dipropylamine, dibutylamine complexes of the mixture of alkylarylsulfonic acids were synthesized. Amines used in the experiment were purchased from Sigma Aldrich company. 15% solutions of synthesized complex salts in water, water+ethyl alcohol, water+isopropyl alcohol were prepared and some physico-chemical parameters of the obtained complex salts were investigated. Indicators were determined by the accepted standard methods - density by ASTM D5002 method in DMA 4500 M device, freezing temperature by GOST 20287-91, refraction coefficient in Abbemat 500 device, and pH indicator in HANNA pH-ISE-EC HI 5522 device. The accuracy of the pH measuring device is ± 0.5 % . The results are given in table 1.

Table 1. Physico-chemical properties of diethylamine, dipropylamine, dibutylamine complexes of the mixture of alkylarylsulfonic acids

Symbol of the complexes	Density, g/cm^3 20°C	Freezing temperature, °C	Refraction coefficient, 20°C	pH
K-1	0.9850	-3	1.4874	8.200
K-2	0.9436	-57	1.3807	8.473
K-3	0.9445	-46	1.3871	8.528
K-4	1.010	-5	1.3628	8.357
K-5	0.9615	-42	1.3744	8.437
K-6	0.9375	-40	1.3862	8.586
K-7	0.9253	-43	1.3757	8.672
K-8	0.924	-40	1.3845	8.875

Experiments to study the bactericidal effects of the obtained alkylarylsulfonate samples were carried out in pre-sterilized test tubes according to the known method [15]. 1143 strains of "Desulfovibrio desulfuricans" species of the sulfate-reducing bacteria were taken for the experiment. The bactericidal property of the reagents was studied by keeping them in a thermostat at 32ºC for 15 days and calculating the amount of H_2S formed at the end. At the end of the study, the amount of H_2S in the tested samples was determined by the iodometric method, and based on the results, the reduction rate of sulfate-reducing bacteria was calculated. (OST 39-234-89). The obtained results are given in table 2.

Table 2. Bactericidal effects of diethylamine, dipropylamine, dibutylamine complexes of the mixture of alkylarylsulfonic acids

The content of alkylarylsulfonic acids	Concentration of a substance, C-mg/l	The number of bacteria (number of cells/ml)	Content H_2S, mg/l	Bactericidal effect, Z-%
Solution of diethylamine complex in water (K-1)	50	10^1	4	99
	75	-	-	100
	150	-	-	100
Solution of diethylamine complex in water + ethyl alcohol (K-2)	50	10^2	65	82.6
	75	10^1	39	89.6
	150	10^1	21	94.4
Solution of diethylamine complex in water + isopropyl alcohol (K-3)	50	10^3	116	69
	75	10^3	98.2	73.8
	150	10^2	54.9	85.3
Solution of dipropylamine complex in water (K-4)	50	10^1	5.5	98.5
	75	-	-	100
	150	-	-	100
Solution of dipropylamine complex in water + ethyl alcohol (K-5)	50	10^2	70	81.3
	75	10^1	10.8	97.1
	150	-	-	100

Solution of dipropylamine complex in water + isopropyl alcohol (K-6)	50	10^1	52.3	86
	75	10^1	24.5	93
	150	10^1	16.9	95.4
Solution of dibutylamine complex in water + ethyl alcohol (K-7)	50	10^2	62.5	83.3
	75	10^1	29	92.2
	150	-	-	100
Solution of dibutylamine complex in water + isopropyl alcohol (K-8)	50	10^4	145	61.3
	75	10^3	102	72.8
	150	-	-	100
Control-1. Amount of H_2S in without SRB conditions -24 mg/l				
Control-2. Amount of H_2S in with SRB conditions -375 mg/l				
Control-3. Number of bacteria in the nutrient medium -10^8 number of cells /ml				

It is important to firstly ensure complete solubility of amino salts of alkylarylsulfonic acid in various solvents during the study. Additionally, the physico-chemical properties of the solutions obtained in different solvent environments vary depending on the nature of the solvent and the structure of the substance taken. The different solvents widen the application opportunities of the complex salts. When the compositions of the complex salt and solvent change, the size of the resulting micelles varies, as a result, the contact with the surface changes. Even at a low concentrations, synthesized complexes show complete inhibitory effect.

As can be seen from the table, the aqueous solution of the diethylamine complex of the mixture of alkylarylsulfonic acids showed a high bactericidal effect (99%) at the low concentration (50 mg/l) and significantly reduced the number of bacteria, while at the concentration of 75 mg/l it showed a 100% bactericidal effect and completely stopped the life of bacteria. The solution of diethylamine complex in water + ethyl alcohol at the concentration of 150 mg/l showed a result of 94.4% and reduced the number of bacteria from 10^8 to 10^1. Also, the solution of dipropylamine complex in water at the concentration of 75 mg/l showed 100% bactericidal effect, while the solutions in a mixture of water + ethyl alcohol and water + isopropyl alcohol showed 97.1% and 93% bactericidal effect, respectively. Solutions of dibutylamine complex in water + ethyl alcohol, water + isopropyl alcohol mixture completely destroyed bacteria at the concentration of 150 mg/l. The bactericidal effect results of the synthesized complex samples were compared with the bactericidal inhibitors applied as standard in the industry and the results are expressed in the following picture.

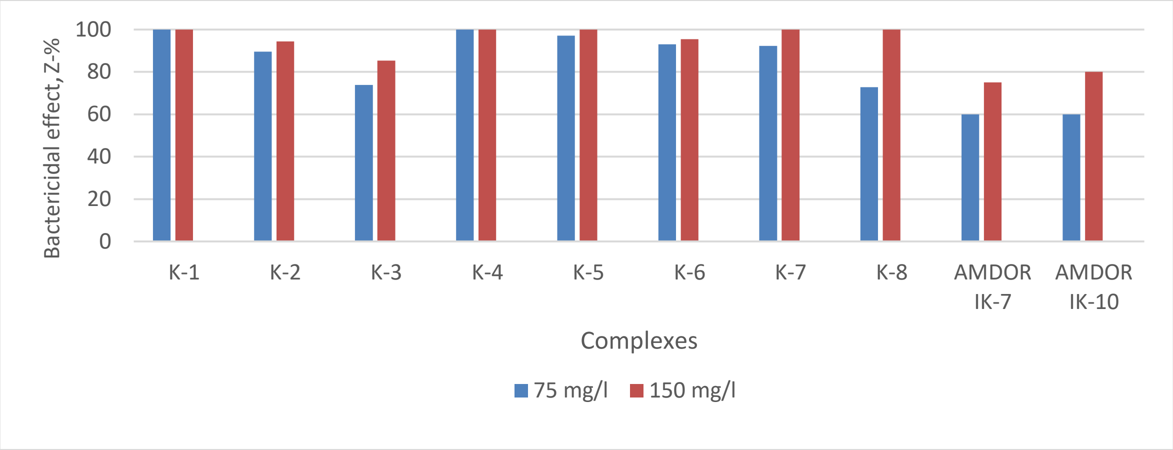

Figure. Comparison of bactericidal effect results of complex samples with standard samples

As can be seen from the figure, each of the samples has a higher corrosion protection property at all concentrations compared to the standard bactericidal inhibitor AMDOR-IK-7 and AMDOR-IK-10. Thus, the highest result shown by standard bactericidal inhibitors was 93% at the concentration of 200 mg/l.

Conclusion

Thus, the aqueous solution of the diethylamine complex of the mixture of alkylarylsulfonic acids showed a bactericidal effect of 99% at the concentration of 50 mg/l, and 100% at the concentration of 75 mg/l, showing successful results in combating microbiological corrosion. Also, it was determined that the solution of dipropylamine complex in water at the concentration of 75 mg/l has 100% bactericidal effect, while the solutions in water + ethyl alcohol and water + isopropyl alcohol have bactericidal effects of 97.1% and 93%, respectively. Based on the obtained results, it was determined that the synthesized complex samples are more promising than AMDOR IK-7 and AMDOR IK-10 bactericidal inhibitors, which are used as standard bactericidal inhibitors in the industry.

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SIMULATION STUDY ON ENHANCED OIL RECOVERY USING LOW-SALINITY WATER TREATED WITH A MAGNETIC FIELD

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ABSTRACT

The waterflooding technique is one of the most widely used and efficient technique for increasing oil recovery. In an oil-wet reservoir, however, the higher the water mobility, the lower the oil production. The following research will look into the effects of high and low saline waterfloods on oil recovery and water mobility with application of magnetic field. This research also looks at how varied water salinity injections affect wettability and salt production rates. The design of a three-dimensional, two-phase model, i.e., water and oil, is the first step in this research. Initially, the reservoir is oil-wet. To show the wettability change, relative permeability curves are generated during simulation. The impact of salinity on oil production, water mobility, and salt production is examined by a comparison of high and low saline waterfloods. In order to identify an effective well injection technique, a sensitivity analysis was done for two possible injections well patterns: five spot and direct line drive. The recovery attained by lowering the salinity of the water was found to be around 80%, with a cumulative oil production of 0.45 MMSTB. The water cut is prolonged to a large extent by lowering the salinity of the water.

1. Introduction

Based on formation characteristics, fluid characteristics, reservoir heterogeneities, and PVT characteristics of the reservoir, oil recovery during the life of a reservoir is split into three stages (Ahmed 2006) [1]. According to Abubaker H. Alagorni (2015), the main recovery is based on the natural energy of the reservoir and has a recovery factor that is less than 30% of OIIP. Primary recovery also includes artificial lift techniques. The recovery from the secondary mechanism is between 30 and 50 percent of OIIP [2]. Waterflooding was first utilized as a pressure maintenance source for oil recovery in 1880, but it is now universally acknowledged as one of the most popular fluid injection techniques, mainly from the United States, between 1930 and 1950 (Cobb 1997) [3].

The low salinity waterflooding (LSF) EOR technology improves oil recovery by reducing the salinity of the injection water. In the last ten years, low saline waterflooding (LSW) has emerged as a new and promising enhanced oil recovery strategy for carbonate and sandstone reservoirs

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[4]. The low saline waterflooding has gained a lot of interest from the oil sector due to its simplicity and inexpensive cost. When Bernard and his colleagues tested the oil recovery using (NaCl) sodium chloride brine injection varying from 0-1 percent with distilled water injection. Additionally, their research has indicated that the injection of sodium chloride brine, ranging from 1 to 15%, has no impact on oil recovery (Bernard 1967) [5].

Recently, the application of magnetic fields has been investigated as an innovative approach to enhancing the efficiency of waterflooding. Magnetically treated water exhibits altered physicochemical properties that influence interactions with reservoir rock and fluids. Studies suggest that exposure to a magnetic field can modify ion interactions, enhance the dissolution of salts, and influence fines migration, all of which contribute to improved oil recovery. Furthermore, the magnetic field may facilitate wettability alteration and reduce interfacial tension, enhancing the displacement of oil in the porous media. This integration of magnetic fields with low-salinity waterflooding represents a novel enhancement to traditional EOR strategies, offering additional recovery potential with minimal cost and complexity.

In the laboratory core flood test and at the field scale, it is demonstrated that Low Salinity waterflooding improves oil recovery The suggested mechanisms for low-salinity waterfloods are listed below [6,7]:

- Increased pH
- Fines migration
- Multicomponent Ionic Exchange (MIE)
- Double Layer Expansion (DLE)
- Wettability Alteration

Thus, integrating magnetic field technology with low-salinity waterflooding has the potential to revolutionize oil recovery processes by further enhancing recovery efficiency while maintaining operational simplicity and cost-effectiveness.

2. PROBLEM STATEMENT

In this study, water is injected through an injector using both low- and high-saline water injection procedures, and oil is recovered from the production well. The following undesired issues were discovered in this simulation study:

- Earlier water breakthrough
- High salt production rate
- Unaltered oil-wet reservoir conditions

Predictive modelling can be used to identify and fix the existing challenges.

3. OBJECTIVES OF STUDY

The objectives of this study are:

- To choose an optimum injection design (such as direct line drive and five spot pattern) for an effective displacement of the oil.
- To study the effect of low and high saline water injection in oil wet sandstone reservoir.

The objective of this study is to evaluate the performance of a sandstone reservoir following the injection of low and high salinity water. The reader is intended to develop a clearer understanding of the mechanisms by which low saline water removes oil from reservoirs and changes the wettability of formations from oil-wet to water-wet, improving oil recovery. For the purpose of choosing an optimized injection method to achieve maximum oil recovery, a sensitivity analysis for various injection well patterns are also performed.

The performance of an oil-wet sandstone reservoir under low and high salinity waterflooding is determined in this experiment. A flowchart in Figure 1 shows a brief overview of the steps that have been followed in this work.

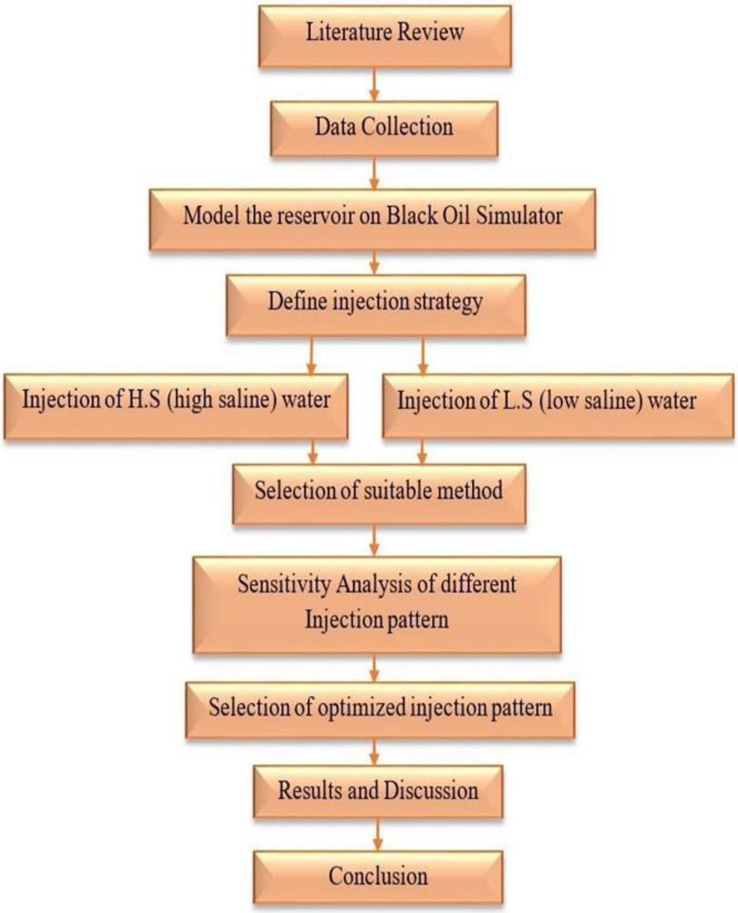

Fig. 1 A systematic workflow diagram for analysis of salinity effects in waterflooding technique.

The reservoir data was first obtained via a literature review, and after that, a simulation model was created using a black oil simulator, such as Eclipse-100 (a commercially available simulation software). In order to determine the best injection technique, simulations for continuous low- and high-saline water injection were run. Later, a sensitivity analysis was performed using simulated data for the five-spot pattern and direct line drive well injection techniques. After that, based on technical factors including water cut, oil output, and salt production, the best injection well plan was chosen in the conclusion section.

4. CASE STUDY

A part of Shaybah oil field is under consideration in this study which is located in Rub'al Khali desert in Saudi Arabia. A well was spud in this field and is now under a need to waterflood, this study gives a brief consideration whether high saline or low saline water will be most efficient in order to produce oil from this field in commercial quantity. Reservoir specifications are taken and a simulation model was generated by considering that this model replicate the original reservoir conditions and methods that are tested in the simulation will be best applicable on the actual reservoir. The description of reservoir simulation model is as follow:

Description of reservoir model:

In this study, a 3D reservoir model with a square geometry of 334 acres area is simulated on a black oil simulator. The reservoir model has dimensions of 492 ft, 492 ft, and 30 ft in I, J, and K directions, respectively. The developed model is heterogeneous so, it compromises 50, 50 grid blocks in the I and J direction respectively but has 6 layers in the K direction. At the Initial stage, there are two active phases present in the reservoir i.e., oil and water. The reservoir has a permeability of 275-525 md and porosity of 23-31% (Fig. 2).

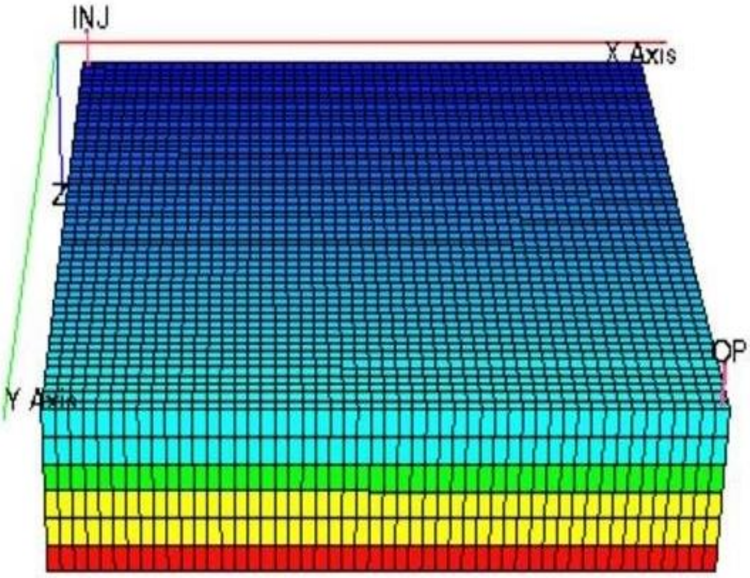

Fig. 2 A 3D reservoir model representing Injector (INJ) and Producer (OP) wells.

An injection well and a production well are located on the opposite corners of the model. Injection well is represented by INJ and production well is represented by OP. The simulation is carried out for a period of 5 years.

Developing a Reservoir Model

In this study, the simulation for the base case is carried out in the following steps:

Model Dimension

In Eclipse 100, the first step for developing a model is to define the title of the run, geometry to be used, number of cells in each direction, number of wells in the model, and starting date of the simulation. This information is defined in the "RUNSPEC" section.

Grid and Rock Properties

The second step for developing a model is to define the number of grid cells in I, J, and K directions, dimensions of cells, the permeability of cells, and porosity of cells. This information is defined in the "GRID" section.

As the reservoir is heterogeneous it has different permeability and porosity in the I, J, and K directions.

Fluid Properties

The third step for developing a model is to define the concentration of oil and water at the surface, the formation volume factor, viscosity of water and oil, reservoir pressure, rock compressibility, and water compressibility. This information is defined in the "PROPS" section.

Initial Conditions

The fourth step for developing a model is to define initial reservoir pressure, saturation conditions, and water-oil contact. This information is defined in the "SOLUTION" section.

Production Schedule:

The last step for developing a model is to define the names of wells, their positions and groups, the completion period for each well, and specify the injector and producer controls. This information is defined in the "SCHEDULE" section.

Salinity limits and relative permeability:

The literature research revealed that the threshold limit for low saline waterflooding effects is between 500 and 5000 ppm [8]. As a result, the range of low saline waterflooding is kept within the threshold limit in this study. As a result, depending on the salt content, it is important to change the relative permeability for oil-water phases and the saturation endpoints for the modelling of low saline waterfloods. Therefore, the reservoir's wettability has a significant impact on low salinity. The following Corey model equations have been applied to produce the relative permeability and saturation profiles that depict oil-wet and water-wet conditions in the reservoir [9]:

$$K_{rw} = S*^{N_w} + E_w \quad (1)$$

$$K_{ro} = (1 - S*)^{N_o} E_o \quad (2)$$

$$E_w = K_{rw}(S_{or}) \quad (3)$$

$$E_o = K_{ro}(S_{wi}) \quad (4)$$

$$S^* = \frac{S_w - S_{wi}}{1 - S_{wi} - S_{or}} \quad (5)$$

K_{rw} - Relative permeability to water

K_{ro} - Relative permeability to oil

N_w - Empirical constant for water

N_o - Empirical constant for oil

S^* - Normalized water saturation

S_w - Water saturation

S_{or} - Residual oil saturation

S_{wi} - Irreducible water saturation

E_w - Endpoint relative permeability for water

E_o - Endpoint relative permeability for oil

To generate relative permeability curves the data used has been summarized in Table 1.

Table 1. Corey parameters for the base model [9].

Oil Wet Conditions		Water Wet Conditions	
Parameters	**Values**	**Parameters**	**Values**
S_w	0.3	S_w	0.1
S_{wi}	0.2	S_{wi}	0.2
N_o	3.0	N_o	2
N_w	3.0	N_w	3
$E_o=K_{ro}(S_{wi})$	0.5	$E_o=K_{ro}(S_{wi})$	0.8
$E_w=K_{rw}(S_{or})$	0.8	$Ew=K_{rw}(S_{or})$	0.6

Figure 3 illustrates how varied residual oil saturation (S_{or}) during waterflooding results from altered wettability profiles.

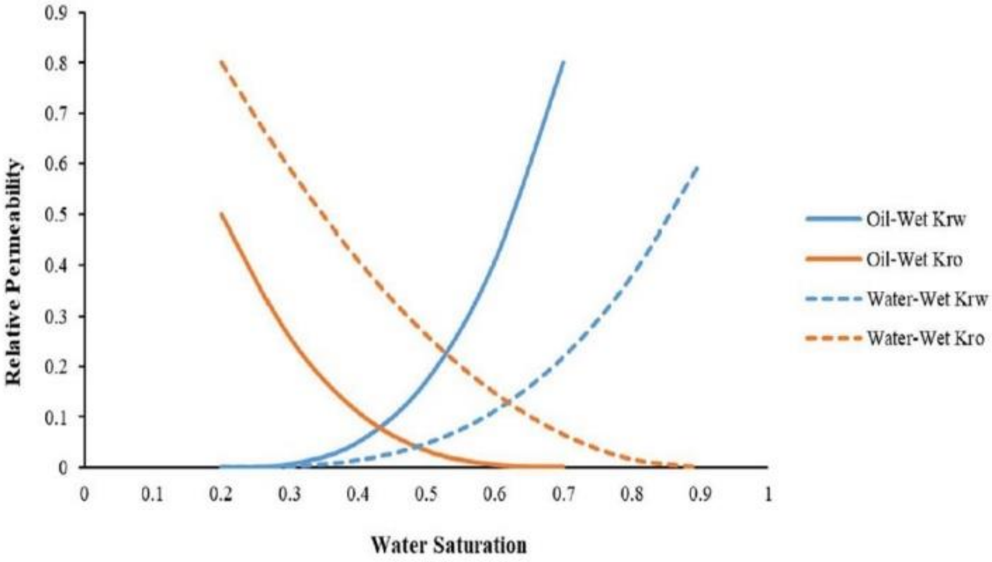

Fig. 1 Relative permeability curves for oil-wet and water-wet conditions.

Additionally, rock wettability has a significant impact on the saturation endpoints for both water- and oil-wet systems. High water relative permeability, low oil relative permeability, and high residual oil saturation are the characteristics of an oil-wet reservoir. In an oil-wet reservoir, significant salty waterflooding results in low ultimate oil recovery. The cross-over point for the oil-water relative permeability curve intersects at a fraction below 0.5 water saturation. A water-wet reservoir, on the other hand, has high oil relative permeability, low residual oil saturation, and low water relative permeability. The convergence of the oil-water relative permeability curves may be shown in Figure 3 to be at 60% of water saturation. Thus, it is demonstrated in this situation that the eventual oil recovery is maximized [10,11].

5. RESULTS & DISCUSSIONS

The underlying reservoir model in this work was first simulated for continuous low salinity (LS) and high salinity (HS) water injection. After that, a sensitivity analysis for different well injection methods, including a direct line and a five-spot pattern, was carried out. For a total of five years, the simulation was run. In this study, primarily, two cases are simulated to inspect the effects of salinity on the behavior of oil-wet sandstone reservoirs. The two cases are defined as:

- Continuous injection of Low Saline (LS) water treated with magnetic field (1000 ppm)
- Continuous injection of High Saline (HS) water treated with magnetic field (45000 ppm)

Oil Saturation Response

According to the simulation's findings, low saline water injection produced a significant amount of oil. Whereas high saline water injection left almost 53% of residual oil behind. Saturation response of both high salinity waterflooding and low salinity waterflooding is represented in Figure 4 and 5 respectively.

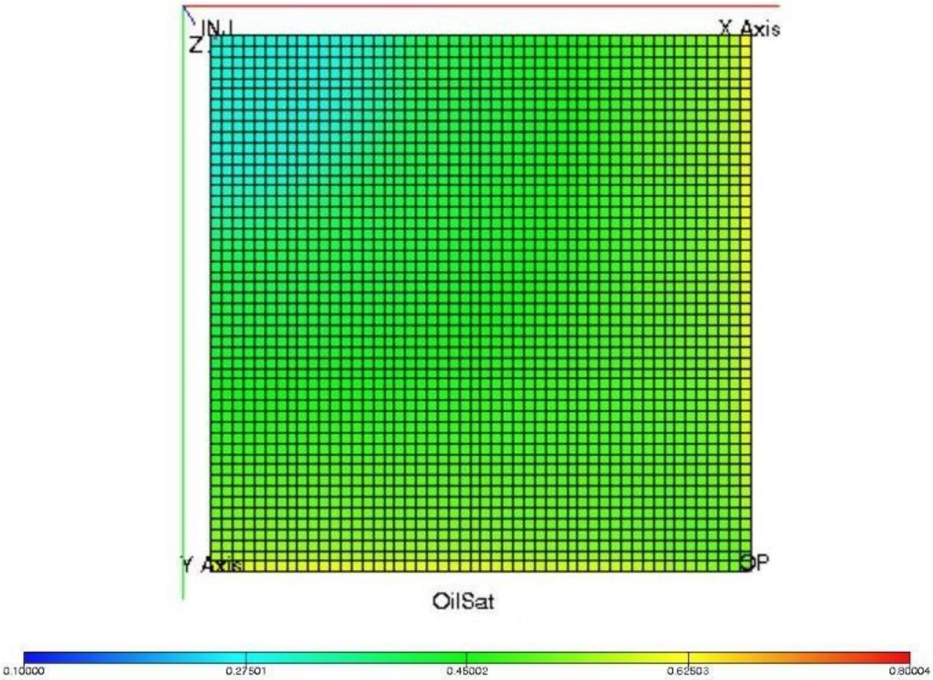

Fig. 4 Saturation response over high saline waterflooding.

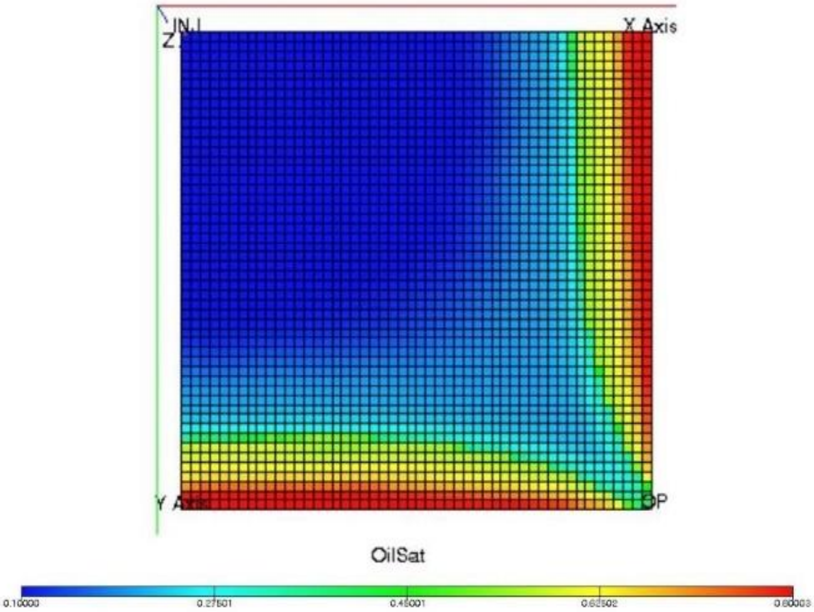

Fig. 5 Saturation response over low saline waterflooding.

The wettability alteration is what caused the considerable oil displacement from the reservoir. Additionally, the clay particles are retained undistributed because the rock is held in an oil-wet condition, which contributes to the reduced displacement effectiveness in high saline water injection.

Field Oil Production Rate

Figure 6 shows that the oil production rate for both low- and high-saline waterflooding is constant for the first year at the controlled volume of 630 STB/Day.

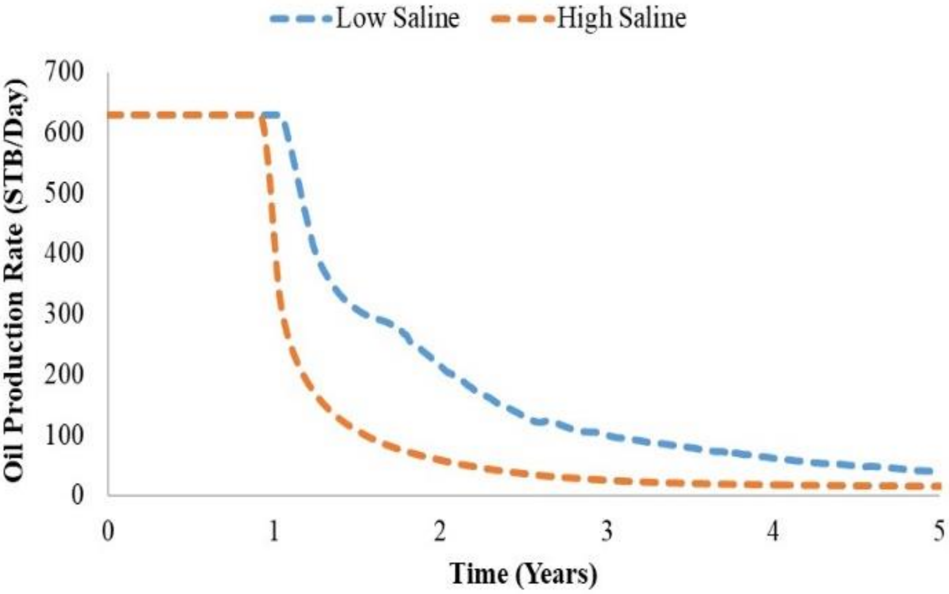

Fig. 6 Oil production rate response for low and high saline waterflooding.

At the conclusion of the first year, the production rate tends to decline, and by the end of the second year, it has reached 100 STB/Day for the low saline water injection and 25 STB/Day for the high saline water injection.

Similar trends may be seen for the third, fourth-, and fifth-years' producing periods. The field production rates for low salinity and high salinity are 39 STB/Day and 15 STB/Day, respectively, at the end of the fifth year.

Field Cumulative Oil Production with Oil Recovery

The rates of oil production have a direct impact on the total amount of oil produced. Since oil is producing quite rapidly when low saline water is injected than when high saline water is injected, the cumulative oil production obtained during low saline waterflooding is also higher, coming in at 0.45 MMSTB at the end of five years as opposed to 0.3 MMSTB for the high saline flooding. Figure 7 displays a summary of the total oil production during the past five years.

After five years of cumulative oil production, the recovery of oil acquired through the injection of low saline water is around 80%, whereas the recovery of oil gained through the injection of high saline water is 57%. When the water's salinity is changed when the wettability is changed from oil-wet to water-wet, the amount of recovered oil increases, which reduces the saturation of remaining oil.

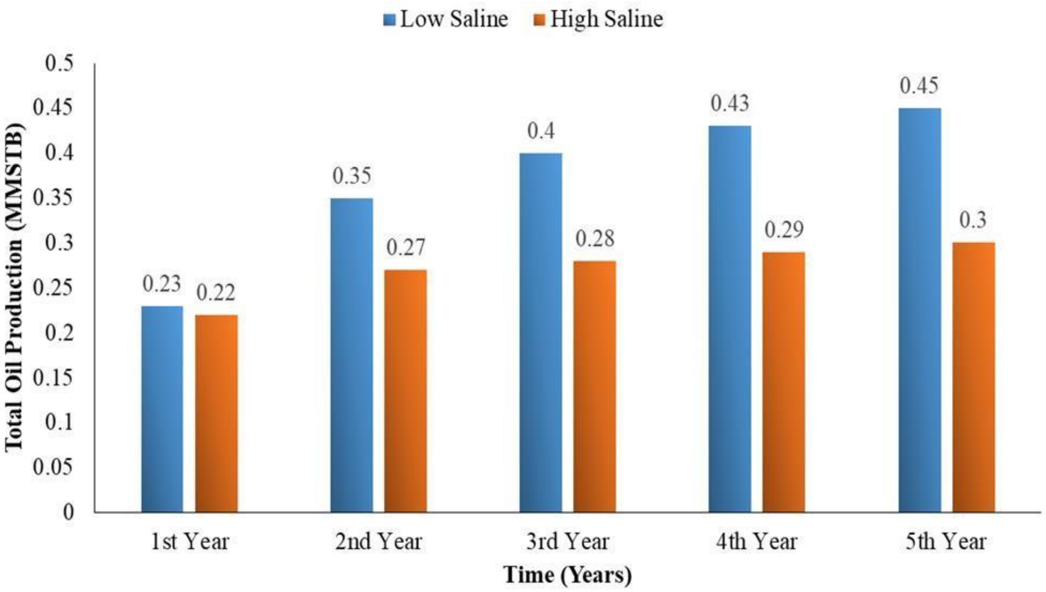

Fig. 7 Cumulative oil production response for low and high saline waterflooding.

6. CONCLUSIONS

Based on simulation results, the following conclusions have been drawn:

- Low saline water injection demonstrated superior oil recovery performance compared to high saline water injection, leaving significantly less residual oil in the reservoir.
- Wettability alteration from oil-wet to water-wet conditions played a critical role in enhancing oil displacement during low saline water injection.
- The results showed that the salinity threshold limit determines whether the water-flooding process for an oil-wet reservoir is successful, and we saw that low salinity values prove to be a successful technique to enhance oil recovery and decrease water mobility in comparison to high salinity.
- At the conclusion of five years, the cumulative oil production obtained during low saline waterflooding is also better, peaking in at 0.45 MMSTB compared to 0.3 MMSTB for the high saline flooding. Additionally, a five-spot design produces 0.43 MMSTB of total oil production, compared to 0.45 MMSTB for a direct line drive.
- The results underscore the significant role of water salinity in influencing oil recovery. The lower salinity of LS water, combined with magnetic field treatment, enhanced wettability alteration and limited the redistribution of clay particles, improving oil displacement.

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SPECTROPHOTOMETRIC METHOD OF DETERMINING THE QUANTITY OF OIL PRODUCTS IN NATURAL AND WASTEWATER

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ABSTRACT

Oil products are the strongest toxic substances on the earth's surface, and their permissible levels in water bodies are 0.1 mg/dm^3. However, until now, insufficient attention has been paid to determining the amount of oil products in natural and waste water. The article presents the results of spectrophotometric determination of the amount of oil products in water samples taken from lakes in the Absheron Peninsula and compares them with the existing gravimetric method. Extractants were selected to determine oil products, and the improved spectrophotometric method was applied to real objects under optimized conditions. The aim of this work was to select an organic extractant for the extraction of petroleum products from natural and waste waters and to apply an improved spectrophotometric method to natural objects. The aim of this work was to select an organic extractant for the extraction of petroleum products from natural and waste waters and to apply an improved spectrophotometric method to natural objects. The waters taken from the lakes of Gu and Girmizy on the territory of the Absheron Peninsula were selected as objects of the study. Spectrophotometric, gravimetric and chromatographic methods of analysis were used in the study. A mixture of organic reagents was selected to determine oil products in the waters of the lakes. Using the selected organic reagent, the oil products contained in the objects of study were isolated and analyzed using the GX-MS method. A new improved separation method using a mixture of organic reagents was proposed for the spectrophotometric determination of oil products. An improved spectrophotometric method for determining oil products in natural waters was developed. Optimal conditions for the extraction of oil products were found and the extraction method using a new organic reagent was optimized. The proposed method was tested on natural waters.

Introduction

The development of the production of oil and gas products, unfortunately, leads to the problem of processing or disposal of the waste of these industries. Currently, the most common pollutants in the hydrosphere are oil and its products. A monomolecular layer of oil reduces gas permeability by 50%, pollution of the atmosphere and hydrosphere with oil products causes disruption of normal gas and heat exchange. The result of these disturbances can lead to uncontrollable changes in our planet's climate, as well as the mass extinction of phytoplankton, which produces about 70% of the oxygen, [1] causing serious imbalances in the Earth's oxygen balance. Therefore, the development of modern, highly sensitive chemical analysis methods for controlling and determining the amount of oil products is one of the urgent problems in Uzbekistan. Oil and its products are the most common and dangerous substances that pollute natural waters. Oil and its products consist of a complex and diverse mixture of organic substances, and the concept of "petroleum products" in hydrochemistry is conventionally understood as a hydrocarbon fraction consisting of non-polar and low-polar aliphatic, aromatic, alicyclic hydrocarbons that can be extracted from water [2].

The results of man-made accidents in the process of extraction, processing and processing of oil products are considered the main factors that pollute the hydrosphere and atmosphere. Contamination of water with oil products makes it unsuitable not only for consumption, but also for various household needs. Currently, the most common polluting petroleum products include fuel oil, kerosene, gasoline, and petroleum oils. These oil products are extremely dangerous not only for the human body, but also for the environment [1, 4].

One ton of oil can form a film on the surface of 12 km^2 of water. When petroleum products enter water, they are mostly in a coarse dispersion and easily float to the surface of the water to form a floating film. Low molecular weight components evaporate easily. Depending on the type of oil products, it can evaporate from 10% to 75% [3]. Such atmospheric processes increase the density of the remaining oil products and cause the oil products to lose their ability to remain on the water surface. Under the influence of sunlight, oil products are oxidized, and oil products that have formed a thin layer on the water surface are oxidized more easily and faster. Water flow and vibrations cause oil emulsions to form. Emulsions formed on the surface of water remain stable for a long time.

The main sources of oil products entering natural waters include:

- oil warehouses;
- oil bases;
- oil processing enterprises;
- enterprises engaged in transportation of oil and its products.

The amount of petroleum products in water is 0.5 mg/dm^3 and the amount of petroleum acid is 0.01 mg/dm^3, which has a sharp effect on the smell and taste of water [4]. The presence of oil products in water of 100-500 mg/dm^3 causes a sharp change in the chemical effect of water. The oil layer formed on the water surface disrupts the gas exchange between the water and the atmospheric layer, slows down the aeration rate, and removes carbon dioxide formed from oil oxidation. If the layer of oil products is 4.1 mm in water and the amount is 17 mg/dm^3, the amount of dissolved oxygen will decrease by 40% in 20-25 days [5].

To control the amount of oil and its products in water, periodic water sampling and chemical analyzes are required. Chemical analyzes [6-14] are performed based on one of the methods listed in Table 1.

Table 1. Comparative table of modern methods of determining oil products

Method	Description	Measuring tools and equipment	Chemical reagents	Sampling and storage	Test execution process
Spectrophotometry method [9,11,14].	The amount of oil products is determined by spectral analysis of the separated oil extract. The analysis is based on the absorption intensity of S-N bonds in the infrared region of the spectrum. The measurement range is from 0.02 to 2.0 mg/dm3	Spectrophotometer, photometer, volumetric flasks, pipettes, drying cabinet, muffle furnace, solvent drive, glass cooler, glass slide, indicator paper	Carbon tetrachloride, aluminum oxide, sodium sulfate, sulfuric acid, distilled water	The sample is taken in a glass container. It can be stored for 6 hours at a temperature of 15-25 C and 24 hours at a temperature of 6 C. A preserved sample can be stored at 15-25 C for 5 days, at 6C for 1 month	Extraction; Purification of the extract; Taking measurements; Calculation of results;
Gravimetric method [6,12,13].	It is based on separation of oil products using an organic solvent, purification of polar compounds using a column chromatography column, and determination of the amount of oil products by gravimetric method. The measurement range is from 0.3 to 50.0 mg/dm3	Analytical balance, thermometer, glass cooler, magnetic stirrer, funnel, cylinder, beaker, measuring cups	Hexane, chloroform, aluminum oxide, sodium sulfate, sulfuric acid, glass wool, distilled water	The sample is taken in a glass container. If it is not possible to perform the analysis on the same day, the sample is preserved.	Extraction; Purification of the extract; Solvent evaporation; Residue measurement; Calculation of results;
Fluorimetry method [7,10].	The amount of extracted oil products is based on the measurement of fluorescence intensity using a liquid analyzer. The measurement range is from 0.005 to 50.0 mg/dm3	Liquid analyzer "Fluorate-02", measuring flasks, pipettes, drying cabinet, magnetic stirrer, desiccator, indicator paper, glass cooler	Hexane, hydrochloric acid, nitric hydroxide, distilled water	The sample is taken in a glass container. The analysis should be done on the day of sampling. If it is not possible to perform the analysis on the day of sampling, the sample can be extracted and the analysis can be continued during the week.	Extraction; Purification of the extract; Taking measurements; Calculation of results;
Gas chromatography method [8].	Extraction of oil products, purification of the extracted extract from polar compounds and analysis of the purified eluate in a gas chromatograph. The measurement range is from 0.01 to 2.0 mg/dm3	Gas chromatograph (MS, FID), volumetric flasks, pipettes, drying cabinet, glass cooler, chromatographic column	n-hexane, n-octane, eicosane, tetracontane, sorbent (magnesium silicate), sodium sulfate, hydrochloric acid, stearyl stearate, distilled water	The sample is taken in a glass container. Can be stored in a tightly closed container for 1 day, and a preserved sample for 1 month.	Extraction Purification of the extract from polar compounds Taking measurements Calculation of results

The correct performance of laboratory analysis also depends on the environmental factors necessary for conducting the analysis, and it is important to create the necessary environmental conditions for performing the tests based on the methods discussed above [6-16]. Table 2 presents a comparative table of environmental conditions (temperature, humidity and atmospheric pressure) required for quantitative analysis of oil products in water bodies.

Table 2. Environmental requirements

Methodology	Room temperature,° C	Air humidity, %	Atmospheric pressure, kPa	Literature
RD 118.3897485.13-92, Fluorimetry	20±5	80±5	84,0-106,7	[10]
O'z O'U 0697:2015, Gravimetry	20±5	not specified		[6]
O'z O'U 0791:2019, Gravimetry	20±5	80±5	84,0-106,7	[16]
HDPE F 14.1:2:4.5-95, Infrared-spectrometry	20±5	<80	84,0-106,7	[9]
HDPE F 14.1:2.116-97, Gravimetry	20±5	80±5	84,0-106,7	[12]
State standard 4.1.1013-01, Infrared-spectrometry	20±5	<80	84,0-106,7	[15]
State standard of Russia 51797-2001, Infrared-spectometry	not specified			[14]
State standard 31953-2012, Gas chromatography	not specified			[8]
HDPE F 16.1.41-04, Gravimetry	20±5	25 °C да <80	97,3-104,6	[13]

1. Research method and research

Equipment. The accuracy of the solutions to determine the hydrogen index was measured in MI-150 ionomer at 0.01 units. Chromatographic column for separating the oil layer from water, UF-spectrophotometer SPECORD 210 PLUS providing measurements at a wavelength of 3.42 microns with an absorbent layer thickness of at least 40 mm, Agilent 7872A gas chromatograph for determining the purity of standard samples, 0.0001 g for gravimetric analysis of oil products. precision analytical balance VL-224 and laboratory glassware according to GOST 25336-82 were used.

The following conditions must be observed when performing the test.

- ambient temperature (20 ± 5) °C;
- air humidity should not exceed 80% at 25 °C;
- atmospheric pressure from 84.00 to 106.70 kPa;

To measure the amount of petroleum products in water using the IR-spectrophotometric method, it is based on extracting the amount of petroleum products from water using an organic solvent extraction method and purifying the extracted extract using an aluminum oxide filter.

2. Discussion of research method and its results

For analysis, water samples taken from existing effluent and monitoring boreholes in the territory of Fergana Oil Refinery (FORP) were used. The collected water samples were first chemically analyzed for pH value and mineral content. Based on the obtained results, it can be seen that the amount of minerals and other chemical parameters in oil-polluted waters are higher than the permissible standards. Table 3 shows a comparative analysis of the water sample by chemical parameters.

Water samples taken from Absheron lakes were also used for the analysis. The collected water samples were first subjected to chemical analysis for pH and mineral content. Based on the results obtained, it is evident that the amount of minerals and other chemical indicators in oil-polluted waters exceed permissible standards. Table 4 presents a comparative analysis of the water sample by chemical indicators[17-19].

Table 3. Results of chemical analysis of water sample

Sampling location (well)	Hydrogen index (pH)	Total hardness (mg*eq/ dm^3)	Amount of total minerals (g/dm^3)	Note [17,18]
Monitoring borehole No. 121	6.80	8.12	0.62	The chemical composition of the water is within the permitted standards
Monitoring borehole No. 121 № 0.14	7.38	7.80	0.78	
Treated wastewater	7.82	6.20	2.24	
The outlet of the wastewater from the plant	6.96	29.60	4.62	The total mineral content and hardness of the water is above normal
Wastewater pool	7.38	29.20	4.28	

Table 4. Results of chemical analysis of the water sample

Water sample	Hydrogen index (pH)	dissolved O_2 (mgO_2/l)	COD	BOD	salinity (mg/l)
Girmizy lake	7.81	12,6	72	43	1580
Gu lake	7.2	0.7	60	38	3152

The chemical composition of the lakes water is within the permitted standards, the total mineral content and hardness of the lakes water is above normal[17-19].

Preparation of chromatographic column. Chromatographic column - washed thoroughly first in chromium mixture and then in water. It is then rinsed in the organic solvent used for analysis. 6 g of aluminum oxide dried in a drying cabinet at a temperature of 100-110 °C for 2 hours is placed in a 50 cm^3 beaker. A suspension is formed by adding 5-6 cm^3 of organic solvent on top. Passing the resulting suspension through a filter, a layer containing 1 g of sodium sulfate is formed on the remaining aluminum oxide, which is dried in a drying cabinet at a temperature of 100-110 °C for 2 hours.

Choose a pure organic extractant. The main analytical process for the determination of oil products in water is the extraction of oil products from water. Therefore, the choice of organic reagent for extraction is important. Chloroform, hexane and carbon tetrachloride were selected as the most used organic solvents as organic reagents. Solvents were checked for purity by gas chromatography before starting the analytical procedures. Table 5 shows the percentages of purity specified in the regulatory documents for the production of extractants and the results of real analysis of extractants.

Table 5. Table for determination of purity level of organic reagents

Solvent name and production regulatory document number	Purity level of solvents specified in regulatory documents, %	Results obtained in the analysis, %
Chloroform GOST 20015-88	≥99,60	99,60
Hexane GOST 4517-2016	≥99,00	97,60
Carbon tetrachloride GOST 20288-74	≥99,00	96,20
Petroleum ether TC 2631-074-44493179-01	>40,00	60,00
Isohexane GOST 24676-2017	≥94,00	90,50
Pentane T ES TC COMP 1-178-10	≥85,00	86,00

Based on the results of the analysis, three extractants, chloroform, hexane and carbon tetrachloride, were selected for extracting the samples. Figures 1, 2, 3 show chromatograms of selected extracts.

```
File        :C:\msdchem\1\DATA\2024\Other\BSB\20240123_Chl-3.D
Operator    : Bobakulov Kh.M.
Acquired    : 23 Jan 2024  18:53     using AcqMethod SOLVENT.M
Instrument  :   GC MSD
Sample Name: Chloroform
Misc Info   :
Vial Number: 1
```

Fig 1. Chromatogram of chloroform obtained for extraction

```
File        :C:\msdchem\1\DATA\2024\Other\BSB\20240123_Hex-2.D
Operator    : Bobakulov Kh.M.
Acquired    : 23 Jan 2024  20:14     using AcqMethod SOLVENT.M
Instrument  :   GC MSD
Sample Name: Hexane
Misc Info   :
Vial Number: 2
```

Fig 2. Chromatogram of hexane obtained for extraction

```
File        :C:\msdchem\1\DATA\2024\Other\BSB\20240125_CC14-1.D
Operator    : Bobakulov Kh.M.
Acquired    : 25 Jan 2024  16:58     using AcqMethod SOLVENT.M
Instrument  :   GC MSD
Sample Name: CC14
Misc Info   :
Vial Number: 7
```

Fig 3. Chromatogram of carbon tetrachloride obtained for extraction

The extractant should not contain impurities adsorbed on aluminum oxide. If the extractant does not meet the requirements, it must be cleaned.

Purification of the extractant. Add 2 g of aluminum oxide to 200 ml of organic solvent and shake for 5 minutes. After the aluminum oxide is completely precipitated, the liquid is decanted and driven at normal pressure using a bottle cooler. Fractions driven at 46-47 oS or 76-77 oS are collected during the driving process. When driving, 1.0-1.5 g of activated carbon is added to 100 ml of organic solvent.

Creating a graduated graph. A standard sample consisting of a mixture of hydrocarbons with a mass content of 50 mg/dm^3 is used to make a graduated graph.

Primary standard sample preparation. To prepare a standard sample with a mass of 1.00 mg/dm^3, 1 cm^3 of the standard sample is taken into a clean 50 cm^3 volumetric flask and the volume is brought up to 50 cm^3 using an organic solvent.

Preparation of working solution. To prepare a standard sample with a mass content of 0.100 mg/dm^3, 5 cm^3 of the primary standard sample is measured using a pipette and placed in a 50 cm^3 volumetric flask and made up to 50 cm^3 using an organic solvent.

0.025 to 25 cm^3 volumetric flasks using 1 and 5 cm^3 pipettes; 0.50; 1.00; 2.50; 5.00; 10.00; 15.00 cm^3 of the working solution is added and mixed with an organic solvent until the volume is 25 cm^3. The number of hydrocarbons is 0.0001 by volume; 0.002; 0.004; 0.01; 0.02; 0.04; It is 0.06 mg/cm^3. A standard sample of 0.10 mg/cm^3 can be used for the final graduated solution.

Table 6. Gradation graph chart

Standard sample, ml	0,025	0,50	1,00	2,50	5,00	10,00	15,00
C(concentrated) mg/dm³	0,0010	0,0020	0,0040	0,0100	0,0200	0,0400	0,0600
Device indicator 1	0,003	0,006	0,015	0,040	0,078	0,150	0,232
Device indicator 2	0,003	0,006	0,016	0,041	0,078	0,148	0,236
Device indicator 3	0,002	0,005	0,017	0,040	0,078	0,146	0,235
Average indicator	0,003	0,006	0,016	0,040	0,078	0,148	0,234
C(concentrated), mg/dm³	0,0010	0,0020	0,0040	0,0100	0,0200	0,0400	0,0600
Average indicator	0,003	0,006	0,016	0,040	0,078	0,148	0,234

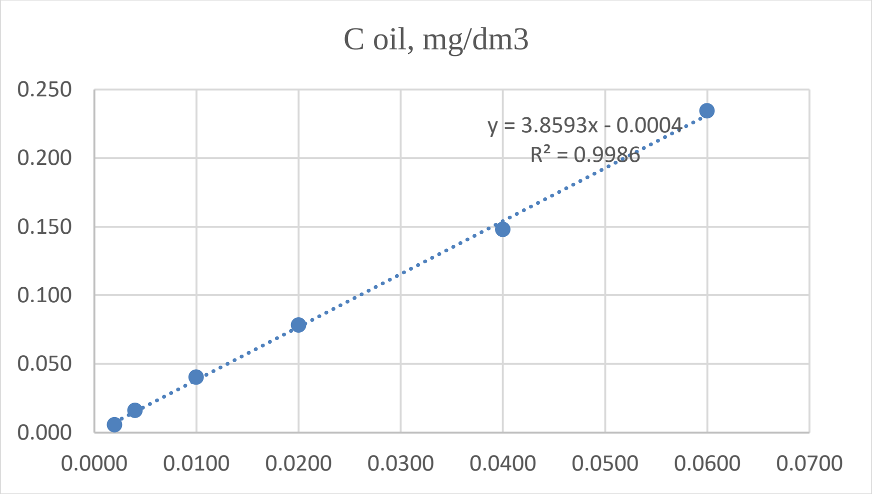

Fig 4. A graduated graph for the identification of petroleum products

Table 7. Determining the coefficient a and b using mathematical calculations on a graduated graph

n= 6

C concentrated mg/dm3	0,0010		0,002	0,004	0,010	0,020	0,040	0,060
Average indicator	0,0027		0,0057	0,0160	0,0404	0,0782	0,1480	0,2343

Calculation of coefficients a and b

∑x=	0,136	**x^2:**	0,0000	0,0000	0,0001	0,0004	0,0016	0,0036
∑y=	0,523	**y^2:**	0,0000	0,0003	0,0016	0,0061	0,0219	0,0549
x¯=	0.022	**xx¯:**	-0,0206	-0,0186	-0,0126	-0,0026	0.01733	0.03733
y¯=	0.087	**yy¯:**	-0,081	-0,071	-0,047	-0,009	0,061	0,147
∑(xx¯)^2=	0,002	**(xx¯)^2:**	0,00042	0,0003	0,00016	0,000007	0,00030	0,00139
∑(yy¯)^2=	0,039	**(yy¯)^2:**	0.006	0,0050	0,00218	0,00007	0,00370	0,02167
∑xy=	0,022	**xy:**	1.1333	0,00006	0,000403	0,0015	0,00592	0,01406
∑(xx¯)(yy¯)=	0,010	**(xx¯)(yy¯):**	0,00168	0,00132	0,000591	2.3719	0,00105	0,00549
∑x^2=	0,0057							
∑y^2=	0,0848		**∑(U^2)=**	0,0026	**∑(V^2)=**	0,03933	**∑(UV)=**	0,01017

a= 0,00038212 b= 3.8592602

100-500 ml of the samples brought for analysis are measured in a glass flask, 20 ml of organic solvent is added and mixed by shaking well. The walls of the glass container are rinsed with an organic solvent. The well-mixed sample is placed in a separatory funnel, and the organic layer is separated from the aqueous phase in a 50 cm^3 glass beaker with a tightly closed mouth. The remaining sample is reextracted with another 20 ml of organic solvent, and the organic layer is separated again into the glass beaker from which it was first extracted. The resulting eluate is passed through a filter prepared with aluminum oxide and placed in a test tube. Measurements are made after rinsing the spectrophotometer cuvettes with an organic solvent. In order to confirm the accuracy of our results, an artificial mixture of organic compounds was prepared in pure distilled water. The amount of oil products in the artificial mixture is 8.00-8.50 mg/dm^3.

Table 8. The results obtained when extracting the amount of petroleum products in the sample in three different organic solvents

Location of taken sample	Total mineral content of the sample, mg/dm^3	Hydrogen indicator of the sample, (pH)	The result of chloroform extracted sample, mg/dm^3	The result of hexane-extracted sample, mg/dm^3	The result of carbon tetrachloride extracted sample, mg/dm^3
Observation well № 131	0.56	7.08	0.10	0.05	0.06
Observation well № 014	0.84	7.12	0.12	0.10	0.08
Waste water (discharge point in the pond)	3.44	5.54	14.50	10.10	11.60
Sewage pool	3.64	5.40	16.20	12.20	14.40
Waste water after treatment	1.20	6.86	1.64	1.10	1.24
Artificial mixture	-	-	8.40	8.38	8.34

According to the results of the analysis, it can be seen that chloroform is the strongest separator as an organic reagent in the spectrophotometric determination of oil products (in the case of the Fergana oil refinery).

Table 9. The results obtained when extracting the amount of petroleum products in the lakes waters samples in three different organic solvents

Location of taken sample	Total mineral content of the sample, mg/dm^3	Hydrogen indicator of the sample, (pH)	The result of chloroform extracted sample, mg/dm^3	The result of hexane-extracted sample, mg/dm^3	The result of carbon tetrachloride extracted sample, mg/dm^3
Girmizy lake	0.56	7.81	0.14	0.07	0.08
Gu lake	0.84	7.2	0.16	0.10	0.09

As can be seen from Table 9, the results of the analysis show that chloroform is the strongest separator as an organic reagent in the spectrophotometric determination of petroleum products in water samples from Lakes Gu and Girmizy [20-21].

In order to confirm spectrophotometric results, oil products were analyzed gravimetrically. Tables 10 and 11 shows the results of spectrophotometric and gravimetric analysis.

Table 10. Results of spectrophotometric and gravimetric analysis of oil products

Location of taken sample	Total mineral content of the sample, mg/dm3	Hydrogen indicator of the sample, (pH)	The results of spectrophotometric analysis, mg/dm^3	The results of gravimetric analysis, mg/dm^3
Observation well № 131	0.56	7.08	0.11	<0.3
Observation well № 014	0.84	7.12	0.14	<0.3
Waste water (discharge point in the pond)	3.44	5.54	14.54	14.30
Sewage pool	3.64	5.40	16.80	16.54
Waste water after treatment	1.20	6.86	1.70	1.62
Artificial mixture	-	-	8.44	8.34

Table 11. Results of spectrophotometric and gravimetric analysis of oil products

Location of taken sample	Total mineral content of the sample, mg/dm^3	Hydrogen indicator of the sample, (pH)	The results of spectrophotometric analysis, mg/dm^3	The results of gravimetric analysis, mg/dm^3
Girmizy lake	0.56	7.81	0.15	0.13
Gu lake	0.84	7.2	0.18	0.2

Conclusion

In the course of scientific research, the chemical and biological impact of petroleum products in the hydrosphere and atmosphere, exceeding permissible levels on the human body, toxicological properties, quantitative analysis of petroleum products in water from various lakes of the Absheron Peninsula, as well as the development (verification) of the spectrophotometric method in laboratory conditions were studied, taking into account the results of the analysis, the following conclusions were made:

- since the gravimetric method of analysis of oil products currently used in our country does not allow to determine the presence of oil products in small amounts (<0.3 mg/dm^3), it is not possible to analyze oil products in samples taken from monitoring wells and water facilities using the method;

- spectrophotometric method - accurate quantitative analysis, fast and high sensitivity, low sample requirement, the possibility of detecting large and very small amounts of the method, low time consumption, taking into account the small error rate, the minimum amount of oil products in the sample (>0, 05 mg/dm^3) that it is also possible to determine;

- based on the analysis results, it can be concluded that hexane is the strongest separator as an organic solvent (extractant) by spectrophotometric method (in the case of the Fergana oil refinery facility).

For the quantitative analysis of the water samples taken for analysis, the quantitative analysis of petroleum products in water using the spectrophotometric method was carried out for the first time in the "Geoecologist-chemistry" laboratory of the "Institute of Hydrogeology and Engineering Geology" State Institution and the method was verified. Based on the obtained results, it is proposed to use spectrophotometric methods in the analysis of oil products in the waters of "Hydrochemistry" laboratories in Uzbekistan Republic in the future.

Also for the quantitative analysis of water samples from lakes Gu and Girmizy taken for analysis, the laboratory of the Ministry of Ecology and Natural Resources of the Republic of

Azerbaijan conducted for the first time a quantitative analysis of oil products in water using a spectrophotometric method, and the method was tested on real objects (in water samples from lakes Gu and Girmizy). Based on the results obtained, it is proposed to use spectrophotometric methods in the future when analyzing oil products in other natural waters.

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SYNTHETIC CHELATING SORBENT BASED ON MALEIC ANHYDRIDE WITH STYRENE AND 4-NITROANILINE-2-ARSONIC ACID FOR PRECONCENTRATION OF SILVER(I)

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Keywords: synthetic chelating sorbent, sorption capacity, silver(I), sorption, desorption.

ABSTRACT

This article is devoted to the extraction of silver (Ag) ions in an acidic medium at pH 5 by a copolymer of maleic anhydride with styrene (MASC), chemically modified with 4-nitroaniline-2-arsonic acid (NAA). The structure of the sorbent CSMA-4-nitroaniline-2-arsonic acid was studied by IR spectroscopy methods. The study of Ag(I) ion sorption was carried out under static conditions. The influence of various parameters on the process of Ag(I) ion sorption was studied. Maximum sorption of metal ions is observed at pH 5. The sorption equilibrium was established after 3 hours. As the concentration of sorbed metal ion increases, it reaches its maximum at $6 \cdot 10^{-3}$ M. To study desorption, the effect of different acids - HNO_3, CH_3COOH with the same concentrations on the desorption of Ag(I) from the sorbent was studied. The experiment showed that the maximum desorption of Ag(I) occurs in 2 M nitric acid (HNO_3).

Introduction

Sorption technologies have been widely used for the preconcentration of heavy and hazardous metal ions [1-7]. Chelating sorbents are of particular interest as sorption material. More efficient is the use of modified forms of the MASC. For example, chelating sorbents, which are fixed on organic compound·s matrices [8–9]. According to recent papers, the MASC is a potential matrix for the synthesis of chelating sorbents, as well as the preconcentration and determination of heavy metal ions [10-13].

Ag(I) is among heavy and toxic metal ions. It can accumulate on skin and prolonging contact with it results in argyria [14-15]. Therefore, it is actual from analytical point of view the sorption preconcentration of Ag(I) as heavy and toxic metal ion from aqueous solutions.

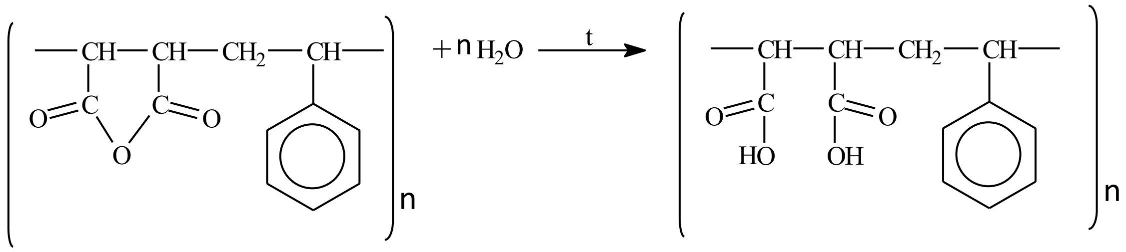
The main goal in the present work is to study the conditions for the preconcentration of Ag(I) with a new chelating sorbent based on MASC modified with NAA, followed by determination of Ag ions by photometric spectrometry to remove Ag(I) from aqueous solutions.

Experimental technique

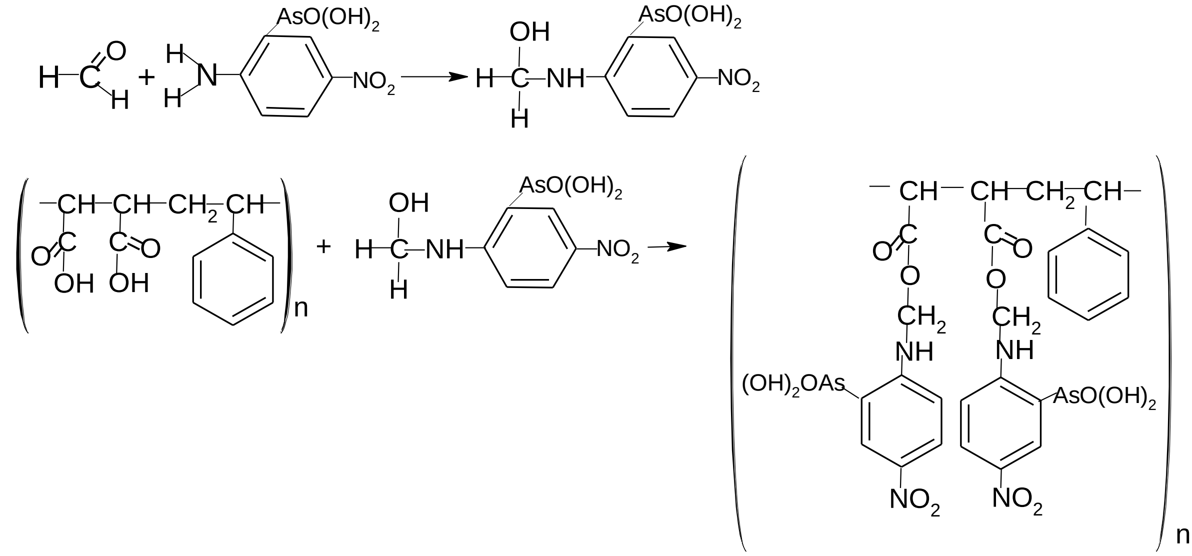
Sorbent. To investigate the sorption preconcentration of Ag, a synthetic chelating sorbent based on MASC and NAA was used for preconcentration of Ag(I).

Synthesis of sorbent.

The sorbent synthesis is carried out according to the method [16]. The sorbent used in this study was created by modifying a macroporous MASC. NAA was applied as an amine. To begin, weigh 3 g of copolymer using an analytical scale before transferring it into the round bottom flask. The appropriate amount of NAA was weighed, dissolved in water, and added to the flask's original contents. In the synthesis, formalin was utilized as a cross-linking agent. The reaction was conducted at 60-70 °C for 30-40 minutes. The following stages were observed in the polycondensation reaction (Scheme 1):



Because the procedure is carried out in an aqueous medium, the polymer's anhydride groups undergo hydrolysis.



The combination of formaldehyde with 4-nitroaniline-2-arsonic acid creates an unstable carbonylamine. Unstable carbonylamine interacts with the macromolecule's carboxyl groups, introducing the amine into it.

Before conducting experimental studies, the synthetic chelating sorbent was purified. To conduct the experiment on the sorption of silver ions, the sorbent was ground in an agate mortar and sifted through a sieve with 14 mm pores.

Figure 1 shows the molecular structure of the amine.

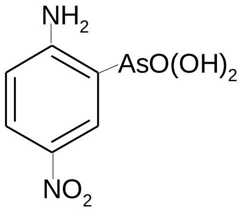


Fig 1. Molecular structure of 4-nitroaniline-2-arsonic acid

Solutions. The standard solution of Ag(I) was prepared by dissolving an accurate mass of the metal salt $AgNO_3$ (chemically pure) in distilled water [17]. Spectrophotometric measurements were performed using a Lambda Perken Elmer spectrophotometer and a KFK-2 photoelectric colorimeter. Working solutions were obtained by appropriate dilution of the stock solutions.

To create the required acidity ammonium acetate buffer solutions (pH 3–11) were used. The determination of silver in solutions was carried out by the spectrophotometric method using the reagent - 2,2',3,4-tetrahydroxy-3'-sulfo-5'-nitroazobenzene.

Study of metal sorption. Metal sorption isotherms were obtained under static conditions at 20°C. The sorption value and the degree of metal extraction were calculated from their equilibrium concentration in the solution by the spectrophotometric method [18]. The degree of extraction (R, %) and the value of sorption (q_e, mg/g) for the studied analyte were calculated using the formulas:

$$R,\% = \frac{C_0 - C_e}{C_e} x100 \ (1),$$

$$q_e = \frac{(C_0 - C_e)V}{m} \ (2),$$

where C_o and C_e are the initial and residual (equilibrium) concentrations of the adsorbate, respectively, $mg\cdot L^{-1}$; V is the volume of the solution, L; m is the mass of the sorbent, g.

When studying sorption in a static mode, $5\cdot10^{-3}$ M of Ag(I) metal aqueous solution was introduced into a test tube with a ground stopper, and an ammonium acetate buffer solution was added to create the required acidity to a total volume of 20 ml. 30 mg of the sorbent was added to a test tube, closed with a cork, and intensively stirred for 1–150 min. The solution was separated from the sorbent by filtration.

Study of metal desorption. The dependence of metal desorption from the modified sorbent surface on acidity and eluent concentration was studied under static conditions. A portion of the modified sorbent weighing 30 mg was placed in a 50 ml conical flask with a metal solution and left for three hours with stirring. Then, the sorbent was separated from solution by filtration. At the final stage, the concentration of desorbed silver(I) ions was determined in the obtained filtrate.

Results and discussions

Sorbent identification.

IR spectroscopy.

The structure of the synthetic sorbent CSMA-4-nitroaniline-2-arsonic acid was studied by IR spectroscopy methods. The following vibrations are observed in the IR spectrum of CSMA-4-

nitroaniline-2-arsonic acid: 3600-3100 cm^{-1} (stretching vibrations of the –OH group, as well as stretching vibrations of the –NH group (3400-3200 cm^{-1})], 1775-1745 cm^{-1} (stretching vibrations of the -C=O group in the carboxyl group), 1585-1565 cm^{-1} (stretching vibrations of C-N and deformation vibrations of N-H), 1605-1515 cm^{-1} (stretching vibrations of C-C in the benzene ring), 730-695 cm^{-1} (deformation vibrations of C-C in the benzene ring).

Influence of pH on sorption. The static sorption capacity of a synthetic chelating sorbent depends on the content of functional-analytical groups in the sorbent matrix and the acidity of the medium. The sorption of silver(I) by synthetic sorbent was influenced by pH.

The study of the effect of pH (in the range of 3-8) on the preconcentration of silver(I) ions under static conditions showed that the quantitative extraction of metal ions is achieved at pH 5.

This effect of the medium pH value on the preconcentration of silver(I) ions can be explained as follows: at a low pH value, $-AsO_3H_2$ and NH_2 functional groups of the polymer sorbent easily form protonation and in this case, competition between the formed protons and silver ions with subsequent electrostatic repulsion of silver ions is observed in the aqueous solution. In this case, the adsorption value decreases. With a further increase in the pH value, these functional groups are no longer protonated and therefore the previously observed process of electrostatic repulsion of the silver ions decreases. The result of this process is an increase in the adsorption value of the silver ion.

At pH=5 of the environment, at which maximum adsorption is observed, the metal ion in the aqueous solution is in the form of Ag^+.

The pH or acidity value of the medium at which hydrolysis of a metal ion begins depends on its charge and radius. Thus, the greater the charge and the smaller the radius of the cation of a metal element, the lower the pH value of the medium at which hydrolysis of the metal begins. [19] For silver ions in aqueous solution, at pH values greater than 8, the hydrolysis process begins.

Figure 2 represents the dependence of adsorption capacity on medium pH.

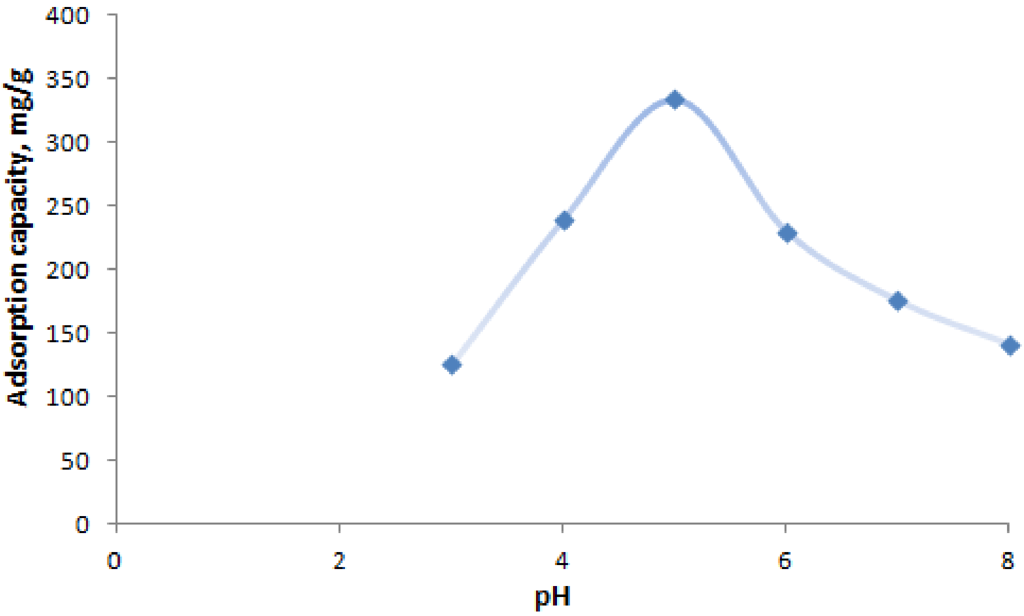


Fig.2. Effect of medium pH on adsorption capacity.

Fig. 2 shows that the maximum degree of silver extraction by sorbent is achieved from solutions with pH 5. So, all further studies were carried out at pH=5.

Effect of time on sorption. It was found that the sorption equilibrium in the "sorbent - liquid phase" system is achieved after 3 hours of contact. For all further experiments, the time to establish the sorption equilibrium was 3 hours.

Influence of silver (I) concentration. The initial concentration of metal affects the value of the sorbent sorption capacity. The study of the dependence of the sorption capacity (SC) on the concentration of silver (I) showed that the sorption value changes with the concentration of the silver ions. Figure 3 shows the dependence of the sorption capacity of the sorbent on the initial concentration of silver ions. As can be seen from the figure, the maximum sorption capacity of the sorbent is achieved at an initial metal concentration of $6{\cdot}10^{-3}$ M. So, with an increase in the concentration of the silver ion in the solution, the amount of adsorbed metal increases, and at a concentration of $6{\cdot}10^{-3}$ M it becomes maximum (pH=5, C_{Ag+} =$6{\cdot}10^{-3}$ mol/l, $V_{tot.}$=20 ml, SC = 334,08 mg/g).

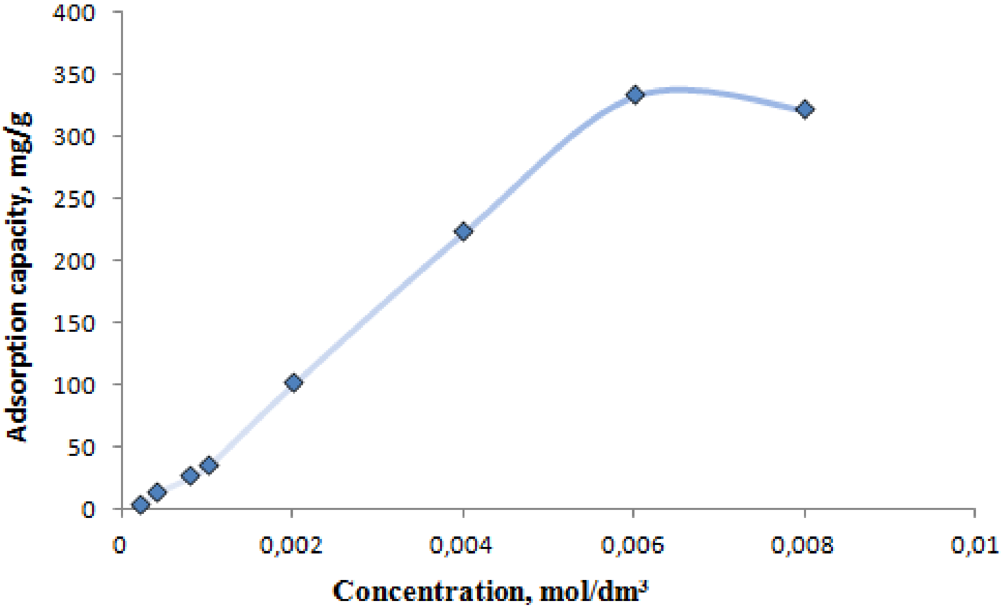


Fig.3. Effect of initial concentration of metal on adsorption capacity.

Study of the desorption of the absorbed silver ion from a polymeric sorbent. The technique of adsorption has a number of benefits, including great reversibility, which enables recycling of wasted adsorbent by desorption.[20] Furthermore, desorption and regeneration of the sorbent is the economical process of removal silver(I) ions. This process allow the repeated use of sorbent. In this process a precipitate of silver (I) with sorbent was formed, filtered off, washed 2-3 times with distilled water in order to remove the diluents, and then dried. To select a suitable eluent, as desorbing agents various acids were tested – mineral HNO_3 and organic CH_3COOH. It was found that the desorption capacity of HNO_3 is higher than that of CH_3COOH. A study of the influence of the HNO_3 concentration showed that Ag(I) ions are maximally desorbed in a nitric acid with concentration of 2.0 M.

Effect of concentration of different acids on the degree of extraction (%) of silver(I)

Acid	Concentration, mol/l	Degree of desorption, %
HNO_3	0,5	65
	1,0	79
	2,0	87
CH_3COOH	0,5	60
	1,0	71
	2,0	76

Adsorption isotherm. The adsorption isotherm depicts the connection between the adsorbate in the surrounding phase and the adsorbate adsorbed on the surface of the adsorbent at equilibrium and constant temperature. This graph is extremely important for research on adsorption studies. [21] Adsorption isotherm will be linear only in small ranges, at low sufficient concentrations the linear adsorption isotherm can be applied. [22-23]

In this work, Langmuir adsorption isotherm model was used to explain adsorption process.

Langmuir isotherm. [Langmuir, 1918]: Langmuir's model is widely used to depict physical and chemical adsorption. The Langmuir isotherm model is defined by the following equation:

$$q_e=\frac{q_m K_L C_e}{1+K_L C_e}, \quad (1)$$

In the equation, C_e (mmol/dm^3) represents the adsorbate concentration in the aqueous phase at the adsorption equilibrium, q_e (mmol/g) represents the equilibrium adsorption capacity or the quantity of metal adsorbed on the adsorbent's surface at the adsorption equilibrium, q_m is the maximum adsorption capacity equal to q_e for the complete monolayer, and K_L (dm^3/mmol) is the Langmuir isotherm constant.

A graph showing the dependence of 1/qe on 1/Ce has been produced. The q_{max} and K_L values were calculated using the plot's slope and intercept, respectively. Table 1 illustrates Langmuir isotherm parameters.

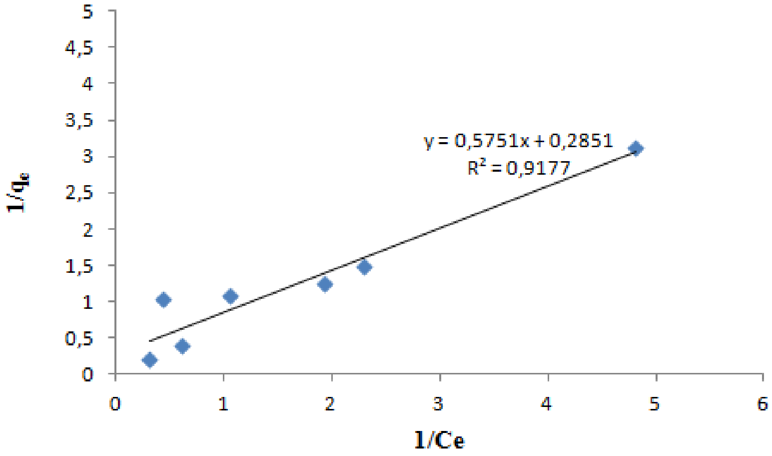


Table 1. Langmuir isotherm parameters .

Langmuir			
q_{max}, mg/g	K_L, dm^3/mg	R_L	R^2
3.507	0.004	0.996	0.9177

R_L is a crucial adsorption equilibrium characteristic that determines whether the isotherm is irreversible ($R_L = 0$), favorable ($R_L<1$), linear ($R_L=1$), or unfavorable ($R_L>1$). The Langmuir isotherm model factor R_L may be derived using the following equation:

$$R_L=\frac{1}{1+K_L C_O}, (2)$$

where K_L is the Langmuir constant(dm^3/mmol), C_0 is the initial concentration of adsorbate (mmol/dm^3).

The results obtained reveal that R_L is between 0 and 1 and equivalent to 0.996, indicating that adsorption is favorable under the given circumstances using the Langmuir model. Furthermore, the coefficient of regression $R^2=0.9177$ indicates that the isotherm model matches well with experimental adsorption values.

Conclusion. For the first time, the preconcentration of silver ions with a synthetic sorbent based on MASC modified with NAA was investigated. The most effective conditions for silver sorption on the adsorbent were identified. Silver removal by adsorbent is most effective in pH 5 solutions. After 3 hours of contact, the "adsorbent - liquid phase" system reached sorption equilibrium. The Langmuir adsorption isotherm was used to describe the adsorption process. As the concentration of silver ions in the solution rises, sorbed metal increases until it reaches its maximum at $6 \cdot 10^{-3}$ M. The results demonstrated that the suggested sorbent may be utilized to preconcentrate silver in aqueous solutions. The regenerated sorbent can be reused for further preconcentration processes.

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УДК 546.42

СИНТЕТИЧЕСКИЙ ХЕЛАТООБРАЗУЮЩИЙ СОРБЕНТ НА ОСНОВЕ МАЛЕИНОВОГО АНГИДРИДА СО СТИРОЛОМ И 4-НИТРОАНИЛИН-2-АРСОНОВОЙ КИСЛОТОЙ ДЛЯ КОНЦЕНТРИРОВАНИЯ СЕРЕБРА(I)

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Аннотация: Статья посвящена извлечению ионов серебра(Ag) в кислой среде при pH 5 сополимером малеинового ангидрида со стиролом(СМАС), химически модифицированным 4-нитроанилин-2-арсоновой кислотой(НАК). Исследование сорбции ионов Ag(I) проводилось в статических условиях. Изучено влияние различных параметров на процесс сорбции ионов Ag(I). Максимальная сорбция ионов металла наблюдается при pH 5. Сорбционное равновесие устанавливается через 3 часа. Количество сорбированного иона металла увеличивается и при концентрации $8 \cdot 10^{-3}$ М становится максимальным. Для изучения десорбции Ag(I) с сорбента исследовано влияние различных кислот - HNO_3, CH_3COOH с одинаковыми концентрациями. Эксперимент показал, что максимальная десорбция Ag(I) происходит в 2М азотной кислоте (HNO_3).

Ключевые слова: синтетический хелатообразующий сорбент, сорбционная емкость, серебро(I), сорбция, десорбция.

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MALEİN ANHİDRİDİ-STİROL SOPOLİMERİ ƏSASINDA 4-NİTROANİLİN-2-ARSON TURŞUSU İLƏ GÜMÜŞ(I) QATILAŞDIRILMASI ÜÇÜN SİNTETİK XELATƏMƏLƏGƏTİRİCİ SORBENT

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Xülasə: Məqalə gümüş(Ag) ionlarının 4-nitroanilin-2-arson turşusu(NAT) ilə kimyəvi modifikasiya olunmuş, malein anhidridi-stirol sopolimeri(MASS) ilə turş mühitdə pH 5 sorbsiya olunmasına həsr edilmişdir. Ag(I) ionunun sorbsiyasının tədqiqi statik şəraitdə aparılmışdır. Ag(I) ionlarının sorbsiya prosesinə müxtəlif parametrlərin təsiri öyrənilmişdir. Metal ionlarının maksimal sorbsiyası pH 5-də müşahidə edilir. Sorbsiya tarazlığı 3 saatdan sonra əldə olunur. Udulmuş metal ionunun miqdarı artır və $8 \cdot 10^{-3}$ M qatılığında maksimuma çatır. Ag(I)-in sorbentdən desorbsiyasını öyrənmək üçün eyni qatılıqlı müxtəlif turşuların - HNO_3, CH_3COOH təsiri öyrənilmişdir. Təcrübə göstərdi ki, Ag(I)-nin maksimum desorbsiyası 2M azot turşusunda (HNO_3) baş verir.

Açar sözlər: sintetik xelatəmələgətirici sorbent, qatılaşdırma, gümüş(I), sorbsiya, desorbsiya.

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INTERACTION OF GAS PHASES WITH ACIDIC RUST MELT AND METAL

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ABSTRACT

After ores are extracted from mines, they undergo various processing processes, after which they are smelted. The smelting process is carried out in various types of smelting furnaces and units. The working areas of these units are built of refractory materials. These refractory materials are eaten, destroyed, and fail for various reasons. One of the reasons that accelerates the erosion of refractory materials is the dross formed during the smelting process. This largely depends on the composition of the dross. The dross contains metal and non-metal oxides of various compositions and nature. Since the composition of the dross is of various nature, the mechanism of action is also different. The article clarifies the effect of dross on the working volume of the furnace during the smelting process, and proposals are put forward for its elimination.

The acid open-hearth process allows steel to be produced with a lower gas content compared to the basic process.

Introduction

Hydrogen permeability of acid steel making rusts the process of hydrogen transfer from the furnace atmosphere through acid rust into metal includes the stage of dissolution of water vapor in the rust melt without considering in detail the data available in the literature on the solubility of water vapor in the rust melt, It should be noted that they were first obtained in a study, the results of which are consistent with our recent research work [2]. The degree of acidity of the rust melt can be described by the equations of hydrogen mass transfer through the slag melt layer to the slag-metal interphase surface and the transition of hydrogen from the rust to the metal.

$$H_2O_г + 0^{2-}_{ru.} = 20H^{-}_{ru.};\ (1)$$

$$H_2O_г + 2Si0^{4-}_{4ru.} = 20H^{-}_{d.} + Si_2\ 0^{2-}_{7ru.}\ (2)$$

$$H_2O_г + Si_2\ 0^{6-}_{7} = 20H^{-}_{ru.} + 2Si0^{2-}_{3ru.}\ (3)$$

The last rust, depending on the process conditions and the degree of oxidation of the metal, can proceed in different ways. For example, the decomposition of hydroxyl into oxygen and hydrogen can proceed with the participation of iron atoms of the surface layer of the metal or without the participation of iron atoms.

In the conditions of experiments on studying the hydrogen permeability of rust melts, all the above-mentioned rustes of hydrogen movement took place [3]. Some researchers claimed that with an increase in the basicity of the rust, the hydrogen content in the steel increases, while others reported a decrease in the hydrogen concentration in the metal with an increase in the basicity of the rust melt. Therefore, in the first series of experimental melts, the effect of the basicity (CaO/SiO_2) of electric steel-making slags on their hydrogen permeability was studied. The technique was similar to that previously described in as applied to the main electric steel-making slags. With the method used for supplying the steam-nitrogen mixture (Fig. 1), which primarily washes the crucible with molten metal and rust, the gas permeability of the crucible could greatly affect the results obtained.

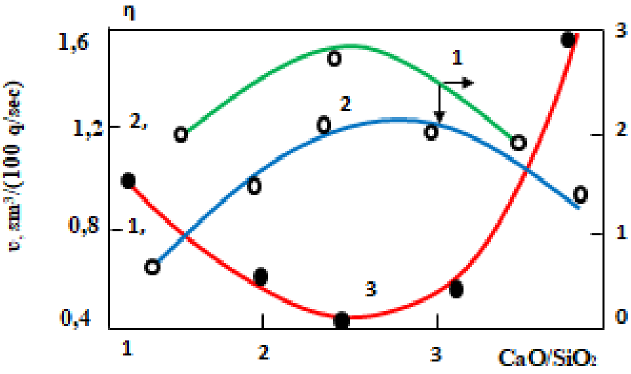

Fig. 1. The influence of the basicity of electric steelmaking rusts of the reduction period on their hydrogen permeability under industrial (1) and laboratory (2) conditions and on their viscosity (3) at 1650 ⁰ C.

In this connection, several melts were carried out to clarify the hydrogen permeability of the zirconium dioxide crucibles used. For this purpose, the molten metal in the crucible was covered with a layer of rust containing 60% SiO_2 , 25% CaO, 25% Al_2O_3 impermeable to hydrogen. A sample of the metal was taken for hydrogen, and then hydrogen was supplied to the system from a cylinder for 20 minutes. Experiments showed that the ones used for hydrogen.

Specially conducted melts with a doubled rust layer thickness showed that its hydrogen permeability also decreased by half. In other words, the hydrogen permeability of the rusts was limited by the process of hydrogen mass transfer through the rust layer [4,5].

Experiments were carried out mainly at 1650 ⁰C and a partial pressure of water vapor in the gas phase of 150 mm Hg. The chemical composition of industrial acid open-hearth slags, selected from a 90 t furnace, is given in Table 1.

The main component of acid steelmaking rusts is silica, so it was necessary to first check the effect of its concentration on the hydrogen permeability of the rusts. As can be seen from Table 1, the silica content in the rusts we studied varied from 39.0 to 61.80%.

Table 1. Chemical composition of acidic open-hearth rust

Rust group	Contents of components, %								SiO_2/ FeO+MnO
	SiO_2	CaO	FeO	Fe_2O_3	MnO	Cr_2O_3	Al_2O_3	MgO	
I	39,00	4,20	36,00	1,70	15,30	1,93	0,90	0,80	0,72
	41,76	4,65	34,82	1,67	14,29	1,82	0,81	0,17	0,81
	46,80	4,70	28,80	1,20	15,00	1,80	0,80	0,17	1,03
	49,07	4,90	22,20	0,60	15,60	1,73	4,38	0,60	1,27
	54,23	4,60	16,70	0,30	17,60	1,38	4,19	0,61	1,56
	56,70	4,40	13,10	-	19,40	0,84	4,18	0,57	1,74
	59,40	4,29	11,20	-	19,60	0,74	4,00	0,62	1,92
	61,80	4,30	10,01	-	19,46	1,13	3,76	0,14	2,11
	56,70	4,40	13,10	-	19,40	0,84	4,18	0,57	1,74
	55,00	6,80	13,00	-	19,00	0,80	4,10	0,50	1,71

II	54,00	9,70	12,10	1,51	17,40	0,96	2,16	0,97	1,71
	52,00	11,70	12,00	1,50	17,30	1,00	2,10	1,00	1,68
	52,20	11,60	11,60	1,26	16,80	0,82	2,10	1,01	1,75
III	59,40	4,29	11,20	-	19,60	0,74	4,00	0,62	1,92
	57,20	4,00	11,00	-	19,00	0,74	7,00	0,60	1,90
	53,40	3,30	12,60	-	17,60	0,80	10,70	0,60	1,76
	52,20	3,10	12,00	-	17,00	0,80	13,00	0,60	1,81
	51,20	3,00	12,30	-	15,10	0,90	16,40	0,62	1,88

The silica concentration in the slag increased mainly due to ferrous oxide from manganese oxide, so Fig. 2 shows the dependence of the hydrogen permeability of the rusts on the SiO/FeO+MnO ratio [5,6]. With an increase in this ratio from 0.72 to 2.11, the hydrogen permeability of the slags decreases from 1.00 to 0.09 cm^3 (100 g/min). This is explained by a significant increase in rust viscosity with an increase in the SiO_2/(FeO+MnO) ratio (Fig. 3) and a decrease in oxygen activity in the slag with an increase in the silica concentration (since SiO_2 is a strong complexing oxide), due to which the reaction of dissolution of water vapor in the rust is hindered.

$$H_2O_r + 0^{2-}_{d.} = 20H^{-}_{d.} \quad (4)$$

The data we obtained on the effect of the SiO_2/(FeO+MnO) ratio on the hydrogen permeability of acid rusts were later confirmed by our colleagues and explained from the point of view of thermionic emission of oxide melts. The authors of studied the work function of electrons from acid rusts that had the same chemical composition as the melts we studied.

It was found that with an increase in the SiO_2 /(FeO+MnO) ratio, the work function of electrons from rusts increases, and, consequently, the thermionic emission of the rust melt decreases:

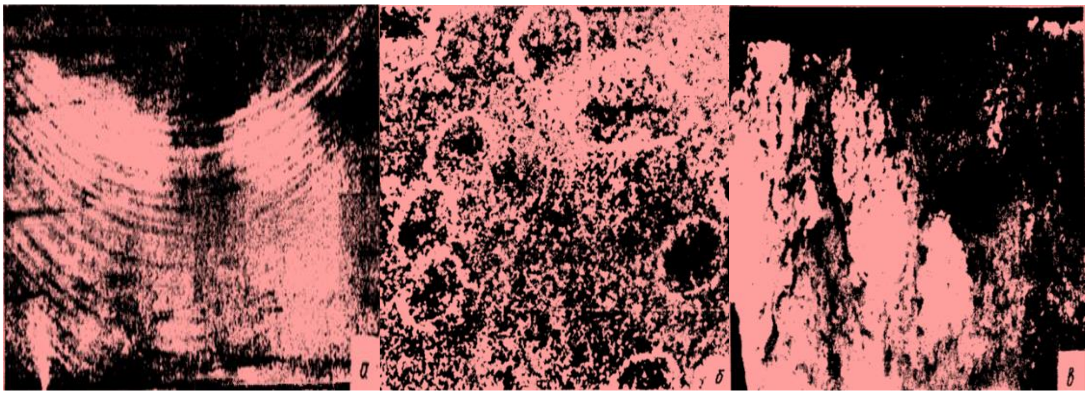

Fig. 2. Inclusions in steel 30KhGSNA. X500: a, b, aluminum additive after alloying steel with silicon; c-aluminum additive before alloying steel with silicon

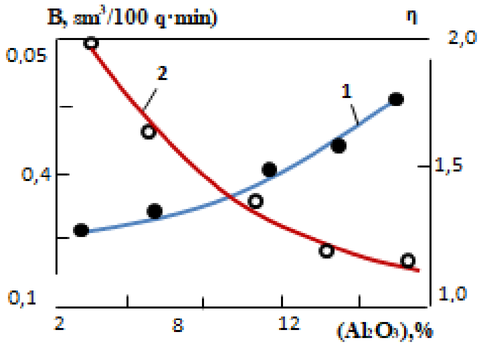

Fig. 3. Effect of Al_2O_3 on hydrogen permeability (1) and viscosity (2) of acidic open-hearth rusts at 1650 ^{0}C and p_{H_2O}= 150 mm Hg.

In this connection, it is extremely important to study the effect of partial pressure of water vapor in the gas phase on hydrogen permeability of steelmaking rusts. Experiments were conducted at 1650 ^{0} C and p_{H_2O} in the gas phase equal to 55, 100, 170 and 260 mm hg**.**

The experimental data (Fig. 4 and Table 2) allowed us to establish a linear dependence of the hydrogen permeability of a rust of a given composition on the square root of the partial pressure of water vapor in the gas phase.

Due to the fact that the solubility of water vapor in rusts changes little within the limits of temperature fluctuations during open-hearth smelting [7] it can be assumed with a certain error that the difference C_1-C_2 in the equation ($\upsilon_H = \beta_H S(C_1-C_2)$) remains constant for a certain point in time when the temperature changes. Then, using the experimentally established dependence of the hydrogen permeability of the rust on temperature, it is possible to estimate the apparent activation energy of the hydrogen permeability process.

To do this, we represent the equation ($\upsilon_H = \beta_H S(C_1-C_2)$) in the following form:

$$\upsilon_H = AB_0\, e^{-E/RT}(C_1-C_2) \quad (7)$$

$$\lg = \upsilon_H = A_0 - B_0/T \quad (8)$$

Where,

$$A_0 = \lg AB_0 \quad (9)$$

$$B_0 = E/R \lg e = E/4{,}575 \quad (10)$$

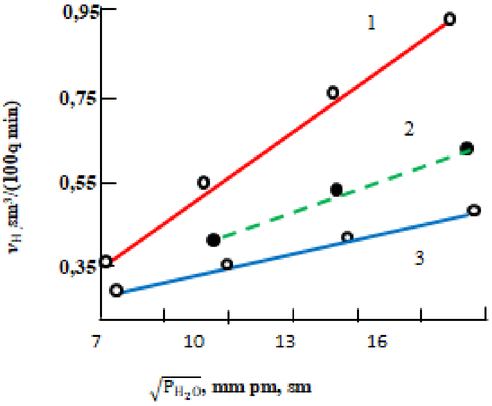

Fig. 4. The influence of p_{H_2O} in the furnace atmosphere on hydrogen permeability of acidic rusts at 1650 ^{0}C
1 – rust, 2 – s rust; 3 – rust, 6 (see table 2).

In this case, the tangent of the angle of inclination of the straight line to the abscissa axis (Fig. 5) will characterize the apparent activation energy of the rust hydrogen permeability process. For the rust containing 49.0% silica, this value was equal to 56.8 kcal/mol, and for the melt with 54.20% silica, 74.6 kcal/mol.

Thus, the study of the hydrogen permeability of unstirred rusts showed that the limiting link in the process is the mass transfer of hydrogen in the rust layer, determined mainly by the viscosity of the latter [8] .

The rate of hydrogen transition from the gas phase through the slag to the metal is expressed as the rate of the first-order reaction and is proportional to the square root of the partial pressure of water vapor in the furnace atmosphere:

$$\upsilon_H = K_{OH^-}(OH^-) = K_{OH^-}\sqrt{K_{H_2O}}(O^{2-})P_{H_2O} = K_H\sqrt{P_{H_2O}} \quad (10)$$

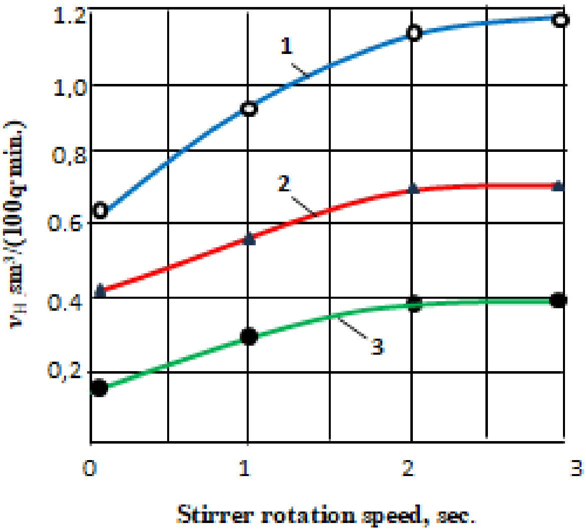

Fig. 5. Effect of mixing intensity on hydrogen permeability of rust with different compositions:

1 - 52,2% SiO_2; 14,6 % CaO; 11,6 % FeO; 16,8 % MnO; 2 – 49,0 % SiO_2; 4,9 % CaO; 22,2 % FeO; 15,6 % MnO; 3 – 59,4 % SiO_2; 4,3 % CaO; 1,1-2,0 % FeO; 19,6 % MnO

A similar phenomenon was observed [9] when stirring slag in an open-hearth furnace at different periods of melting with a steel stirrer. When stirring relatively calm rust at the end of the melting period, the hydrogen content in the metal increased from 3.6 to 4.3 sm^3 /100 g, and stirring at the beginning of pure boiling of mobile rust with a stirrer did not lead to an increase in the hydrogen content in the metal.

When comparing the rust stirring power during the boiling period (υ_C = 0.24 % S/h) in an open-hearth furnace with the maximum power spent on slag stirring in our experiments, it turned out that the stirring power in our case was somewhat lower than the ruts stirring power in an open-hearth furnace at a carbon oxidation rate of 0.24 %/h.

From the above it follows that with intensive rust stirring, the rate of hydrogen mass transfer in it increases so much that it begins to exceed the rate of processes occurring at the interfaces of the rust melt with the gas and metal phases. In other words, the process changes from a diffusion mode to a kinetic mode.

Experiments with stirred slags, conducted by us in crucibles of a special shape [10], showed that the change in the total rate of hydrogen transition from the gas phase through the slag into the metal is proportional to the change in the specific surface area at the rust-metal phase boundary. In this case, the rate of hydrogen transition from the furnace atmosphere through the rust into the metal can be expressed as the rate of a second-order reaction:

$$\upsilon_H = K_{OH^-}(OH^-)^2 = K_{OH^-}K_{H_2O}(O^{2-})P_{H_2O} = K_H P_{H_2O}, \quad (11)$$

i.e., υ_H is proportional to the partial pressure of water vapor in the gas phase.

The latter was confirmed in experiments conducted with stirred slag II (see Table 2) at different P_{H_2O} in the furnace atmosphere. The experiments showed that υ_H in this case changes proportionally to P_{H_2O}

υ_H sm^3 /(100 q·min)……. 1,13 0,72 0,34

P_{H_2O}, mm рт.st……………..150 100 50

With an increase in the MnO/FeO ratio from 0.50 to 1.85, the hydrogen permeability of rusts increases, and a further increase in this ratio is accompanied by a decrease in the value of hydrogen permeability of slags.

With an increase in the content of manganese oxide instead of ferrous oxide, there is an increase in the solubility of hydrogen in rusts, since the strength of the bond of oxygen anions with manganese ($r_{Mn^{2+}}$ = 0,91 Å) is less than with iron ($r_{Fe^{2+}}$ = 0,83 Å), and the reaction $H_2O_r + O^{2-} = 2OH^-_{ru.}$ occurs faster.

A decrease in the hydrogen permeability of rusts with an increase in the MnO/FeO ratio from 1.85 to 2.42 can be explained based on the fact that the transition of hydrogen from rust to metal is accompanied by reactions.

$$2(OH^-) + (Fe^{2+}) = [Fe] + 2[O] + 2[H] \quad (12)$$

$$2(OH^-) + (Mn^{2+}) = [Mn] + 2[O] + 2[H] \quad (13)$$

using the "narrowing" method when processing experimental data on the hydrogen content in the rust and metal, he determined the equilibrium constants of the latter reactions (12) and (13). The values of the changes in the isobaric potential under standard conditions for these reactions are expressed respectively

$$\Delta G = 118000 - 61{,}5T \quad (14)$$

$$\Delta G = 192800 - 91{,}0\,T \quad (15)$$

These equations allow us to conclude that the reactions of hydrogen transfer from rust to metal are sharply endothermic, and the reaction involving iron cations is of greatest importance in the process of hydrogen transfer from rust to metal, because it requires less energy. It is evident from this that at a high value of the MnO/FeO ratio (from 1.85 and above), hydrogen transfer from rust to metal occurs mainly due to manganese cations. This process requires a large energy expenditure, therefore, the hydrogen permeability of rusts, starting from the MnO/FeO ratio of 1.85, decreases. After laboratory studies, the effect of the rust regime on the behavior of hydrogen in the metal of acid open-hearth and electric steelmaking furnaces under industrial conditions was studied. The smelting was carried out using an active and silicon-reducing process. The open-hearth furnaces at both plants (Baku Steel Company) had the same capacity (90 t) with a hearth area of 30.0 and 28.0 m2 and were heated with fuel oil. The electric furnace had a capacity of 5 t.

Silicon reduction smelts were carried out by a duplex process (the main one was acid open-hearth furnaces). The data on these smelts are given in Table 2 (the first six smelts). The last four smelts (see Table 3) were carried out by an active process on a solid charge using 3.5% recycled rust and 0.5% iron ore. The smelts presented were carried out by an active process on a solid charge without the use of recycled rust.

During each smelt, seven metal samples were taken for hydrogen with simultaneous rust samples taken to determine the chemical composition. The metal samples after quenching in water were placed in eudiometric vessels with alcohol, where they were kept for five days. Samples of metal and rust were started to be taken 1 hour before the complete melting of the charge. Figure 6 shows the effect of the duration of the melting period on the hydrogen content in the metal after melting, as well as the effect of the SiO_2 (FeO + MnO) ratio in the rust taken 1 hour before the complete melting of the charge on the increase in the hydrogen content in the metal during the last hour of the melting period. Comparing the effect of these two factors, it can be seen that the hydrogen content in the metal after melting is mainly determined by the chemical composition of the slag, on which the viscosity and hydrogen permeability of the latter depend.

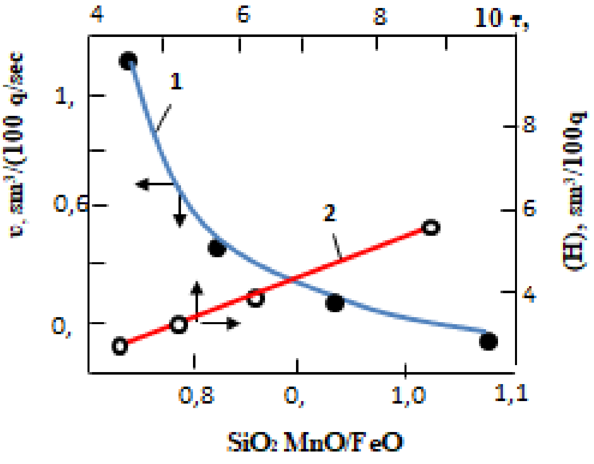

Fig. 6. The effect of the SiO_2 (FeO + MnO) ratio in the rust collected 1 hour before melting on the increase in the hydrogen content in the metal during the last hour of the melting period (1) and the effect of the duration of the melting period on the hydrogen content in the metal (2)

Table 2. Hydrogen behavior in metal during melting carried out by silicon-reducing and active processes using recycled rust.

Melt number	**Sample number**	**[C], %**	**[Mн], %**	**Rust composition, %**						**(H), sm^3/100q**	**υ, sm^3/ (100 q/sec.)**
				SiO_2	Al_2O_3	FeO	CaO	MgO	MnO		
1	1	0,94	0,14	56,30	5,34	15,67	3,56	0,17	16,77	2,60	0,18
	2	0,46	0,25	57,54	4,54	12,48	3,73	0,14	19,47	2,48	
	3	0,33	0,25	58,80	4,32	10,94	4,14	0,15	19,42	2,70	
	4	0,36	0,35	60,56	4,08	9,86	3,77	0,16	19,44	3,90	
2	1	1,04	0,12	50,93	5,50	21,18	4,41	0,12	13,67	4,63	0,14
	2	0,44	0,31	57,37	3,92	12,48	4,36	0,13	18,91	4,18	
	3	0,36	0,27	61,34	3,44	10,15	3,40	0,13	18,91	3,09	
	4	0,36	0,45	61,46	3,04	9,72	4,02	0,14	17,84	4,54	
3	1	0,90	0,28	55,96	4,13	13,78	7,36	0,12	15,75	3,91	0.19
	2	0,36	0,30	59,41	3,10	10,59	4,64	0,13	18,62	3,26	
	3	0,25	0,27	61,74	3,32	10,61	4,13	0,13	15,24	2,84	
	4	0,27	0,27	60,80	3,76	10,01	4,30	0,14	18,46	4,40	
4	1	0,96	0,07	50,82	4,32	19,81	5,02	0,13	17,84	5,02	0,11
	2	0,45	0,16	57,52	4,40	13,54	5,18	0,15	17,91	2,90	
	3	0,35	0,23	60,02	4,30	12,33	4,70	0,13	17,52	2,70	
	4	0,38	0,50	59,92	4,24	12,19	4,58	0,14	18,11	4,30	
5	1	1,01	0,10	54,20	5,82	16,68	7,41	0,15	13,37	3,50	0,15
	2	0,47	0,29	56.08	4,18	13,06	5,83	0,14	19,03	2,81	
	3	0,32	0,20	58,32	4,46	10,83	5,65	0,14	19,61	2,80	
	4	0,33	0,31	58,48	4,48	10,60	5,77	0,13	19,59	4,06	

Samples were taken: 1 - after melting; 2 - at the end of ore boiling; 3 - at the end of clean boiling; 4 - before tapping.

In an acid electric furnace, due to the lower content of water vapor in the gas phase, the concentration of hydrogen in the metal is significantly lower than in open-hearth steel. But even under these conditions, the rust is not a complete insulator of the metal from the hydrogen-containing atmosphere. Based on our data on the study of the behavior of hydrogen in the metal bath during 60 melts in an acid electric furnace, 14 of which are described in detail, the following pattern was revealed for the melting period.

Conclusions and Discussions

1. The reduction in the causticity of the pulp is reduced by properly regulating the amount of basic and acidic oxides in its composition

2. As a result of our research, it was determined that the pulp has a low pickling effect when its content is SiO_2 /CaO<1.2

3. The results of the analyses also allow us to say that this ratio directly depends on the amount of impurities in the pulp

4. The transfer of hydrogen from the furnace atmosphere to the metal through the pulp was also studied as a result of the research

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THE ANTIFUNGAL PROPERTIES OF 1,2,3-TRİAZOLES

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ABSTRACT

Fungicides are very important for agriculture, animal husbandry and medicine, as the various infections induced by certain fungi cause harm to plants and animals which are used as a source of food, as well as directly to humans themselves. More than 1,5 million deaths are caused by fungi each year, both the incidence of fungal infections and the resistance against already existing antifungal drugs are on the rise, which renders the search for inexpensive and new effective fungicides very urgent. On the other hand, some compounds containing 1,2,3-triazole moieties (for example, Radezolid and Cefatrizine) display strong antifungal activity and are used as fungicides. Azoles prevent lanosterol 14-alpha-demethylase enzyme from converting to ergosterol, and therefore inhibit growth of fungi. Today many scientists all across the world synthesize new compounds containing 1,2,3-triazole moieties and research their antifungal properties by applying them against various pathogenic fungal strains. This article is a review of recent scientific literature describing antifungal activity of compounds containing 1,2,3-triazole moieties.

1. Introduction

Antifungal drugs are utilized widely in agriculture, animal husbandry, medicine, because the infections caused by fungi are harmful to plants and animals important for agriculture and even directly to humans themselves. [1] Fungi-induced infections cause deaths of 1,5 million people per year. Moreover, both the the incidence of fungal infections and the resistance against already existing antifungal drugs are on the rise, therefore new efficient antifungals are needed. [2]

Generally speaking, the antifungal properties of azole derivatives were first discovered in 1944, and nowadays there are several antifungal drugs based on 1,2,3-triazoles, for example Cefatrizine, Tazobactam, Carboxyamidotriazole, Radezolid, Tertbutyldimethylsilylspiroaminooxathioledioxide. The antifungal properties of azoles are explained by the fact that these compounds prevent lanosterol 14-alpha-demethylase enzyme from converting to ergosterol, which is used to create cell walls. [3]

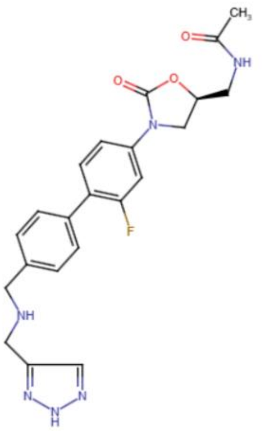


Figure 1. The structure of the radezolid compound.

This article is a review of scientific articles concerning antifungal properties of 1,2,3-triazoles.

2. Result and discussion

Konda and their team [4] synthesized a series of new benzoxazine-6-sulfonamides with excellent yields. Most compounds have shown promising activity against *Candida albicans*. Some compounds have demonstrated activity similar to the reference drug fluconazole. For fluconazole, minimum inhibition concentration (MIC) is equal to 32 μg/mL, the values for these compounds are as follows: 1 (MIC=62,5 μg/mL), 2 (MIC=31,25 μg/mL), 3 (MIC=31,25 μg/mL), 4 (MIC=62,5 μg/mL), 5 (MIC=62,5 μg/mL) and 6 (MIC=31,25 μg/mL).

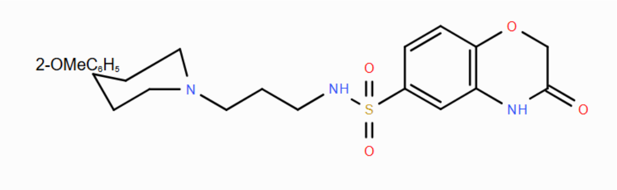


Figure 2. Compound №1.

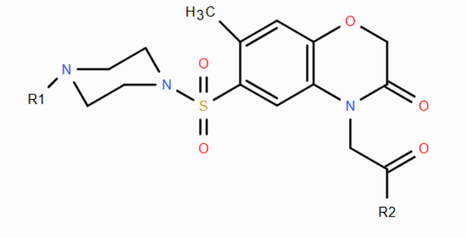
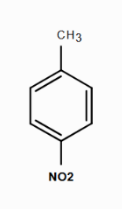


Figure 3. The general scheme of compounds № 2-6. For compounds №2 and 3 R1=4-(trifluoromethyl)phenyl; for compounds № 4-6 R1=2-methoxyphenyl. R2 substituents are: for 2



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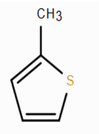

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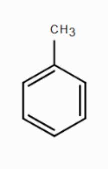

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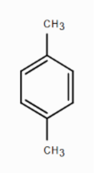

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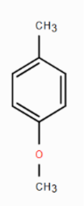


García-Monroy and their colleagues [5] obtained several benzylic 1,2,3-triazole-4-carboxamides via a one-pot procedure and tested their activity *in vitro* against eight fungal strains (*Aspergillus fumigatus, Trichosporon cutaneum, Rhizopus oryzae, Mucor hiemalis, Candida krusei, Candida albicans, Candida utilis* and *Candida glabrata*). The best results were shown by compounds № 7, 8 and 9 against *R. Oryzae* fungi (MIC values, respectively, 0,017 µmol/mL, 0,017 µmol/mL and 0,07 µmol/mL). Itraconazol was used as a reference drug, its MIC against *R. Oryzae* is 0,14 µmol/L. This means that these compounds are stronger fungicides against *R. Oryzae* than itraconazole.

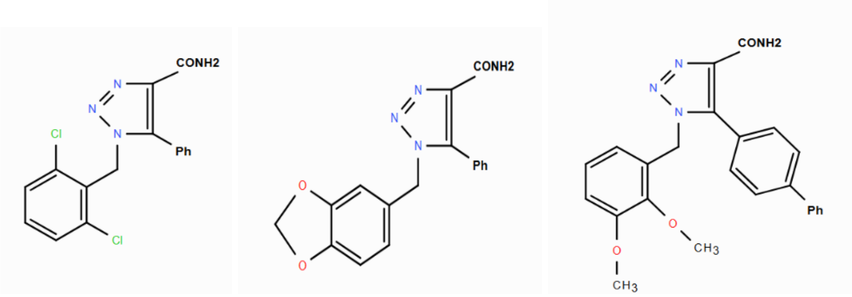


Figure 4. Compounds № 7, 8, 9.

Two other compounds (10 and 11) showed MIC = 0,14 µmol/L against this same fungal strain, which means their antifungal activity is equal to that of itraconazole. The authors expressed a hypothesis that stronger fungicides can be obtained in the future by modifying the compounds №7 and 8.

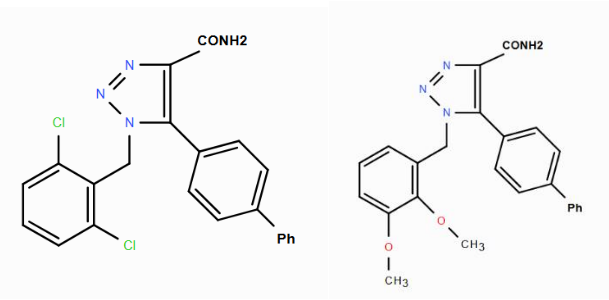


Figure 5. Compounds №10 and 11.

Guiqing Xu and their team [6] synthesized 1,4-disubstituted 1,2,3-triazoles containing indole ring via $CuCl_2$/Zn catalyzed Huisgen cycloaddition and tested their antifungal activities against *Colletotrichum Capsici* and *Cotton Physalospora*. The research has demonstrated that these compounds, especially 12 and 13, show significant inhibitory activity.

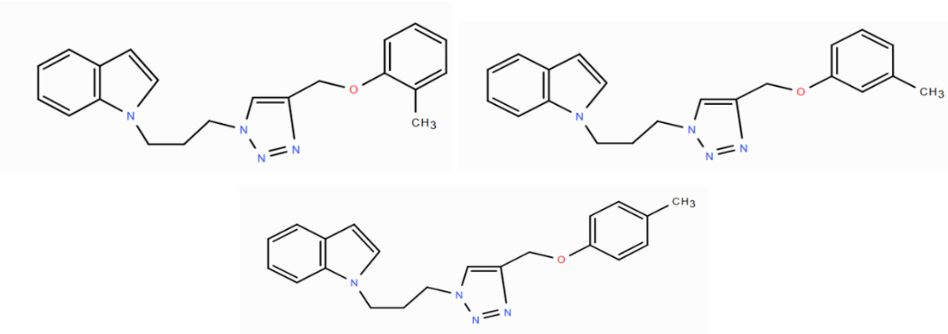


Figure 6. Compounds №12, 13, 14.

Flutriafol was used for a comparison. The best inhibitors of *Colletotrichum Capsici* were 12 (inhibition rate 100%) and 13 (inhibition rate 87,4%), the best inhibitors of *Cotton Physalospora* were 14 (inhibition rate 71,4%) and 13 (inhibition rate 56,2%).

Pertino and their team [7] synthesized twenty four new triazole derivatives starting from carnosic acid and carnosol and tested their antifungal properties against *Candida albicans ATCC 10231* and *Cryptococcus neoformans ATCC 32264* fungi, and used amphotericin B for comparison. All of these compounds fully inhibited the growth of pathogenic fungi with minimum inhibition concentrations (MIC_{100}) >250 $\mu g \cdot mL^{-1}$. The strongest fungicide against *C. Albicans* was compound №15 at concentration 250 $\mu g \cdot mL^{-1}$ (inhibition percentage 57,9 ± 1.0%), but against *Cryptococcus neoformans* the strongest fungicide was the compound №16 at concentration 250 $\mu g \cdot mL^{-1}$ (inhibition percentage 91,3 ± 3.0%).

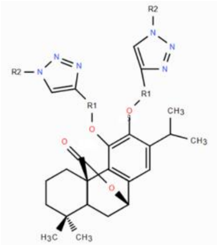
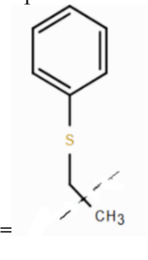
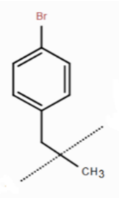


Figure 7. The general scheme of compounds №15 and 16. For both compounds R1 = $CO(CH_2)_3$, but for the compound

№15 R2= 

and for compound №16 R2 = 

It bears mentioning that six compounds at concentrations lower than 250 $\mu g \cdot mL^{-1}$ inhibited 50% growth of *C. Albicans*.

Mallikanti and their colleagues [8] synthesized new benzimidazole-based 1,2,3-triazoles via Suzuki coupling, cyclization and microwave-supported Cu-catalyzed chemical reaction. The impact of all the compounds on *Candida albicans* and *Aspergillus niger* fungi has been tested. Three compounds (with R substituent being 3-fluorobenzyl; 4-fluorobenzyl; R=3-cyanobenzyl) have proven themselves to be strong antifungals.

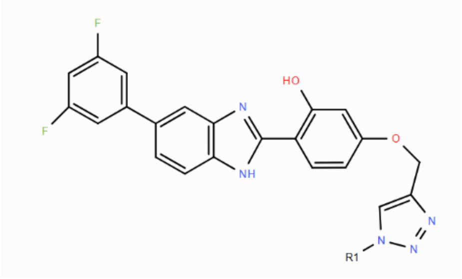


Figure 8. The general scheme of the compounds described in Mallikanti's article.

Dhawan and their colleagues [9] synthesized coumarine-tethered 1,2,3-triazoles via the 1,3-dipolar cycloaddition reaction of coumarine with various substituted azides and tested their antifungal properties. The triazoles at the concentration of 32 µg/mL were applied against two fungal strains (*Candida albicans* and *Cryptococci neoformans*), and fluconazole's percentage inhibition was also mentioned (0,41 against *Candida albicans*; 26,1 against *Cryptococcus neoformans*). Neither of the synthesized triazoles was active against *Cryptococci neoformans*, but some activity was observed against *Candida albicans*, and the structures of the three most active compounds (17 (percentage inhibition 10,43%), 18 (percentage inhibition 6,08%) and 19 (percentage inhibition 6,04%)) are presented below (figures 9,10,11).

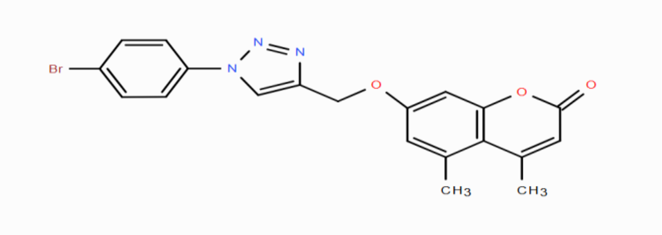


Figure 9. Compound №17

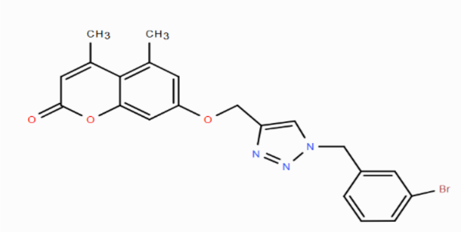


Figure 10. Compound №18.

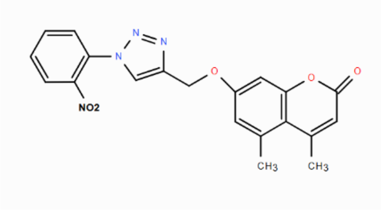


Figure 11. Compound №19.

Akolkar and their team [10] synthesized 1,4-disubstituted-1,2,3-triazoles via ultrasonic radiation and applied them against various fungal strains (*Candida albicans*, *Fusarium oxysporum*, *Aspergillus flavus*, *Aspergillus niger*, and *Cryptococcus neoformans*) in order to test their antifungal activity. Miconazole was used as a reference drug. Two compounds were inactive against all fungal strains, but some others have proven themselves to be very good antifungals. The compounds №20, 21, 22 had MIC = 12 µg mL^{-1} against *Candida Albicans*, while compounds №23, 24, 25 have shown MIC = 25 µg mL^{-1} (for comparison: the reference drug miconazole's MIC against the same fungal strain is 25 µg mL^{-1}). The strongest antifungal against another fungal strain (*Fusarium oxysporum*) was compound № 22, which was even stronger than miconazole (MIC=12,5 µg mL^{-1} and MIC=25 µg mL^{-1} respectively), and five other compounds (20, 21, 24, 26, and 25) have demonstrated activity equal to that of miconazole. The most active compounds against *Aspergillus flavus* were 26 and 25 (both have shown MIC=12,5 µg mL^{-1}, which is equal to that of miconazole). The best result against *Aspergillus niger* was shown by compound №22 (MIC=12,5 µg mL^{-1}), which is better than that of miconazole (MIC=25 µg mL^{-1}), and four compounds (20, 24, 26 and 25) were as active as miconazole. Finally, compounds №22, 25, 26 have demonstrated

MIC=12,5 μg mL^{-1} against *Cryptococcus neoformans*, which is better that the results of miconazole (MIC=25 μg mL^{-1}), and 21 was equal in activity to miconazole.

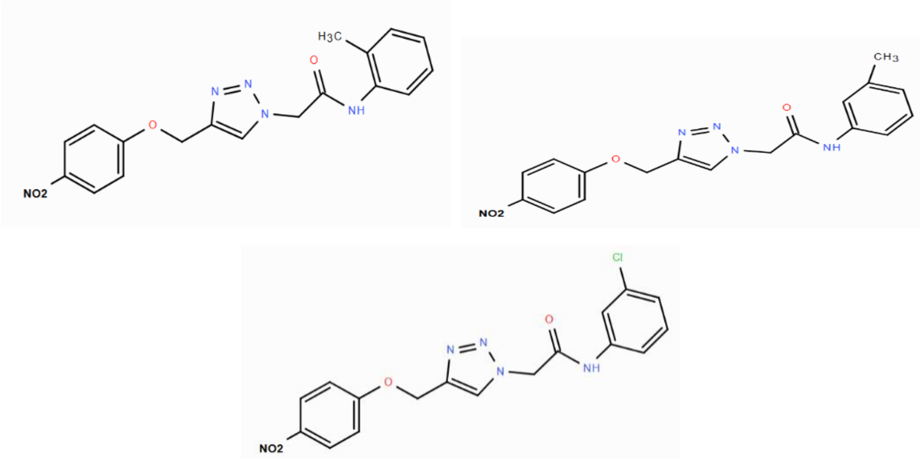


Figure 12. Compounds №20, 21, 22.

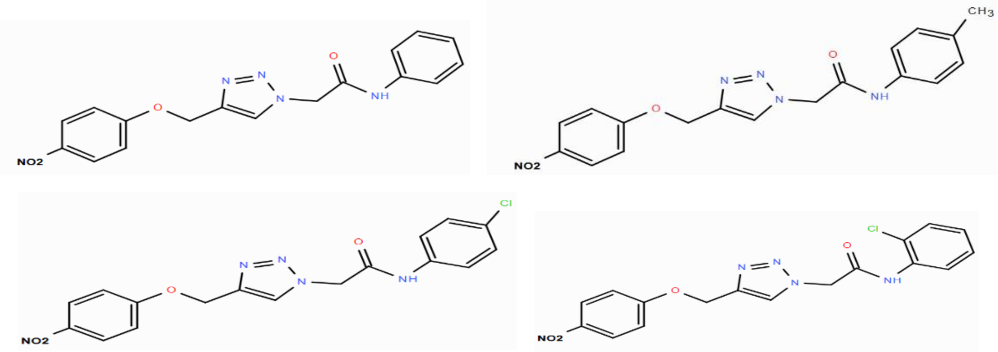


Figure 13. Compounds №23, 24, 25, 26.

P.A.R. Gazolla and their colleagues [11] synthesized twenty two vaniline derivatives with 1,2,3-triazole fragment via click reaction copper-catalyzed alkyne-azide cycloaddition with good yields and tested their antifungal activity against *Candida albicans*, *Candida glabrata*, *Candida parapsilosis*, *Candida tropicalis*, *Cryptococcus neoformans*, *Cryptococcus gattii*, *Trichophyton rubrum*, and *Trichophyton interdigitale* fungi. The minimum inhibition concentrations of these compounds varied between 32 μg mL^{-1} and 512 μg mL^{-1}. With the exception of 3-methoxy-4-((1-(4-nitrobenzyl)-1H-1,2,3-triazole-4-yl)methoxy)benzaldehyde against *C. gattii* R265, all vaniline derivatives have shown themselves to be fungicides. Molecular docking calculations have demonstrated that all compounds bind to the active site of lanosterol 14α-demethylase enzyme (binding energies being in the range between –9,1 and –12,2 kcal/mol). Based on the analysis and the calculations, researchers claim that the synthesized compounds have a potential of becoming drugs in the future.

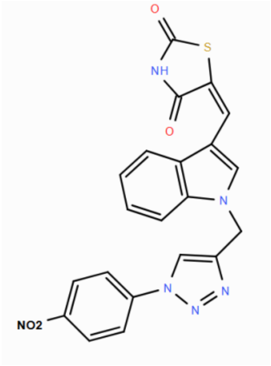


Figure 14. According to Gazolla's article [11], this compound shows minimum inhibition concentration 56 µM against *Ca. Albicans*.

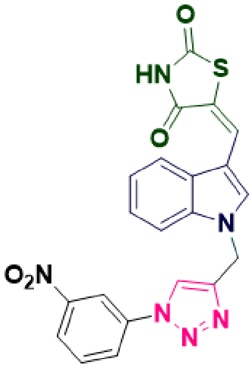


Figure 15. According to Gazolla's article [11], this compound shows MIC=56 µM against *As.niger*.

L. S. de Magalhães and their colleagues [12] synthesized eighteen new glucosyl-1,2,3-triazoles and tested their anti-*Candida* properties. Nine compounds have shown anti-*Candida* potential, and among them the strongest fungicides were 27 (2-[1-(2,3,4,6-tetra-O-acetyl-β-D-glikopyranosyl)-1,2,3-triazole-4-(methyl)oxy]-4-allyl-2-methoxy-benzene) and 28 (2-[1-(2,3,4,6-tetra-O-acetyl-β-D-glycopyranosyl)-1,2,3-triazole-4-(methyl)oxy]-2-methoxy-4-propyl-benzene). The compound № 27, which is the derivative of eugenol, has shown remarkable activity against the three *Candida* strains (26,1–52,1 µM) and was specifically very active against *Candida krusei* (four times stronger than fluconasole). The compound №28, which is dihydroeugenol derivative, has shown activity similar to the compound № 27, and it was four times stronger and less toxic against *C. Krusei* than fluconasole. Respective deacetylated glucosydes and non-glucosylated derivatives didn't demonstrate significant activity, which proves the critical role that acetyl groups play in the anti-*Candida* properties. Molecular docking and molecular dynamics studies, 14α-lanosterol enzyme is a valid molecular target for the compounds №27 and 28, because they can be deacetylated and bind to this enzyme. Furthermore, the article emphasizes the importance of hydrophobic substituents in the phenyl ring.

V.K.R. Tangadanchu and their colleagues [13] synthesized isomannide monoundecenoate-based 1,2,3-triazoles via click chemistry method with good yields and tested their activity against *Candida* fungi. Phenyl-substituted №29 and hydroxyphenyl-substituted №30 compounds have shown excellent antifungal properties (MIC=3,9 µg/mL).

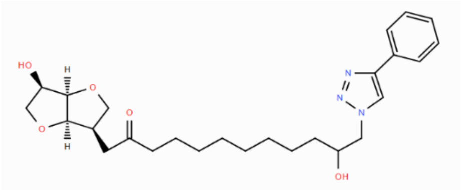


Figure 16. Compound №29

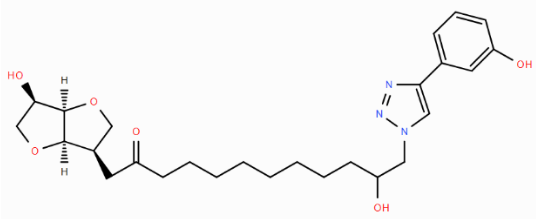


Figure 17. Compound №30

Danne and their team [14] synthesized new 1,2,3-triazole-appended bis-pyrazoles via molecular hybridization and tested their activity against *Candida albicans*, *Cryptococcus neoformans*, *Candida glabrata*, *Candida tropicalis*, *Aspergillus niger*, and *Aspergillus fumigatus* fungi. The best antifungal properties were demonstrated by compound № 31 against *Candida glabrata* (minimum inhibition concentration was 2 μg/mL). Except from the aforementioned compound, the highest antifungal properties were shown against *Candida albicans1* by compounds №32, 33, 34, 35 (MIC=4 μg/mL). Compounds №31 and 36 have shown MIC=8 μg/mL, which is also a good value. Besides these, the MIC=8 μg/mL was demonstrated by compounds № 33 and 36 *C. albicans2*, compound №33 against *C. Neoformans*, compound №34 against *C. Glabrata*. Authors conducted molecular docking study and concluded that the molecules can behave like inhibitors of sterol 14α-demethylase. The authors also expressed their conviction that these compounds can be used as antifungal agents in medical research.

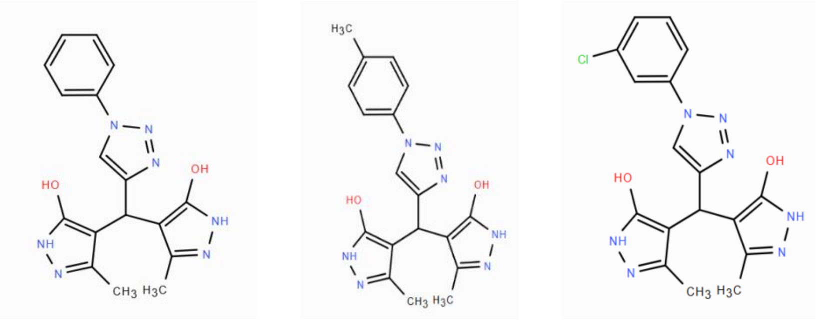


Figure 18. Compounds № 31, 32, 33.

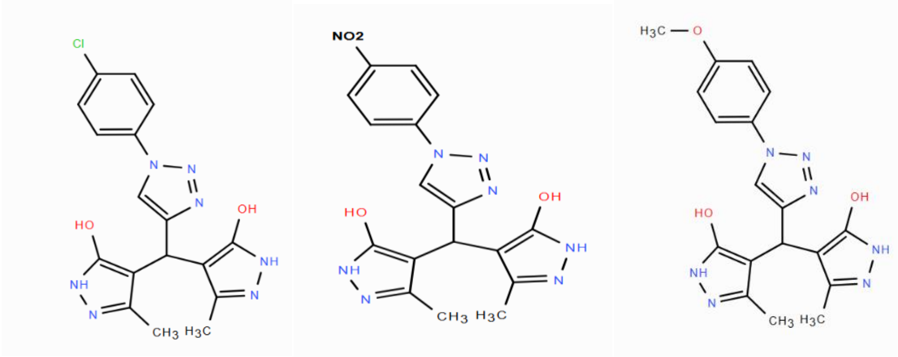


Figure 19. Compounds №34, 35, 36.

Considering all this, 4-azido-2,5-diphenyl-2H-1,2,3-triazole derivatives have been synthesized [15-16]. The presence of a triazole group would lead to antifungal activity in the compounds.

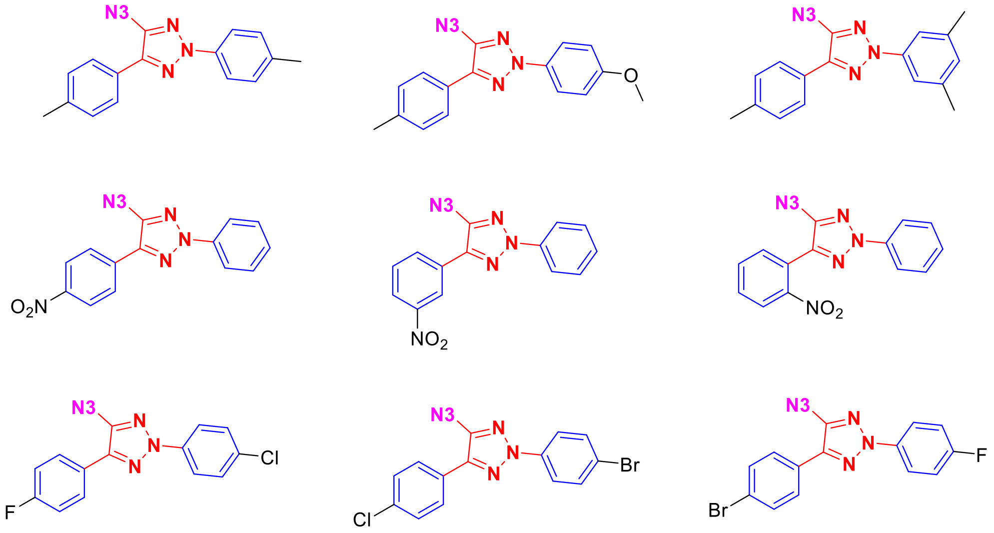


Figure 20. 4-azido-2,5-diphenyl-2H-1,2,3-triazole derivatives

3. Conclusion

In this article, we presented a review of several scientific articles about antifungal properties of compounds containing 1,2,3-triazoles. The MIC values and/or percentage inhibitions for most active antifungals were provided. This review will aid specialists in organic chemistry and mycology who are working on developing new fungicides containing 1,2,3-triazoles.

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SYNTHESIS AND ANTIMICROBIAL PROPERTIES OF Zn, Co and Cu COMPLEXES

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ABSTRACT

We have been synthesized hydrogenated Schiff base ligand with Co(II), Cu (II) and Zn(II) complexes. Ligand was synthesized hydrogenation of salicylidene-aniline. Ligand and three metal complexes structure have been proved by spectral analyses. The antimicrobial properties of synthesized compounds have been investigated. Synthesized compounds have shown high antifungal and antibacterial properties. Comparing Schiff bases metal complexes with hydrogenated Schiff base complex compounds hydrogenated complex compounds has shown higher antimicrobial properties, because when azomethines group double bond break down and hydrogen atom enter the structure of ligand it changes complex formation ability of ligand and also influence antimicrobial properties. Other positive side of of our ligand and complex compounds, they have shown antimicrobial properties even 0,25% concentration and they are durable 6 month.

1. Introduction

Microelements are metals which plays important role of life process.In living systems they generally include the structure of enzymes, catalyst different chemical reactions.Zinc is microelement which includes all enzymes structure and plays lifely role in human body [1-5]. Zinc also controls action of immune systems and cell metabolism

Copper after iron and zinc form importance stands in the third stage and protect cell membrane damages [8]. Cobalt includes the structure of B_{12} vitamin and several enzymes. All three microelements in our body form different complex compounds, because they have free d orbital [9].

Schiff Bases are condensation of primary amines with carbonyl compounds and they were first reported by Schiff in 1864 [10-12]. Because of the relative easiness of preparation, synthetic flexibility, and the special property of C=N group [16]. Schiff bases are generally excellent chelating agents, especially when a functional group like –OH or –SH is present close to the azomethine group so as to form a five or six membered ring with the metal ions verstality of Schiff base ligands and biological, analytical and industrial applications of their complexes make further investigations in this area highly desirable [17-22]. Nowadays, the research field dealing with Schiff base coordination chemistry has expanded enormously. The importance of Schiff base complexes for bioinorganic chemistry, catalysis and material science, separation and encapsulation processes, and formation of compounds with unusual properties and structures has been recognized and reviewed [23-28].

Schiff Bases are compounds which form many metal complexes [29]. These compounds have shown large application. Antimicrobial, anticancer, antiallergic antinflammatory properties of compounds give to scientists continue their research in this field [30-34].

After synthesis and successful antitumor investigation of iron (III) N, N^1 bis-(salicyclidene)-1,2(phenylidenediamine (SAP) scientist decided to continue next triad elements Co(II) and Ni(II) SAP complexes. Nowadays many Schiff bases derivatives have been synthesizing. In this work we are going to show synthesis and hydrogenation of Schiff bases ligand and synthesis of metal complexes [35].

2. Experimental part

Synthesis of Schiff base ligand

The ligand was synthesized by the condensation of o-salicyclic aldehyde and aniline in 1:1 molar ratio using absolute alcohol as the reaction medium. The mixture was refluxed on water bath for 1 and a half an hour and then allowed to stand overnight at room temperature. The product was crystallized from the same solvent.

IR spectra (◎, sm-1): 1678 (C=N), 1610 (C=C), 1470, 1180 (C-N (CH3)2. NMR spectra (◎, ppm): 8.146 (C=N), 3.641-3.028 (CH3)2N, 2.050 (4H), 1.205-1.131 (CH2).

The IR spectra of the complexes C=N zone is observed at 1650 sm-1. In comparison with its position in the spectrum of the ligand (1678 sm-1) it is shifted to low-frequency zone. Such a change proves presence of coordination of metal with N atom C=N bond (635-620 sm-1, M=N). On the base of above-mentioned we can conclude that complexes should have such a structure: M(L)2X2, where X-anion. The following is the NMR spectrum.

Synthesis of hydrogenated Schiff Base

Schiff base ligand were added in sodium-borhydride in water solution molar ratio 1:4, solution were filtered out. White crystals separated from solution.

Synthesis of metal complexes

They were prepared by reacting ethanolic solution of metal acetate (Co,Cu, and Zn) in 1:2 molar ratio. The settled down solid coloured complexes were filtered, washed with ethanol, dried in oven.

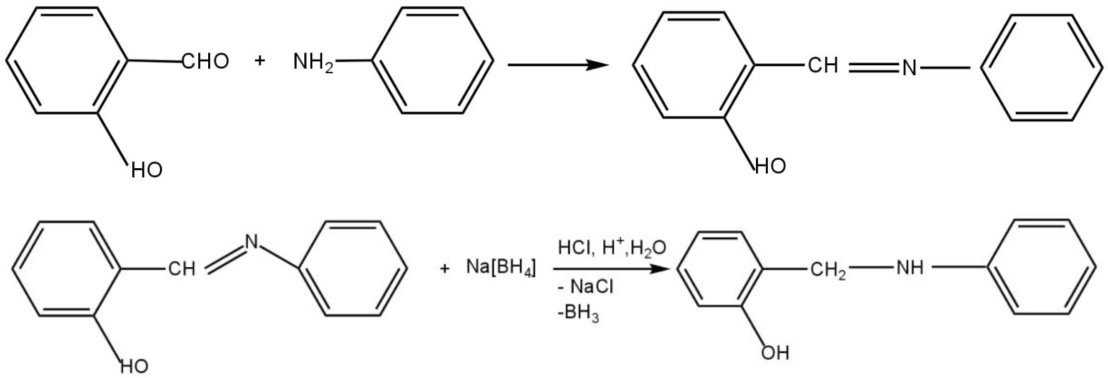
Antimicrobial properties

In literature, it is maintained that ligands and their metal complexes are considerably active against Baccilus megaterium and Candide tropicals, but that the effect of metal complexes is stronger than that of lgands.It was also reported that ligands and their metal complexes are active against Fuherica Coli, Barilum sp and Pseudomanan acurtuginan, while that Cu are more effective.Morever, Cu complexes of ligands were reported to be inhibiting active agents against bacteria and fungus.It was also determined that ligands could produce an inhibiting effect on the development of Aspergillus niger, Penisilum rubium and Augergillus ferreus.Furthermore, it was also established that ligands had an actibacterial effect at 100ppm concentration and they had and antifungisid effect [6].

Antimcrobial activity of the compounds of tested against using Pseudomonas Aeruginosa, Mycobacterium lacticolium, Aspergillus niger, Cladasporium resinale, Penicillium Chrosegenum, Chastomium gloloodium Trichoderma viride. The sterilized (autoclaved 121^0 C for 15 min) medium (40-50^0) was poured into the Petri dishes to give a depth of 3-4 mm and allowed to solidfy. The suspension of the microorganism the steaked on plates.The paper discs impregnated with the test compounds was placed on the solidified medium.The plates were pre-incubated forth at room temperature and incubated at 37^0 C for 24 hour[7].

3. Result and discussion.

We have described the synthesis and antimicrobial properties of Co, Cu and Zn. The structure of ligands and metal complexes were proved IR spectra. First ligand were synthesized by de condensation salicylic aldehyde and aniline. Second ligand were synthesized saliclidene-aniline with sodiumborhydride reaction.



2L+M=L$_2$M M-Cu(II), Co(II), Zn(II)

The synthesized compounds structure were proved by IR spectra fig.1,2 In the first spectra we can easily observe azomethine fragment in first spectra 1678 sm^{-1}, but when Schiff base hydrogenated the bond between -CH=N- break down and new fragment CH$_2$-NH formed in 3448 sm^{-1}

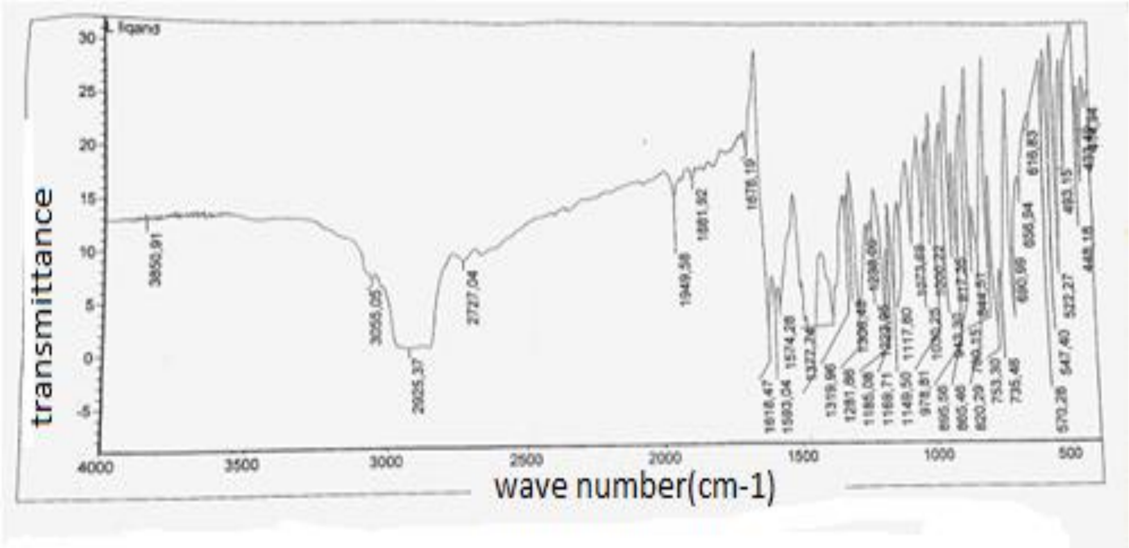


Fig 1. L ligand IR spectra

Fig 2. L$_1$ligand IR spectra

We have also been synthesized three metal complex of hydrogenated Schiff base. We can also describe structure of three complex, here observable all spectra of complexes fig 3,4..

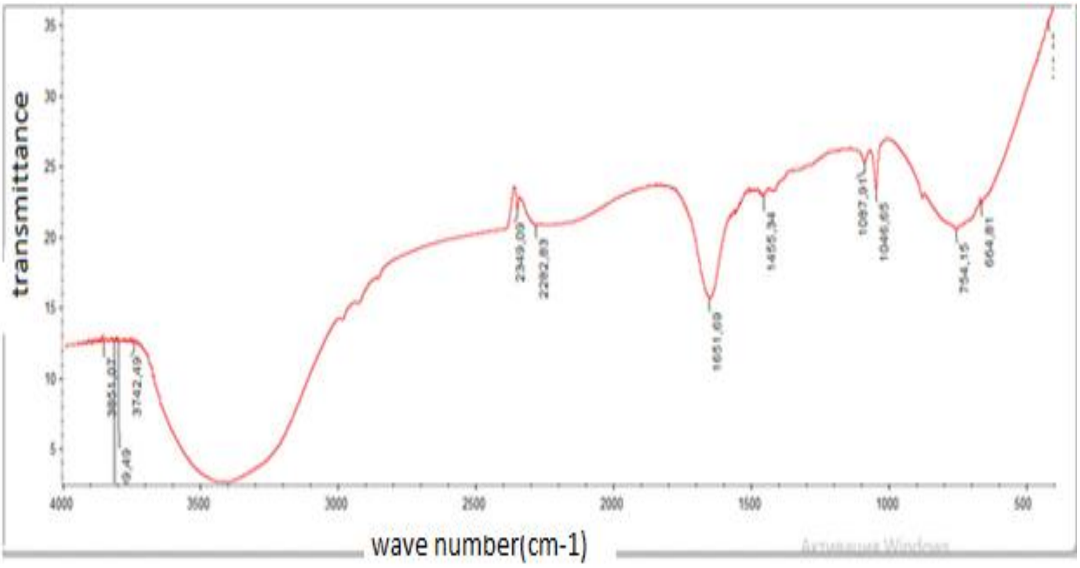


Fig 3. Co complex IR spectra

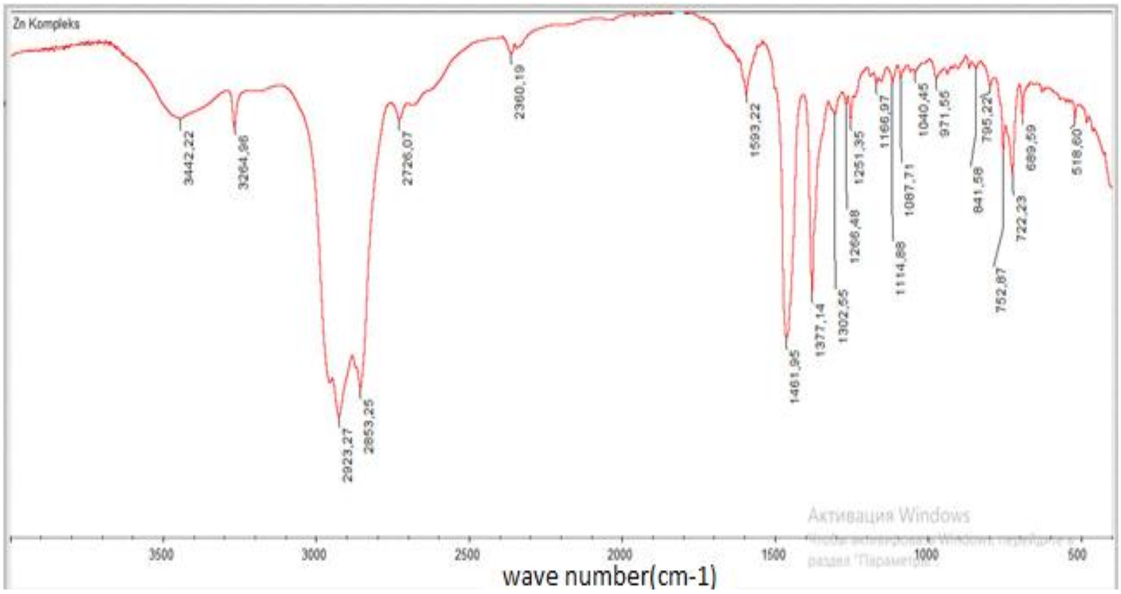


Fig 4. Zn complex IR spectra

If we compare IR Specta of ligands and complexes. By the formation of hydrogenated ligand the azomethine group break down.-CH_2-NH- group appeared higher than 3000 sm^{-1}. In metal complexes appeared 4-5 sm^{-1} differences comparing with ligand.

We firstly have checked by the express method antimicrobial properties of synthesized ligands. When we observed the antimicrobial feature, we checked the antimicrobial properties of the ligand and metal complexes table 1.

From the table, we observed high antimicrobial properties. When we hydrogenated the ligand, we evaluated the antimicrobial properties.

Table 1. Antimicrobial propertiesof synthesized compounds

№	Ligand and complexes	Concentration%	Bactericidial	Fungicidial
1	Ligand	1,0	2,8-2,8	2,80-2,8
		0,5	2,4-2,4	2,4-2,4
		0,25	2,3-2,3	2,3-2,3
2	hydrogenated ligand	1,0	2,9-2,9	2,9-2,9
		0,5	2,5-2,5	2,5-2,6
		0,25	2,4-2,3	2,4-2,4
3	Complex of Co	1,0	3,0-3,0	3,3-3,3
		0,5	2,6-2,6	2,8-2,8
		0,25	2,4-2,4	2,6-2,6
4	Complex of Cu	1,0	3,0-3,0	3,0-3,0
		0,5	2,5-2,6	2,5-2,5
		0,25	2,4-2,4	2,2-2,2
5	Complex of Zn	1,0	3,3-3,4	3.3-3.3
		0,5	2.8-2.8	2,8-2,8
		0,25	2.7-2.7	2,7-2,7

If we give attention of above table we have witness high antibacterial and antifungal properties of metal complexes. Comparing with ligands metal complexes have shown high killing effect of microbe. Zinc complexes has shown highest both bacterial and fungi, Co has shown moderate bacteria and highest fungi, copper has shown moderate antimicrobial properties both anti fungi and anti bacterial properties.

Comparing Schiff bases metal complexes with hydrogenated Schiff base complex compounds hydrogenated complex compounds has shown higher antimicrobial properties, because when azomethine group double bond break down and hydrogen atom enter the structure of ligand it changes complex formation ability of ligand and also influence antimicrobial properties. Other positive side of of our ligand and complex compounds, they have shown antimicrobial properties even 0,25% concentration and they are durable 6 month.

4. Conclusion

We have been synthesized hydrogenated Schiff bases metal complexes. We have investigated antimicrobial properties of ligand and Co, Cu, Zn complexes. Comparing with ligand complexes have shown high antimicrobial properties.Zn complex has shown highest antimicrobial properties. Co has shown moderate bacteria and highest fungi, copper has shown moderate antimicrobial properties both anti fungi and anti bacterial properties.

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SYNTHESIS OF MONO AND BİS A-KETOACIDIC ESTERS AND STUDY OF THEIR ANTIMICROBIAL PROPERTIES

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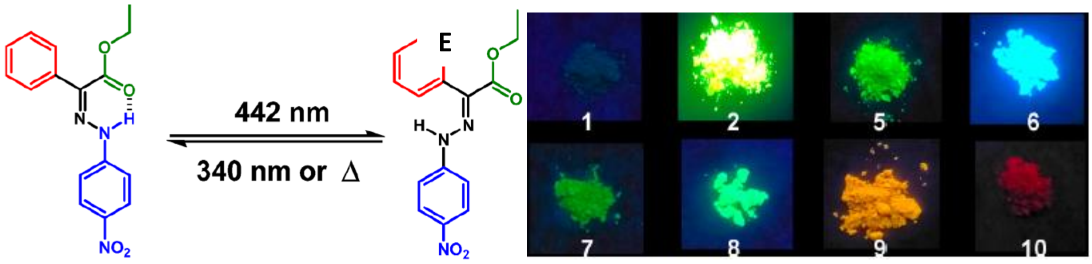
ABSTRACT

Recently, our scientific group has been studying in detail the synthesis and structural properties of dichlorodiazadienes obtained from the interaction of N-substituted hydrazones of benzoyl and terephthalaldehyde with polyhalogen methanes in the presence of a CuCl catalyst. This class of compounds, in addition to their application as azo dyes, can be used as important synthons in the synthesis of other organic compounds. Various research works have been carried out in this area. Mainly, their reactions with nucleophiles have been widely studied. Taking all this into account, we have studied the solvolysis reactions of mono and bis dichlorodiazadienes and synthesized the corresponding compounds.Four novel compounds were synthesized and their antimicrobial activities were evaluated using agar well diffusion method. The results revealed that fungal strains were more sensitive to all compounds compared to bacteria. Pseudomonas aeruginosa was the most sensitive gram-negative bacterium to compound III (Methyl (Z)-2-(2-(4-chlorophenyl) hydrazineylidene)-2-phenylacetate) with 20.0 mm as the diameter of inhibition zone. Escherichia coli and Bacillus mesentericus were highly resistant to compounds I. Candida albicans was the most susceptible fungal strain to compound IV ((E)-1-(4-chlorophenyl)-2-(2,2-dichloro-1-phenylvinyl) diazene) with an inhibition zone of 24.0 mm.

4. Introduction

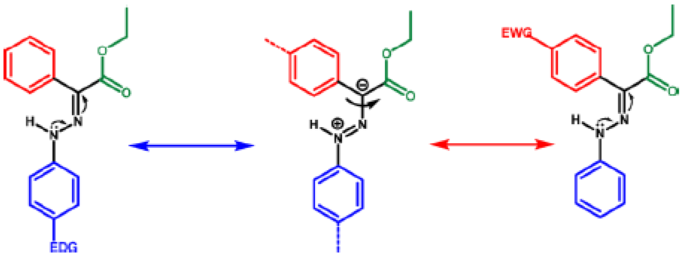
Dichlorodiazadienes have a strong electrophilic centre, which facilitates interactions with various nucleophiles.[1] The reactions of dichlorodiazadienes with several nucleophiles have been reported in scientific literature [2]. Our team synthesized arylhydrazo derivatives of α-keto acidic esters via solvolysis of mono- and bis- dichlorodiazadienes with methyl alcohol. The areas of application of arylhydrazo derivatives of α-keto acidic esters are becoming wider and wider[3]. There's a lot of material pertaining to the application of these compounds [1]. The fact that arylhydrazo derivatives of α-keto acidic esters display absorption and emission properties and also the fact that these properties vary when Z and E isomers interconvert, are now in the centre of attention of organic synthesists [4]. Interconversion of Z and E isomers in the band where they look differently shows itself in the changing of their absorption properties.



A b

Scheme 1. (a) Interconversion and (b) emission under 365 nm UV rays of Z and E isomers at various wavelengthes.

Because of this, the interconversion of Z and E isomers is called "ON/OFF hydrazon transition" in scientific literature [5]. These interconversions are utilized in the regeneration of amines with deformed structure. Furthermore, these esters are active photochromic conductors [6-8]. A brief look at Scheme 2 shows that introduction of electrondonor and electronacceptor functional groups facilitates the interconversion of Z and E isomers.



Scheme 2. The impact of electrondonor and electronacceptor groups on the interconversion of Z and E hydrazones

There is an extensive amount of data in regards to the high antimicrobial activity of these compounds. Hydrazone derivatives are part of many bioactive molecules and display biological activity, such as antibacterial, antitubercular, antifungal, anticancer, anti-inflammatory, anticonvulsant, antiviral and antiprotozoal effects. The antimicrobial activity of the compounds that belong to this class is the most widely reported in the scientific literature [10], because many derivatives of this class are highly active even against persistent strains, which is especially important in modern times when many bacteria are resistant to frequently used drugs. Shirinzadeh et al. synthesized a series of new hydrazid-hydrazones of lactic acid and tested their antibacterial activity against four bacterial strains (S. aureus, S. pneumoniae, E. coli and P. aeruginosa) using broth microdilution method. The compounds 1 and 2 are display higher antibacterial activity (Minimal Inhibitory Concentration MIC = 64-128 μg/mL), but lower than the reference drug gentamicine (Figure 1). The high antibacterial activity of compound 1 is probably due to the presence of electronegative substituent NO2. The authors concluded that compounds with electronwithdrawing groups like I, Br, NO2 are more antibacterial than compounds with electrondonating groups like OCH3 or OH [11].

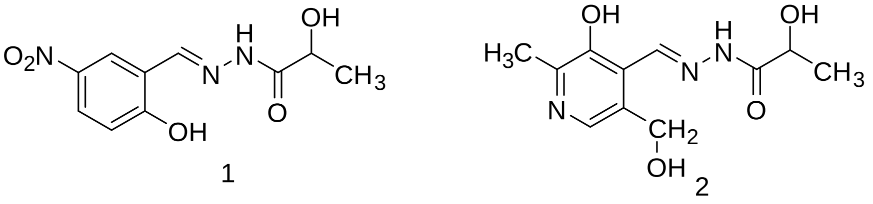


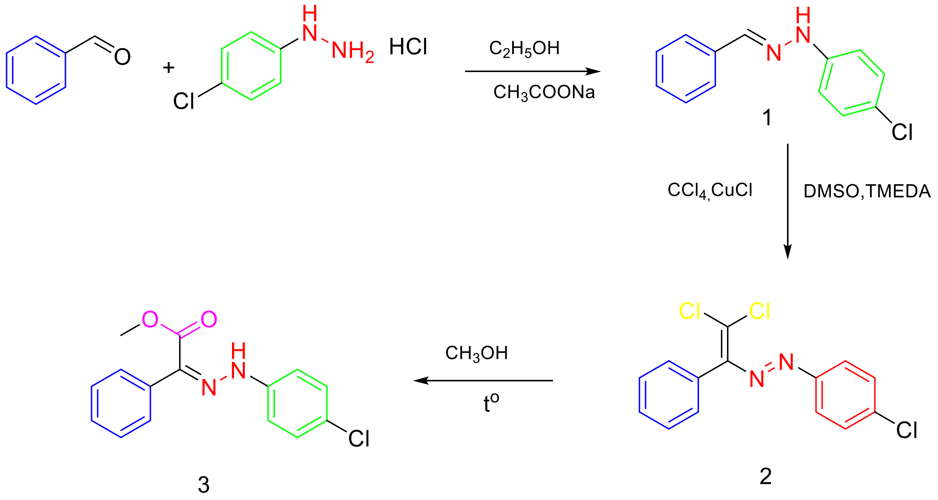
Figure 1. The structure of hydrazide-hydrazones

Taking all of that into consideration, our team synthesized arylhydrazo derivatives of mono- and bis-α-keto acidic esters via methanolysis of mono and bis dichlorodiazadienes and studied their antimicrobial properties.

Results and discussion

2.1.Synthesis of arylhydrazo derivatives of mono and bis α-ketoacidic esters

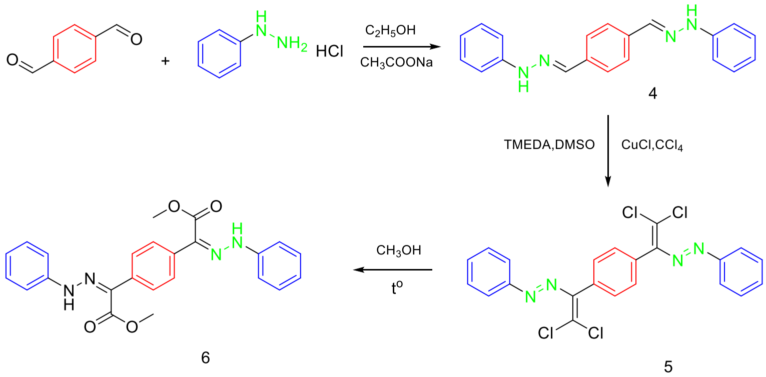
The synthesis of arylhydrazo derivatives of α-ketoacidic esters on the basis of benzaldehyde is a very complicated process. Our team controlled the process via thin-layer chromatography, and it was determined that the products are obtained as a mix of Z and E isomers. The separation of these isomers was conducted via column chromatography.



Scheme 1. Step-by-step synthesis of arylhydrazo derivatives of α-ketoacidic esters

The structures of synthesized compounds were confirmed via NMR method. Due to the presence of hydrogen bonding in the Z isomer, the proton of NH group shifts downfield. There is no hydrogen bonding in the E isomer, therefore the signal of H shifts upfield. Thus the structures of Z and E isomers were confirmed.

We used terephtale aldehyde in the synthesis of bis-adducts. In the course of the step-by-step synthetic process based on terephtale aldehyde, firstly, bis-phenylhydrazones were obtained[12], then bis-dichlorodiazadienes (via the cathalytic olefination reaction of bisphenylhydrazones) [13], and finally, via the process of methanolysis, arylhydrazo derivatives of bis α-ketoacidic esters.



Scheme 2. Step-by-step synthesis of arylhydrazo derivatives of bis-α-ketoacidic esters

2.2.The study of antimicrobial properties of the obtained compounds

Bis adducts are bis arylhydrazo derivatives of α-ketoacidic esters, therefore the antimicrobial character of these compounds is more pronounced than that of mono adducts. Keeping all this in mind, the antimicrobial properties of these compounds were deeply studied, and positive results were obtained. The rise of antimicrobial resistance poses a serious threat to global health and emphasizes the need for new medicines.[14,15]. Compounds based on hydrazone and diazene are promising antimicrobial agents due to their unique structural properties targeting both bacterial and fungal pathogens. [16] This study will research the antimicrobial potential of these compounds by evaluating their activity against seven pathogen bacteria and three Candida species. The table summarizes the antimicrobial efficacy of five organic compounds against pathogenic bacteria and fungi. In gram-negative bacteria, the diameter of inhibition zones ranged from 0.0-20.0 mm.However, these two compounds were not effective against Escherichia coli. Compounds I (Dimethyl 2,2'-(1,4-phenylene) (2Z,2'Z)-bis (2-(2-phenyl hydrazineylidene) acetate)) were 1.5 times more active against Pseudomonas aeruginosa than Klebsiella pneumoniae and Acinetobacter baumannii. The highest inhibition zone found against Pseudomonas aeruginosa was 18.0 mm. In contrast, Escherichia coli was found to be resistant to compound I. On the other hand, compound I equally inhibited the growth of Acinetobacter bauma*nnii, Klebsiella pneumoniae and Pseudomonas aeruginosa. However, Escherichia coli was the only resistant gram-negative bacterium to compound II. In addition, these compound I had the common zone of inhibition of 12.0 mm on Acinetobacter baumannii, and 18.0 mm against Pseudomonas aeruginosa. Furthermore, compound II ((E)-1-(4-bromophenyl)-2-(2,2-dichloro-1-phenylvinyl) diazene) was 1.3 times more effective against Pseudomonas aeruginosa than Acinetobacter baumannii, Escherichia coli and Klebsiella pneumoniae. The average of inhibition zone (17.0 mm) was observed against Pseudomonas aeruginosa. However, the size of inhibition zone (13.0 mm) showed that compound II had similar action against Acinetobacter baumannii, Escherichia coli and Klebsiella pneumoniae. Compund III (Methyl (Z)-2-(2-(4-chlorophenyl) hydrazineylidene)-2-phenylacetate) was 1.3, 1.6 and 1.7 times more active against Pseudomonas aeruginosa than Klebsiella pneumoniae, Escherichia coli and Acinetobacter baumannii, respectively. Compound IV ((E)-1-(4-chlorophenyl)-2-(2,2-dichloro-1-phenylvinyl) diazene) was 1.5 and 1.6 times more efficient against Pseudomonas aeruginosa than Escherichia coli and Klebsiella pneumoniae, respectively. In contrast, this compound did not inhibited the growth of Acinetobacter baumannii. Thus, in gram-negative bacteria, Escherichia coli was the most resistant bacterium to compound I, while Acinetobacter baumannii was found to be resistant to compound IV. Pseudomonas aeruginosa was the most sensitive bacterium to all four compounds with inhibition zones ranged from 17.0-20.0 mm. Compound I had the same inhibition zone (18.0 mm) against Pseudomonas aeruginosa, and 12.0 mm against Acinetobacter baumannii. Therefore, compound III was the most active against Pseudomonas aeruginosa with 20.0 mm as the maximum size ofinhibitionzone

Microorganisms		Diameter of inhibition zone (mm), M ± m			
		I	II	III	IV
Gram negative bacteria	Acinetobacter baumannii	12.0±0.1	13.0±0.2	12.0±0.1	0.0
	Escherichia coli	0.0	13.0±0.2	12.3±0.1	12.2±0.1
	Klebsiella pneumoniae	12.0±0.1	13.0±0.2	15.0±0.3	12.0±0.1
	Pseudomonas aeruginosa	18.0±0.4	17.0±0.4	20.0±0.6	19.0±0.5
Gram positive bacteria	Bacillus mesentericus	0.0	13.0±0.2	13.0±0.2	13.0±0.2
	Bacillus subtilis	12.0±0.1	14.0±0.3	12.0±0.1	12.0±0.1
	Staphylococcus aureus	12.0±0.1	12.0±0.1	12.0±0.1	0.0
Fungi	Candida albicans	14.0±0.3	14.0±0.3	17.0±0.4	24.0±0.6
	Candida guilliermondii	14.0±0.3	12.0±0.1	12.0±0.1	21.0±0.6
	Candida tropicalis	12.0±0.1	15.0±0.3	13.3±0.2	20.0±0.5

Table. Antimicrobial activity results of compounds against bacteria and fungi

Note: I-Dimethyl 2,2'-(1,4-phenylene) (2Z,2'Z)-bis (2-(2-phenyl hydrazineylidene) acetate) ; II -(E)-1-(4-bromophenyl)-2-(2,2-dichloro-1-phenylvinyl) diazene ; III -Methyl (Z)-2-(2-(4-chlorophenyl) hydrazineylidene)-2-phenylacetate ;IV-(E)-1-(4-chlorophenyl)-2-(2,2-dichloro-1-phenylvinyl)diazene

In gram-positive bacteria, the diameter of inhibition zones ranged from 0.0-14.0 mm. Compound I was not active against Bacillus mesentericus. On the other hand, compound I inhibited the growth of Bacillus subtilis with 12.0 mm as the size of the inhibition zone. Staphylococcus aureus was sensitive to compounds I, with inhibitory zones measuring 12.0 mm, respectively. Compound II was 1.1 and 1.2 times more efficient against Bacillus subtilis than Bacillus mesentericus and Staphylococcus aureus, respectively. Compound III had almost the same effect on Bacillus mesentericus, Bacillus subtilis and Staphylococcus aureus. Compound IV did not prevent the growth of Staphylococcus aureus. However, Bacillus subtilis and Bacillus mesentericus were susceptible to compound IV, with 12.0 and 13.0 mm as the respective diameter of inhibition zones. Thus, in gram-positive bacteria, compounds II and III were most efficient against Bacillus mesentericus, Bacillus subtilis and Staphylococcus aureus. These two compounds demonstrated similar antibacterial actions on the three microorganisms. However, Bacillus mesentericus was the most resistant to compounds I. Bacillus subtilis was sensitive to compounds I, II, III and IV, nevertheless Staphylococcus aureus was susceptible to compounds I,II and III. Bacillus mesentericus was the most resistant bacterium, whereas Bacillus subtilis and Staphylococcus aureus were the most vulnerable

A comparative study of the antibacterial activity results of gram-negative and gram-positive bacteria revealed that gram-negative bacteria were more sensitive to all four compounds compared to gram-positive bacteria. Compound I was ineffective against Escherichia coli and Bacillus mesentericus. Compounds II and III inhibited the growth of both gram-negative and gram-positive bacteria. These two compounds were the most effective. Compound III exhibited the highest inhibition zone (20.0 mm) was found against Staphylococcus aureus.

In fungal strains, the size of inhibition zones varied between 12.0 and 24.0 mm. The average of inhibition zone was 16.0 mm. Compound I was 1.2 times more efficient against Candida albicans and Candida guilliermondii, than Candida tropicalis. This compound exhibited the same antifungal action against Candida albicans and Candida guilliermondii, with an inhibitory zone measuring 14.0 mm. Compound II was 1.1 and 1.3 times more active against Candida tropicalis than Candida albicans and Candida guilliermondii, respectively. Compound III was 1.3 and 1.4

times more effective against Candida albicans than Candida tropicalis and Candida guilliermondii, respectively. The average of inhibition zone (17.0 mm) was observed against Candida albicans. Compound IV was 1.1 and 1.2 times more efficient against Candida albicans than Candida guilliermondii and Candida tropicalis, respectively. Thus, fungal strains were all sensitive to all four compounds with inhibition zones ranged from 12.0-24.0 mm. Compound IV was the most efficient against Candida tropicalis, Candida guilliermondii and Candida tropicalis with inhibition zones of 20.0, 21.0 and 24.0 mm, respectively.

A comparative assessment of the antibacterial and antifungal properties of the four compounds revealed that fungal strains were more sensitive to all compounds than bacteria. Compound IV had the largest inhibitory zone (24.0 mm) on Candida albicans. The most resistant bacterial strains were Escherichia coli and Bacillus mesentericus.Compound I was 1.3 and 1.5 times more effective against Pseudomonas aeruginosa than Candida albicans, Candida guilliermondii, Bacillus subtilis and Staphylococcus aureus, respectively. Compound II was 1.1 and 1.2 times more effective against Pseudomonas aeruginosa than Bacillus subtilis and Candida tropicalis, respectively. Compound III was 1.2 and 1.5 times more effective against Pseudomonas aeruginosa than Candida albicans and Bacillus mesentericus. Compound IV was 1.3 and 1.8 times more effective against Candida albicans than Pseudomonas aeruginosa and Bacillus mesentericus, respectively. Thus, Pseudomonas aeruginosa was the most sensitive bacterial strain, whereas Candida albicans was the most fungal one.

Experimental part

3.1. Method of synthesis

NMR ^{1}H and ^{13}C spectra were also recorded in $CDCl_3$ and DMSO on Bruker Avance 300 (operating frequency 300 MHz spectrometer. $SiMe_4$ was used as an internal standard. UB-254 was performed on NTX Silufol plate, and acidified $KMnO_4$ solution was used for clear visibility of the formed spots and UV lamp rays were used. Column chromatography was performed on silica gel from Merck (63-200). Information regarding compounds 4 and 5 have been reported in the existing literature [12-13].

General Procedure for the Synthesis of Hydrazones

To a solution of 1 mmol of the corresponding phenylhydrazine in 50–100 mL of ethanol, 0.082 g (1 mmol) of sodium acetate is added. Next, 1 mmol of the desired aldehyde is introduced into the reaction mixture, which is then stirred and heated. Once the temperature reaches the boiling point of ethanol, the mixture is maintained under reflux with continuous stirring for an additional 20 minutes. After this period, the reaction mixture is allowed to cool to room temperature. Subsequently, 50 mL of water is added, and the mixture is reheated with vigorous stirring until it reaches 60°C. Heating is then discontinued, and the mixture is left to cool. The resulting precipitate is collected by filtration, and the synthesized hydrazone is air-dried at room temperature for approximately 15–20 hours.

Compound 1. It is a white solid compound. The experimental yield of the substance is 90%. The melting point is 145°C. ^{1}H NMR (300 MHz, DMSO-d6) δ 10.49 (s, 1H), 7.87 (s, 1H), 7.64 (d, *J* = 5.5 Hz, 2H), 7.42 – 7.28 (m, 5H), 7.02 (d, *J* = 5.9 Hz, 2H). ^{13}C NMR (75 MHz, DMSO) δ 145.02, 144.90, 137.83, 135.98, 132.19, 129.12, 128.65, 126.22, 114.35, 109.96, 109.61, 108.58, 99.98.

Synthesis Procedure for ([{2,2-Dichloro-1-phenylvinyl}diazenyl]phenyl)methanes

To begin the synthesis, 1 mmol of the starting hydrazone is dissolved in 10–15 mL of dimethyl sulfoxide (DMSO). To this mixture, tetramethylethylenediamine (TMEDA) is added as a mild base in an amount of 290 mg (1.25 equivalents). The reagents are introduced sequentially into a reaction flask. Following this, copper(I) chloride (CuCl) is added as a catalyst at 3 mg (1 mol%). Finally, carbon tetrachloride (CCl_4) is introduced in a 10-fold molar excess (1.5 g). The reaction progress is monitored using thin-layer chromatography (TLC), and typically reaches completion within 2–3 hours. Upon completion, the reaction mixture is transferred to a separatory funnel and subjected to aqueous workup. Approximately 50–70 mL of water is added, and the mixture is extracted with dichloromethane (CH_2Cl_2) in three portions of 30 mL each. The combined organic layers (approximately 3 × 50 mL) are washed with water, followed by a single wash with saturated sodium chloride (NaCl) solution (1 × 70 mL). The organic layer is then dried over anhydrous sodium sulfate (Na_2SO_4). After filtration, the solvent is removed under reduced pressure using a rotary evaporator. The crude product is further purified by column chromatography using a gradient of methylene chloride:hexane mixtures (1:7, 1:5, or 1:3) as the eluent. The reaction course and the purity of the isolated product are verified via thin-layer chromatography (TLC).

Compound 2. Red crystallic substance. Practical yield of this substance is 65%. Melting point is 95°C. ^{1}H NMR (300 MHz, Chloroform-d) δ 7.67 (d, *J* = 8.8 Hz, 2H), 7.59 (d, *J* = 8.8 Hz, 2H), 7.45 (dd, *J* = 4.8, 1.9 Hz, 3H), 7.22 – 7.15 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.5, 150.2, 132.3, 129.9, 128.8, 128.7, 128.2, 126.1, 124.6.

General Procedure for the Synthesis of (Z)/(E)-Methyl 2-Phenyl-2-(2-phenylhydrazono)acetates

A quantity of 10 mg of 1,1-dichlorodiazadiene is dissolved in 30 mL of methanol and stirred using a magnetic stirrer under reflux conditions for 2 hours. After completion of the reaction time, the solvent is removed under reduced pressure using a rotary evaporator. The resulting crude mixture is subjected to column chromatography for separation of the reaction products.

For chromatographic purification, a mixture of dichloromethane and n-hexane (1:1), as well as dichloromethane and ethanol, are used as eluents. The major fractions corresponding to the desired reaction products, identified via thin-layer chromatography (TLC), are collected and concentrated again using a rotary evaporator. The product yield is then calculated based on the final dried material.

Compound 3. It is a yellow solid substance. The experimental yield of the substance is 45%. The melting point is 75°C. ^{1}H NMR (300 MHz, DMSO-d_6, δ, m.h) δ11.5 (s, 1H, NH), 7.3 (dd, *J* = 8.3, 6.7 Hz, 2H, arom), 7.2 (ddt, *J* = 9.4, 6.8, 2.0 Hz, 1H, arom), 7.1 (m, 2H, arom), 7.0-7.1 (m, 2H, arom), 6.8 – 6.8 (s, 1H, arom), 3.83 (s, 3H, -OCH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.1, 141.8, 136.2, 129.3, 128.7, 128.4, 128.0, 127.9, 127.3, 115.4, 51.9.

Compound 6. It is a yellow solid substance. The experimental yield of the substance is 45%. The melting point is 75°C. ^{1}H NMR (300 MHz, Chloroform-d) δ 12.46 (s, 2H), 7.69 (s, 4H), 7.23 (d, *J* = 8.5 Hz, 4H), 7.16 (d, *J* = 8.4 Hz, 4H), 3.91 (s, 6H), 2.35 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.2, 140.87, 135.61, 132.16, 129.89, 128.04, 114.28, 113.1, 99.98, 51.7

3.2 Method for the Investigation of the Antimicrobial Properties of the Synthesized Compounds

The Organic Chemistry Department of Baku State University in Azerbaijan provided all seven organic compounds. Gram-negative bacteria (Acinetobacter baumannii BDU-32, Escherichia coli BDU-12, Klebsiella pneumoniae BDU-44 and Pseudomonas aeruginosa BDU-49), gram-positive bacteria (Bacillus mesentericus BDU-51, Bacillus subtilis BDU-50 and Staphylococcus aureus BDU-23) and yeasts (Candida albicans BDU MI-44, Candida guilliermondii BDU-217 and Candida tropicalis BDU LK-30) were used as test cultures.

The antimicrobial activity of compounds was evaluated using the agar well diffusion method at 0.1% concentration. Dimethyl sulphoxide (DMSO) was used as a solvent to dissolve the compounds, and for a negative control. The pathogenic bacteria were cultivated on nutrient agar, while the fungal strains were grown on sabouraud dextrose agar [17]. All experiments were repeated four times.

Conclusion

We obtained mono and bis phenylhydrazones based on benzaldehyde and terephtale aldehydes and synthesized their respective mono and bis dichlorodiazadienes via catalythic olefination. Arylhydrazo derivatives of mono and bis α-ketoacidic esters were synthesized via solvolysis reactions of dichlorodiazadienes, and their antimicrobial properties were studied. This study revealed that fungal strains were more susceptible to the five organic compounds than bacteria. Among the gram-negative bacteria, Pseudomonas aeruginosa was the most sensitive, with inhibition zones ranging from 17.0 to 20.0 mm. In contrast, Escherichia coli and Bacillus mesentericus showed the highest resistance. (E)-1-(4-chlorophenyl)-2-(2,2-dichloro-1-phenylvinyl) diazene (compound V) produced the largest inhibition zone (24.0 mm) against Candida albicans.

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1. "Journal of Baku Engineering University-Kimya və Biologiya"- əvvəllər nəşr olunmamış orijinal əsərləri və müəllifin tədqiqat sahəsi üzrə yazılmış icmal məqalələri qəbul edir.
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b) ***Kitab:*** Christie ohn Geankoplis. *Transport Processes and Separation Process Principles*. Fourth Edition, Prentice Hall, 2002

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- İstinat Edebiyatı Rusça olduğu halde orjinal dili parantez içerisinde göstermekle yalnız Latin alfabesi ile verilmelidir.

7. **Şekil, Resim, Grafik** ve **Tablolar** baskıda düzgün çıkacak nitelikte ve metin içerisinde olmalıdır. Şekil, Resim ve grafiklerin yazıları onların alt kısımda yer almalıdır. Tablolarda ise başlık, tablonun üst kısmında bulunmalıdır.
8. **Kullanılan kaynaklar**, metin dâhilinde köşeli parantez içerisinde numaralandırılmalı, aynı sırayla metin sonunda gösterilmelidir. Aynı kaynaklara tekrar başvurulduğunda sıra muhafaza edilmelidir. Örneğin: [7,seh.15].

Referans verilen her bir kaynağın künyesi tam ve kesin olmalıdır. Referans gösterilen kaynağın türü de eserin türüne (monografi, derslik, ilmî makale vs.) uygun olarak verilmelidir. İlmi makalelere, sempozyum, ve konferanslara müracaat ederken makalenin, bildirinin veya bildiri özetlerinin adı da gösterilmelidir.

Örnekler:

a) ***Makale:*** Demukhamedova S.D., Aliyeva İ.N., Godjayev N.M.. *Spatial and Electronic Structure of Monomerik and Dimeric Conapeetes of Carnosine Üith Zinc,* Journal of Structural Chemistry, Vol.51, No.5, p.824-832, 2010

b) ***Kitap:*** Christie ohn Geankoplis. *Transport Processes and Separation Process Principles*. Fourth Edition, Prentice Hall, p.386-398, 2002

c) ***Kongre:*** Sadychov F.S., Aydın C., Ahmedov A.İ. Appligation of Information-Communication Technologies in Science and education. II International Conference. *“Higher Twist Effects In Photon- Proton Collisions”, Bakı, 01-03 Noyabr, 2007, ss 384-391*

Kaynakların büyüklüğü 9 punto olmalıdır.

9. **Sayfa ölçüleri**; üst: 2.8 cm, alt: 2.8 cm, sol: 2.5 cm, sağ: 2.5 cm şeklinde olmalıdır. Metin 11 punto büyüklükte **Palatino Linotype** fontu ile ve tek aralıkta yazılmalıdır. Paragraflar arasında 6 puntoluk yazı mesafesinde olmalıdır.
10. Orijinal araştırma eserlerinin tam metni 15 sayfadan fazla olmamalıdır.
11. Makaleler dergi editör kurulunun kararı ile yayımlanır. Editörler makaleyi düzeltme için yazara geri gönderilebilir.
12. Makalenin yayına sunuşu aşağıdaki şekilde yapılır:

- Her makale en az iki uzmana gönderilir.
- Uzmanların tavsiyelerini dikkate almak için makale yazara gönderilir.
- Makale, uzmanların eleştirel notları yazar tarafından dikkate alındıktan sonra Derginin Yayın Kurulu tarafından yayına sunulabilir.

13. Azerbaycan dışından gönderilen ve yayımlanacak olan makaleler için,(derginin kendilerine gonderilmesi zamani posta karşılığı) 30 ABD Doları veya karşılığı TL, T.C. Ziraat Bankası/Üsküdar-İstanbul 0403 0050 5917 No’lu hesaba yatırılmalı ve makbuzu üniversitemize fakslanmalıdır.

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1. «Journal of Baku Engineering University» - Химии и биологии публикует оригинальные, научные статьи из области исследования автора и ранее не опубликованные.
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- Название статьи, имя и фамилия авторов
- Место работы
- Электронный адрес
- Аннотация и ключевые слова

4. **Заглавие статьи** пишется для каждой аннотации заглавными буквами, жирными буквами и располагается по центру. Заглавие и аннотации должны быть представлены на трех языках.
5. **Аннотация**, написанная на языке представленной статьи, должна содержать 100-150 слов, набранных шрифтом 9 punto. Кроме того, представляются аннотации на двух других выше указанных языках, перевод которых соответствует содержанию оригинала. Ключевые слова должны быть представлены после каждой аннотации на его языке и содержать не менее 3-х слов.
6. В статье должны быть указаны коды UOT и PACS.
7. Представленные статьи должны содержать:

- Введение
- Метод исследования
- Обсуждение результатов исследования и выводов.
- Если ссылаются на работу на русском языке, тогда оригинальный язык указывается в скобках, а ссылка дается только на латинском алфавите.

8. **Рисунки, картинки, графики и таблицы** должны быть четко выполнены и размещены внутри статьи. Подписи к рисункам размещаются под рисунком, картинкой или графиком. Название таблицы пишется над таблицей.
9. **Ссылки** на источники даются в тексте цифрой в квадратных скобках и располагаются в конце статьи в порядке цитирования в тексте. Если на один и тот же источник ссылаются два и более раз, необходимо указать соответствующую страницу, сохраняя порядковый номер цитирования. Например: [7, стр.15]. Библиографическое описание ссылаемой литературы должно быть проведено с учетом типа источника (монография, учебник, научная статья и др.). При ссылке на научную статью, материалы симпозиума, конференции или других значимых научных мероприятий должны быть указаны название статьи, доклада или тезиса.

Например:

a) ***Статья:*** Demukhamedova S.D., Aliyeva I.N., Godjayev N.M. *Spatial and electronic structure of monomeric and dimeric complexes of carnosine with zinc,* Journal of Structural Chemistry, Vol.51, No.5, p.824-832, 2010

b) ***Книга:*** Christie on Geankoplis. *Transport Processes and Separation Process Principles.* Fourth Edition, Prentice Hall, 2002

c) ***Конференция:*** Sadychov F.S, Fydin C,Ahmedov A.I. Appligation of Information-Communication Nechnologies in Science and education. II International Conference. *"Higher Twist Effects In Photon-Proton Collision",* Bakı,01-03 Noyabr, 2007, ss.384-391

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