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ABSTRACT

of the dissertation for the degree of Doctor of Chemical Sciences

DEVELOPMENT OF A SCIENTIFIC BASIS SOLUTIONS TO ENVIRONMENTAL PROBLEMS CAUSED MOTOR VEHICLES BY USING SOME ORGANOMETALLIC COMPOUNDS AND OIL REFINING INDUSTRY

Speciality: 2391.01 – Ecological Chemistry

Field of Science: Chemical Sciences

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GENERAL CHARACTERISTICS OF THE WORK

Topic relevance and development rate: The damage caused by the automobile industry to the environment is one of the main ecological problems of today. Environmental problems caused by smoke gases released into the air during fuel combustion, whether additives added to fuel meet the standards, and other such issues are always rising. Research is ongoing to find a solution to these problems. Synthesis of new derivatives of ferrocene and cymantrene, which are the main representatives of organometallic compounds, is proposed as an urgent issue. It is known that ferrocene and cymantrene are industrially important organometallic compounds and have many important properties from an environmental point of view, e.g.; their derivatives have smoke-reducing properties, use as anti-detonation additives in fuels, and other properties.

As the molecular weight increases, the decrease in the mass share of iron and manganese in the molecule of ferrocene and cymantrene allows to use their derivatives as more effective additives. It is also possible to synthesize new compounds on the basis of more flexible transformations due to the presence of active oxygen in their derivatives. For this purpose, we synthesized derivatives of ferrocene and cymantrene under the conditions of interphase catalysis, and based on them, new studies were conducted.

Recently, due to the rapid development of nanotechnology, the possibilities of using nanoparticles in all fields of science are increasing[1].Therefore, the work done in this direction can be considered both interesting and relevant. In our modern era, the application of nanotechnology for the purpose of wastewater treatment is very important for the protection of the water ecosystem. Thus, in order to protect the environment, various countries use nano technological approaches to partially meet the demand for drinking water and wastewater treatment.

Many developed countries have even succeeded in purifying their

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[1] Yeonsig, N., Yong H.L., Kyoung C.K. Photocatalytic activity of TiO_2 nanoparticles: a theoretical aspect //Journal of Materials Chemistry, - 2019. Vol.23, - p.87.

wastewater to the point where it is fully potable using these methods. As we know, in recent years, the fresh water supply in the world has been decreasing and is on the way to exhaustion. All this makes it very important to find effective ways to treat waste water. From this point of view, based on conducting various researches based on rutile phase TiO_2 nanoparticles, scientific work in the direction of phenol purification from waste water is considered relevant.

Object and subject of the research: The object of the research work was environmental protection, and the subject was the investigation of the possibilities of using modern and new methods in the protection of the air and water ecosystem. In laboratory conditions, the anti-detonation properties of the new organometallic derivatives obtained on the basis of ferrocene and cymantrene under the conditions of interphase catalysis were investigated. In addition, photochemical decomposition of phenol under ultraviolet radiation in the presence of TiO_2 nanoparticles was carried out with a high percentage of wastewater samples. It has been determined that when a nitrogen-containing component is included in such an environment, it is possible to extend the ultraviolet radiation range to the visible range. The adsorption property of TiO_2 nanoparticles was also studied. As a result, it was determined that it does not show adsorption capacity.

The aim and tasks of the research: The aim was to minimize the negative effects of motor vehicles on the environment by using metal-organic compounds (ferrocene and cymantrene) and to develop a scientific basis for solving the ecological problems caused by the oil refining industry. To achieve this goal, the following was implemented:

- based on ferrocene and cymantrene, which are used as an anti-detonation additive in motor vehicles, is environmentally non-toxic, and does not have a carcinogenic effect, new derivatives have been synthesized and studied in the medium of interphase catalysis;
- diethylammonium naphthenate (DEAN) was used as an interphase medium;
- a complex chemical analysis of wastewater samples taken from H. Aliyev Oil Refinery was carried out and the effects of the plant's

wastewater on the water ecosystem were investigated from an environmental point of view;

-a method of phenol purification from wastewater was developed using TiO_2 nanoparticles with the rutile phase;

-photochemical decomposition of phenol in the TiO_2+phenol system was carried out in the presence of ultraviolet radiation;

-in the TiO_2+methyl3-aminocrotonate+phenol system, it was possible to extend the photochemical decomposition of phenol from the ultraviolet radiation area to the visible area;

-the adsorption capacity of phenol was studied using TiO_2 nanoparticles with the rutile phase;

-the adsorption of phenol in the presence of TiO_2 nanoparticles was studied and compared with the adsorption in the presence of graphene oxide and activated carbon. Exponential and logistic models of the adsorption process were established.

-the adsorption of phenol in the presence of TiO_2 nanoparticles with the rutile phase was studied;

-general regularities in the studied processes were determined and a mathematical model of several processes was drawn up.

Research methods: modern research methods were used at certain stages of the dissertation work, including the following:

- Agilent 6890N/5975 GC/MS gas chromatography-mass spectroscopy;
- ICP-OES, Optima 2100DV emission analysis method;
- IR spectroscopy;
- UV spectroscopy;
- PMR spectroscopy;
- Specord 250 spectrophotometer;
- Varian Cary 50 spectrophotometer;
- PHS-25 device;
- TEM-transmission electron microscopy;
- SEM-scan electron microscopy;
- XRD- X-ray diffraction method.

- a number of reactions were carried out in order to ensure the environmental safety of the air and water ecosystem;

- the use of new derivatives based on ferrocene and cymantrene in fuels as anti-detonation additive was investigated and their role in air environment protection was studied;
- it was determined that new metal organic derivatives based on ferrocene and cymantrene obtained in DEAN/H_2SO_4 interphase catalysis medium have better anti-detonation properties and smoke reduction capabilities;
-industrial waste water samples were taken from various areas near the Caspian Sea, as well as from the Oil Refinery and analyzed. Heavy metals, polycyclic aromatic hydrocarbons and phenolic compounds were studied in waste water samples. In many cases, the considered substances exceeded the permissible concentration limit.
- the ecological bases of photochemical reactions in the presence of TiO_2 with the rutile phase nanoparticles were studied for the purpose of protecting the water ecosystem;
- 99% photochemical decomposition of toxic phenol was achieved with the TiO_2 nanoparticles in the presence of ultraviolet radiation;
- adsorption properties of TiO_2 nanoparticles were studied. It was determined that although TiO_2 nanoparticles have very good photo catalytic properties, they do not show adsorption properties.

The scientific novelty of the research: New perspective directions have been proposed and developed in solving the ecological problems caused by motor vehicles and the oil refining industry. As we know, derivatives based on ferrocene and cymantrene do not have toxic or carcinogenic effects from an environmental point of view.

Also, the presence of iron and manganese compounds in the biosphere is one of the important factors, as they accelerate the process of photosynthesis and the formation of chlorophyll, which gives plants their green color. For this purpose, metal-organic complexes of iron and manganese (ferrocene and cymantrene) were used.

Reactions of ferrocene and cymantrene with cyclic ketones in DEAN/H_2SO_4 (1:2) medium were synthesized and studied. For this purpose, their reactions with cyclopentanone and cyclohexanone were considered. It was determined that the reactions of organometallic compounds with ketones take place in an acidic medium and proceed with electrophilic substitution.

The obtained new derivatives were studied by IR, EA, PMR methods.

-Industrial wastewater taken from the catalytic cracking area of the Oil Refinery was comprehensively studied, phenol and its derivatives, polycyclic aromatic hydrocarbons, as well as heavy metals were determined.

- For the first time, photochemical decomposition reactions of phenol in the presence of ultraviolet radiation (UV) with TiO_2 nanoparticles with rutile phase were carried out. The photochemical decomposition of phenol was 99%. The presence of rutile phase of TiO_2 nanoparticles used in the process was investigated by XRD method, and their size by SEM method. TiO_2 nanoparticles used as photo catalysts were synthesized by sol-gel method and their size was between 10-30 nm.

  By using TiO_2 nanoparticles and methyl3-aminocrotonate + TiO_2 + phenol system, it was possible to extend the process from the ultraviolet radiation area to the visible area, at which time the photochemical decomposition of phenol was 60-80%.
- The effect of the pH of the medium on the course of the process in photochemical reactions was also studied. It was found that the photochemical reaction goes better in an acidic medium (when pH=4).
- The adsorption properties of phenol in the presence of rutile phase TiO_2 nanoparticles with sizes of 10-30 nm were studied. It was determined that phenol adsorption does not occur in the presence of TiO_2 nanoparticles.

The theoretical and practical significance of the research: Ensuring the ecological safety of the air and water ecosystem in the research work is one of the main indicators of the work. Modern methods were used to protect the atmosphere and water ecosystem. The transition to carbon-free fuel and the use of alternative energy is not completely possible at the moment. Therefore, it is very important to use fuels that cause less damage to the environment from an ecological point of view. If the additives added to the fuel do not have a toxic effect, they can be considered effective from an ecological point of view. For this purpose, derivatives used against detonation in fuels based on organometallic compounds were obtained. Thus, new derivatives of ferrocene and cymantrene with cyclic ketones were synthesized in DEAN/H_2SO_4 (1:2) medium.

The problem of water ecosystem pollution is currently one of the most important environmental problems in the world. Such waters cause pollution of other water bodies. For this purpose, we took and analyzed water samples from the Oil Refinery and different areas of the Caspian Sea. Polycyclic aromatic compounds, phenolic compounds and heavy metals were studied in them.

Currently, making waste water useful through effective treatment is one of the main priority issues in the world. Using modern methods, it is possible to solve these problems based on nano approaches. In this regard, effective purification of phenol from waste water was achieved by applying nano technological methods. TiO_2 nanoparticles with the rutile phase and size 10-30 nm were used for 99% photochemical decomposition of phenol in the ultraviolet radiation area. The same process was carried out in the presence of nitrogenous compounds. At this time, it was possible to extend the photochemical decomposition of phenol from the ultraviolet radiation area to the visible area, which increased the practical importance of the work. At the same time, in all considered photochemical processes, TiO_2 nanoparticles were used in powder form rather than in any materials or doped systems, which means that the practicality and usability of the process is facilitated. Along with the photochemical properties of TiO_2 nanoparticles with rutile phase, its adsorption capacity was also studied. Mathematical modeling of the studied processes has been developed.

Approval and application: Scientific works have been published following the requirements set by the Higher Attestation Commission of Azerbaijan Republic. The results of the research conducted in the dissertation work were discussed and reported in the materials of International and Republican Conferences: Materials of the Republican Scientific Conference "Organic Reagents in Analytical Chemistry" dedicated to the 95th anniversary of Professor A.A. Verdizade (Baku 2009), Republican Conference dedicated to the 90th anniversary of BSU Materials of the scientific conference (Baku 2009), the scientific conference dedicated to the 88th anniversary of the birth of H.A. Aliyev (Baku 2011), the scientific conference dedicated to the 89th anniversary of the birth of H.A. Aliyev (Baku 2012), the III Republican Scientific Conference dedicated to the 91st anniversary of the birth of the national leader Heydar Aliyev. "Actual problems of ecology and soil sciences in the 21st century" (Baku 2014), "Actual problems of modern natural and economic sciences" International Scientific conference (Ganja 2018), "Actual problems of modern natural and economic sciences" International Scientific conference (Ganja 2019), WoS (IOP) Conference Series: Materials Science and Engineering (United Kingdom 2019), 3rd International Unidokap Black Sea Symposium. Sustainable Agriculture and Environment (Tokat 2019), "Human development" dedicated to the 96th anniversary of the birth of national leader Heydar Aliyev. II International Scientific Conference on "World Integration" (Baku 2019), Actual problems of ecology and soil sciences in the XXI century: materials of the VIII Republican Scientific Conference (Baku 2019), II International Envirochem Congress (Antalya 2019),

III International Scientific Conference. Technogenic systems and environmental risk (Obninsk 2020), International Conference on Building Energy Conservation, Thermal Safety and Environmental Pollution Control (ICBTE). Ecology and Energy Saving. E3S Web of Conferences (Brest 2020), International scientific ecological conference "Environmental protection - the basis of country's safety" (Kuban 2022), V International Scientific Conference. Technogenic systems and environmental risk (Obninsk 2022), V International Scientific Conference. Technogenic systems and environmental risk (Obninsk 2022), Modern problems of theoretical and experimental chemistry. International conference devoted to the 90th anniversary of academician Rafiga Aliyeva (Baku 2022), 4th International Environmental Chemistry Congress (Antalya 2022).

Publications: 50 scientific works related to the dissertation (29 articles and 21 conference materials) were published in local and foreign press. The articles were published mainly in journals indexed in Web of Science Clarivate Analytics and Scopus:

“Reports of the Azerbaijan National Academy of Sciences” Department of Chemistry (Baku 2009), “Chemistry and chemical technology” (Ivanovo 2010), “Chemical Problems” (Baku 2010), “Azerbaijan Chemical Journal” (Baku 2010), “News of Baku University” (Baku 2013), “News of Baku University” (Baku 2014), “Azerbaijan Chemical Journal” (Baku 2014), “News of Baku University” (Baku 2015), “Advances in Biology $ Earth Sciences” (Baku 2018), ANAS of Ganja Department “Collection of News” (Ganja 2019), “Proceedings of Universities. Applied chemistry and Biotechnology” (Russia 2019), “Azerbaijan Chemical Journal” (Baku 2020), “Journal of Molecular Structure” (Amsterdam 2021), “Azerbaijan Chemical Journal” (Baku 2021), “Advances in Biology & Earth Sciences” (Baku 2021), “Azerbaijan journal of chemical news” (Baku 2021), “Processes of Petrochemistry and Oil Refining” (Baku 2021), “Fundamental Sciences. Scientific works” (Baku 2021), “Processes of Petrochemistry and Oil Refining” (Baku 2022), “Ecological chemistry” (Russia 2022), “Processes of Petrochemistry and Oil Refining” (Baku 2022), “Azerbaijan journal of chemical news” (Baku 2022), “Water and Water Purification Technologies. Scientific and Technical News” (Poland 2022), “Ecological Chemistry” (Russia 2022),“Russian Journal of General Chemistry” (Russia 2022), “Ecological Chemistry” (Russia 2022), “Advances in Biology & Earth Sciences” (Baku 2023), “Journal of the Chemical Society of Pakistan” (Pakistan 2023), “Processes of Petrochemistry and Oil Refining” (Baku 2023).

Personal contribution of the author. The main role of the author in the implementation of the dissertation work is determined by setting the problem, determining the direction of research, developing the technical task, and conducting experiments, as well as analyzing, summarizing, and interpreting the obtained results on a scientific basis. The presented work is the result of the author's independent research.

The place where the dissertation work is done: The name of the institution where the dissertation work was performed. Baku State University, Institute of Radiation Problems of Ministry of Science and Education of the Republic of Azerbaijan, Institute of Catalysis and Inorganic Chemistry named after Academician M.F. Nagiyev of Ministry of Science and Education of the Republic of Azerbaijan.

Scope, structure and content of the work: The total volume of the dissertation with a sign indicating the volume of the structural sections of the dissertation separately. The dissertation consists of a total of 281 pages of computer text. The dissertation work consists of the introduction, I, II, III, IV, V, and VI chapters, conclusions, and literature list. Excluding the bibliography and appendices, its volume covers – 361856 marks: including introduction (17215), chapter I (61236), chapter II (60873), chapter III (52324), chapter IV (64185), chapter V (86260), and chapter VI (17691) signs. At the end, the main results (2072) and a literature review of 250 names are given. 2 schemes, 3 graphs, 51 tables and 108 pictures are included in the dissertation.

In the introduction, the relevance of the problem to which the dissertation is devoted is justified, the goals and directions of the research, scientific innovations, theoretical and practical importance, and the total number of published scientific works are given.

In the first chapter, the literature information related to the considered dissertation work is given. Modern literature information on environmental pollution, mainly the factors that cause water ecosystem pollution, was used.

In the second chapter, the synthesis of ferrocene and cymantrene with cyclic ketones in the medium of interphase catalysis was carried out, and the structural study of the obtained new derivatives was carried out. The structure of the synthesized new compounds was mainly studied and confirmed by IR, EA, PMR spectroscopy.

In the third chapter, the possibility of using ferrocene and cymantrene derivatives as anti-detonators to raise the octane number was investigated.

In the fourth chapter, water samples taken from the Oil Refinery named after Heydar Aliyev and from different areas of the Caspian Sea were analyzed, and polycyclic aromatic hydrocarbons, phenol and phenolic compounds, as well as heavy metals were determined in them.

In the fifth chapter, photochemical reactions in the presence of TiO_2 nanoparticles were studied. TiO_2 had a rutile phase. All reactions were carried out in the presence of ultraviolet (UV) radiation.

In the sixth chapter, the adsorption capacity of TiO_2

nanoparticles was checked. It was found that TiO_2 nanoparticles with rutile phase do not show adsorption capacity, despite having very good photo catalytic properties. The thesis is completed with the main results and the list of used literature sources.

THE CONTENT OF THE WORK

Ecological basis of the use of organometallic compounds

In this section, new derivatives obtained on the basis of iron and manganese-based organometallic compounds are discussed. Iron (Fe) and manganese (Mn) elements are biogenic elements. Their role is especially important in the development of plants and the process of photosynthesis.

It is known that tetraethyl lead has been used for many years to raise the octane number in fuels.

After the ecological toxicity of tetraethyl lead (TEL) was determined, the need for less dangerous or completely safe compounds for the environment increased. The increased detonation potential of tetraethyl lead when added to fuel is explained by the following probable mechanism:

According to the Sokolik theory, the free radicals generated in the process slow down the formation of peroxide-type compounds during ignition in the fuel-air environment. This causes their density to decrease before ignition, which makes it difficult for normal combustion to detonate.

$$Pb(C_2H_5)_4 \rightarrow Pb + 4C_2H_5^*$$
$$Pb + O_2 \rightarrow PbO_2$$

In this case, as a result of oxidation of free lead, PbO_2 is obtained, and when it reacts with hydroperoxides, peroxide-type compounds are decomposed, as a result, less active oxidizing products and PbO are obtained.

$$RCH_2OOH + PbO_2 \rightarrow RCHO + PbO + H_2O + 0.5CO_2$$

Based on the presence of free oxygen in the environment, PbO is oxidized and forms PbO_2 again. In the process, lead4-oxide reacts with peroxides again and prevents radical oxidation. Prevention of radical oxidation process means prevention of detonation.

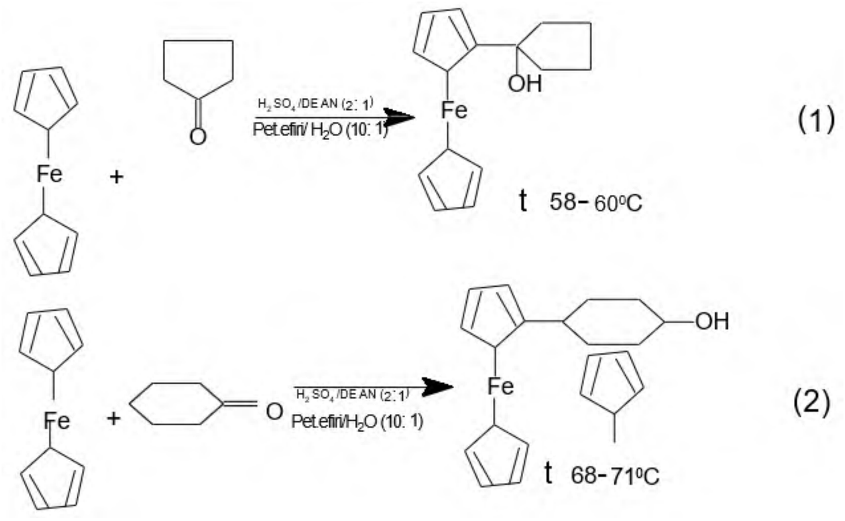
Manganese is directly involved in the formation of chlorophyll in plants. In normal and acidic soils, as well as in soils rich in organic matter , the amount of manganese is low, and plants grown in such soils are deficient in manganese. The elements magnesium and manganese are each trace elements, but they have different functions. While magnesium is a component of the chlorophyll molecule, manganese is not. Manganese participates in photosynthesis, the role of manganese in the formation of chlorophyll, glucose and vitamin C (ascorbic acid) in plants is very large. In case of deficiency of magnesium and manganese in plants, the same problems occur - yellowing of leaves. Magnesium is more mobile than manganese, therefore, due to poor penetration of manganese, yellowing of young leaves occurs first in its deficiency. As can be seen, both iron and manganese elements are considered essential elements in the biosphere, both are biogenic elements and have no toxic effect.

For this purpose, we have synthesized new derivatives based on iron (ferrocene) and manganese (cymantrene) based organometallic compounds.

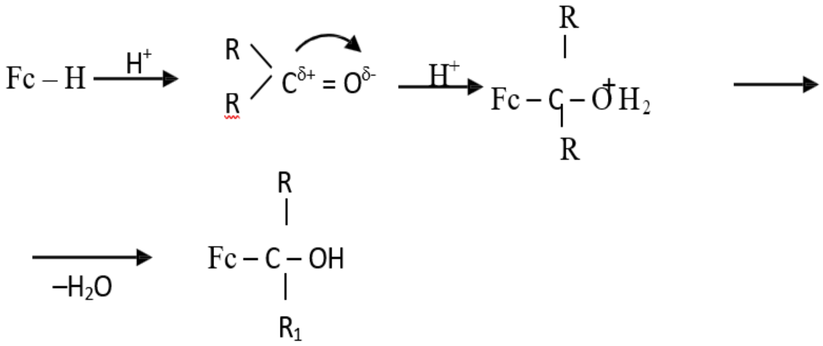
It has been determined that the reactions for obtaining their carbinol derivatives based on organometallic compounds should take place in an acidic environment. In an alkaline environment, the considered reactions do not occur. Since the cymantrene molecule is unstable, these reactions with ferrocene are more characteristic. It was determined that when the acidity number of the C-H bond in the ferrocene molecule is between 10-11, it is impossible to affect the proton in its molecule, in which case the proton is not activated, and as a result, reactions with ketones do not occur.

However, when the acidity number for C-H is above 25, protonation of carbinol groups occurs, the reaction proceeds due to the mobility of hydrogen in the carbinol group. In this regard, reactions with ferrocene should take place in an environment with a high acidity number. An acidic environment was also used to obtain carbinol derivatives of cymantrene. For the reaction to take place, the acidity of the environment should be between 28-30. For this purpose, strong acid-solid sulfuric acid (92%) was used in all the reactions considered. When replacing sulfuric acid with strong hydrochloric and phosphoric acids, the considered reactions did not occur. On the other hand, to obtain carbinol-type compounds of organometallic compounds, it is more appropriate to take the ratio of 1:40 or 1:50 of aliphatic and cyclic ketones with 92% sulfuric acid in an acidic environment. The considered reactions occur with the formation of an intermediate complex. The main purpose of taking sulfuric acid at a high concentration was to prevent hydrolysis of the intermediate complex obtained from the interaction of the ketone with the acid. The intermediate complex obtained at low concentrations disintegrates.

Derivatives of ferrocene and cymantrene are widely used as anti-detonators by increasing the octane number of fuels. They react with aliphatic and cyclic ketones under H_2SO_4/DEAN (2:1) conditions of interphase catalysis with cyclic ketones to form corresponding derivatives. The newly obtained derivatives show better anti-detonation properties than ferrocene and cymantrene. Due to these properties, they have a wide range of uses and applications, as well as a positive role in solving many problems from an environmental point of view. Below are shown the reactions of ferrocene with cyclopentanone and cyclohexanone in the medium of interphase catalysis:



Since the process takes place in an acidic medium, the probable mechanism of the reaction can be shown as follows:



The formula for metal complex (1) is $C_{15}H_{18}FeO$, and for compound (2) it is $C_{16}H_{20}FeO$. The results of the elemental analysis of compounds (1) and (2) are given below:

$C_{15}H_{18}FeO$ C% 66.66 H% 6.61 O% 5.92
$C_{16}H_{20}FeO$ C% 67.60 H%7.04 O% 5.63

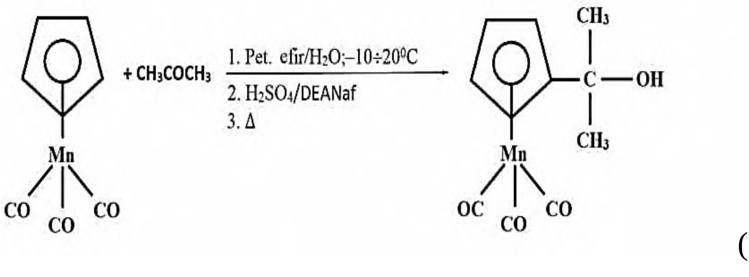
It is known that the reaction of ferrocene with aliphatic ketones occurs more easily than with cyclic ketones, and the yield is higher than with them. This can be explained by the spatial structure of the substance. For this reason, the yield of the product in the considered reactions was low. However, it was possible to increase the yield of the reaction product by using lithium or magnesium derivatives of ferrocene and cymantrene. On the other hand, it has been determined that the reaction of either ferrocene or cymantrene with cyclic ketones is strongly influenced by the temperature factor.

By constantly controlling the temperature, it is possible to obtain a product with a high yield. For this, the considered reactions were carried out by selecting different conditions. At the same time, the temperature factor played an important role in the process. It should be noted that it was possible to increase the yield of the reaction product to 85-87% with the correct selection of the medium. First of all, toluene and a lithium-substituted derivative of ferrocene were used as the phase-forming medium. However, the yield of the reaction product was not high, it was 23-28%. The reaction was exothermic. However, by maintaining a low temperature, it was possible to increase the yield of the reaction product in the medium of interphase catalysis. When studying the factors affecting the course of the reaction, it was determined that the most important thing for the process to go in one direction is the correct selection of the reaction system and the temperature factor. When creating an interphase environment, the resulting two-phase system should not mix with each other.

For this purpose, petroleum ether, a light fraction of gasoline, was used as the organic phase, and water was used as the inorganic phase. The volume ratio of petroleum ether to water was taken as 10:1. The temperature factor played a very important role in the process, so the correct selection of the temperature can increase the yield of the reaction product even 3-4 times. The reaction mixtures were taken in certain proportions and placed in certain phases in sequence. 94-96% sulfuric acid was used in the process. Sulfuric acid has two functions: it has been used both as a catalyst and to neutralize acidic media. First, 94-96% H_2SO_4 was added to the inorganic phase, i.e. water, and then petroleum ether was added. At this time, separation of organic and inorganic phases took place. When left alone, an organic phase is formed in the upper part of the flask, and an inorganic phase is formed in the lower part. After the phase separation is complete, a metal-organic compound (ferrocene or cymantrene) is added to the organic phase, i.e. the upper phase in a 1:1 ratio, and then a cyclic ketone-cyclopentanone or cyclohexanone is added. Only then, the carrier DEAN-diethylammoniumnaphthenate $(C_2H_5)_2NHOCONaf$ is added to the system to initiate the reaction. The process is carried out by heating at a positive temperature: in the temperature range of 30-40^{0}C.

Thus, obtaining the corresponding derivatives of organic metal compounds with cyclic ketones using an interphase catalysis environment, on the one hand, ensures its one-step process, and on the other hand, it can be obtained without loss and with a high yield. At the same time, the degree of purity of the obtained substance is also high. The yield of the reaction product obtained by this method is 85-87%.

The reactions of both ferrocene and cymantrene with ketones occur by an electrophilic substitution mechanism. Below is an example of the reaction of cymantrene with an aliphatic ketone:



(3)

The reactions of both ferrocene and cymantrene with ketones occur by an electrophilic substitution mechanism. In this direction, reactions with ferrocene have been studied more. The hydrolysability of the obtained carbocation, as well as the steric factors created by this carbocation, directly affect the yield of ferrocenylcarbinol derivatives. Compared to ferrocene, these reactions with cymantrene are almost non-existent or with a very small yield. This is explained by the disintegration of the cymantrene molecule in the presence of strong sulfuric acid during the reaction, and as a result, the reaction does not proceed. Corresponding reactions with cymantrene were also carried out in the presence of hydrochloric and phosphoric acids, but no positive results were obtained.

Since the cymantrene core is more unstable than the ferrocene core, it dissipates quickly. Therefore, if the reactions with ferrocene were carried out at a maximum temperature of 20^{0}C, the reactions with cymantrene take place at lower temperatures (-20^{0}C).

A structure study of newly obtained organic metal derivatives based on ferrocene and cymantrene was carried out and they were determined by IR (figure 1 and figure 2) , EA and PMR methods.

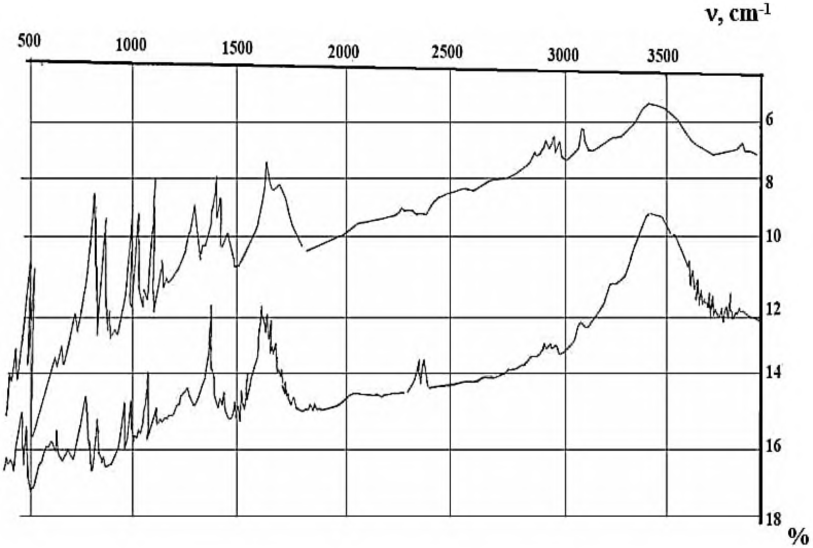


Figure 1. IR spectrum of ferrocenylcyclopentanol and ferrocenylcyclohexanol

According to IR spectroscopy, the valence absorption frequency of the C=O group of the cyclopentanone molecule, which reacts with ferrocene to form ferrosenylcyclopentanol and ferrosenylcyclohexanol, was ν_c=o1678 cm^{-1}, and that of cyclohexanone was ν_c=o1690 cm^{-1}. After the reaction, signals corresponding to these groups were not observed. This is explained by the transition of the ketone group (C=O) to the hydroxyl (OH) group in the molecule.

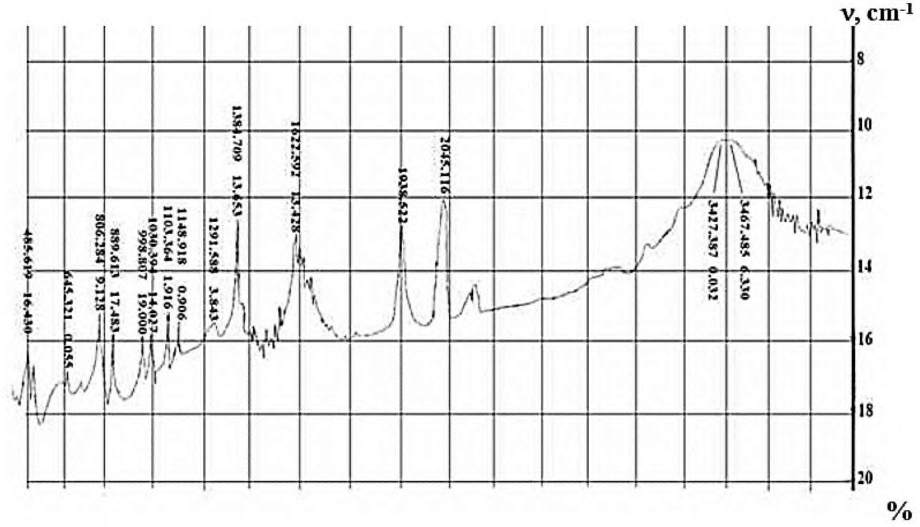


Figure 2. IR spectrum of simantrenylcyclopentanol

In the investigation of metal-organic derivatives of ferrocene obtained with cyclopentanone and cyclohexanone based on IR spectroscopy, signals corresponding to OH-groups were obtained in the region of 3448-3468 cm^{-1} of the field (figure 2). Thus, the valence absorption frequency of ν_{OH} 3468 cm^{-1} and ν_{OH} 3448 cm^{-1} was obtained for ferrocenylcyclopentanol and ferrocenylcyclohexanol, respectively. These groups do not have intramolecular and intermolecular interactions with the central atom. The spectrum was drawn in petroleum jelly.

A valence absorption frequency of ν_{OH} 3415 cm^{-1} was observed for the corresponding derivative of cymantrene.

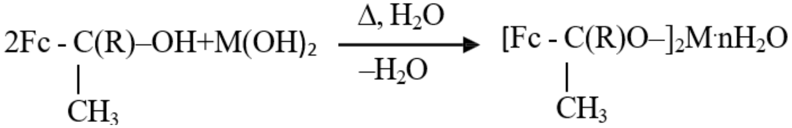
PMR analyses were carried out on a Bruker device. Spectra were recorded at C_4D_8O, 22^0C. In the PMR spectrum, a chemical shift of the site for the -OH group in the molecule of organometallic compounds occurs from 2 m.p to 4.30 m.p., in the unsubstituted ferrocene molecule, the chemical shift of the protons in the cyclopentadiene (C_5H_5) ligand is in δC_5H_5=4.12 million parts of the site, after substitution in the ferrocene ligand due to the violation of symmetry, in the cyclopentadiene ligand (C_5H_4), crossings occur in the α and β positions of the ligand, and the protons become more excited. For protons, chemical shifts occur at 3.82 and 3.91 parts per million of the field.

The EA spectrum of new derivatives of ferrocene and cymantrene was also studied. According to the results of the EA analysis, the obtained new derivatives had an absorption band in the range of λ_{max} 310-335 nm. For ferrocene and cymantrene, EA analyses were between λ_{max} 210-280 nm.

The role of organometallic compounds in motor transport

Antidetonation effect of new derivatives obtained on the basis of ferrocene and cymantrene was studied and their ecologically important reactions were considered. Salts of ferrocenylcarbinols (mainly their barium and calcium salts) generally have a greater smoke reducing effect than ferrocene and cymantrene in gasoline and diesel fuels.

Tests of the smoke reduction properties of ferrocenylcarbinol salts in diesel fuels were conducted in the central laboratory of the Azerbaijan State Oil Company "Azneftyag" (now Oil Refinery) and these compounds had 1.2 times more smoke reduction properties than ferrocene. Smoke reduction properties have been tested on diesel engines. These reactions have an important role in environmental protection.



$$2Fc-\underset{\displaystyle CH_3}{\underset{|}{C}}(R)-OH+M(OH)_2 \xrightarrow[-H_2O]{\Delta,\ H_2O} [Fc-\underset{\displaystyle CH_3}{\underset{|}{C}}(R)O-]_2M\cdot nH_2O$$

M=Ca, Ba.

Here R=CH_3,C_2H_5.

Based on the reaction between ferrocenyldimethylcarbinol and barium hydroxide, a mono-substituted barium salt of the carbinol derivative of ferrocene was obtained. The reaction was carried out by separating two moles of water in boiling tetrahydrofuran (THF).

$Fc–C(CH_3)_2–OH+Ba(OH)_2 \rightleftarrows [Fc–C(CH_3)_2O–]_2Ba*2H_2O$ (4)
$Fc =C_5H_5FeC_5H_4.$

Ferrocenylisopropylatbarium (I) was obtained in 62-70% yield. However, the complex does not have a precise melting and boiling temperature, it decomposes at temperatures above 210^oC. The complex is readily washed, dried, and solidified in low-boiling hydrocarbon solvents such as pentane, hexane, and petroleum ether. When air remains during drying, it turns into a liquid, which indicates the hygroscopicity of the substance. In this case, the obtained complex contains 2 moles of water.

$[Fc–C(CH_3)_2O–]_2Ba*2H_2O$ complex was analyzed by IR and PMR methods.

At the same time, the composition of the complex was determined by the method of microanalysis based on carbon and hydrogen. According to the results of microanalysis, after washing with petroleum ether, the complex corresponded to the formula $C_{26}H_{30}Fe_2BaO_2*2H_2O$. According to IR spectroscopy, an oscillation frequency corresponding to the ν_{OH}=3665 cm^{-1} field is observed in the $Fc–C(CH_3)_2–OH$ complex, but it disappears after interaction with $Ba(OH)_2$. According to the PMR method (the spectrum was recorded in $CDCl_3$), three signals in the $Fc–C(CH_3)_2–OH$ complex were observed at 4-5 m.p. of the field. Thus, two signals from the substituted C_5H_5 ring (C_5H_4) were observed at 4.85 and 4.33 m.p. of the field in the ligand, and one signal was observed at 4.04 m.p. of the substituted C_5H_4 ring. The signal related to the protons of the - CH_3 group is at 2.12 m.p. of the field has been observed. The considered reactions were also carried out on the basis of cymantrene. Cymanthrenylisopropylate barium dihydrate metal complex was obtained based on the reaction of the compound cymantrenyldimethylcarbinol $(OC)_3MnC_5H_4C(CH_3)_2OH$ with $Ba(OH)_2$ in THF. The yield was 60-68%.

$2(OC)_3MnC_5H_4C(CH_3)_2OH+Ba(OH)_2 \rightarrow [(OC)_3MnC_5H_4C(CH_3)_2\text{-}O]_2Ba*2H_2O$ (5)

It should be noted that the cymantrenylcarbinol derivative reacted with $Ba(OH)_2$ at low temperature (-10÷-20°C). Depending on the nature of the reacting ketone, the yield of the carbinol derivative of the cymantrene formed may be lower or higher: e.g.; The yield of the product in the reaction with aliphatic ketones is high, and in the reaction with cyclic ketones (cyclopentanone, cyclohexanone) it is low. This is characterized by the spatial structure of the ketone.

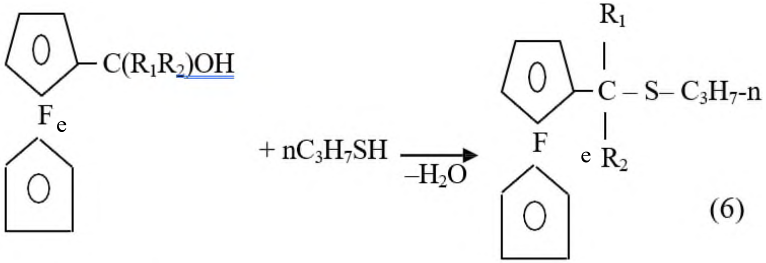
According to the results of the conducted microanalysis, complex (II) corresponded to the element composition $C_{22}H_{20}Mn_2BaO_8*2H_2O$. This compound decomposes at a lower temperature than complex (I), is light yellow in color, does not undergo hydrolysis and does not oxidize.

Complex (II) was studied based on IR spectroscopy (spectra were recorded in petroleum jelly). The vibrational frequencies characteristic of terminal carbonyl (CO) groups fell in the area of 1950, 2018 cm^{-1}. Signals corresponding to coordinated water molecules were obtained in the 3480-3750 cm^{-1} part of the field.

According to the PMR method (the spectrum was recorded in $CDCl_3$) $\delta C_5H_4(a_{,\beta})=4.56-5.08$ m.p. for a,β-protons of the cyclopentadiene ring having a chemical shift indicates substitution in the cyclopentadiene ring.

It has been learned that the anti-detonation properties of new derivatives based on ferrocene and cymantrene are 1.5-3 times more effective than their own.

Later, carbinol-type compounds of ferrocene are used to precipitate sulfur in demercaptanization reactions.



(6)

$R_1 = R_2 = CH_3$.

These reactions are considered ecologically significant.

The structures of the corresponding thioethers obtained from the interaction of carbinol derivatives of ferrocene with H_2S and mercaptans were studied by the IR spectral method. Corresponding vibrational frequencies were observed in the areas of 1134-1151 cm^{-1} for C-S groups. These reactions are considered ecologically significant. The smoke suppression effects for barium-based metal-organic compounds are superior to both ferrocene and cymantrene, as well as to existing smoke suppressants. Thus, these compounds have a smoke reduction effect 1-1.5 times higher than existing smoke reducers in distilled gasoline, as well as diesel fuel, and 0.4-0.6 times higher than ferrocene and cymantrene. In general, it should be noted that compared to ferrocene and cymantrene, the mass fraction of iron and manganese elements in their respective derivatives is lower, and the failure of engines running on such fuel occurs very late. On the other hand, compared to ferrocene and cymantrene (without CO groups), the newly synthesized organometallic derivatives undergo chemical transformations more quickly due to the presence of active oxygen. In this regard, newly synthesized derivatives of organometallic compounds (ferrocene and cymantrene) are considered industrially important compounds. As mentioned, tests of the smoke reduction properties of the investigated metal complexes (1) and (2) were carried out in 2016 at the Azneftyag Oil Refinery, now at the Oil Refinery named after Heydar Aliyev. It should be noted that the damage caused by fuels to the environment causes pollution not only of the atmosphere, but also of the water ecosystem.

In particular, it is necessary to mention the negative impact of waste water from oil refineries and chemical industry on the flora and fauna of other aquatic ecosystems.

For this purpose, water samples were taken and analyzed from the Oil Refinery named after Heydar Aliyev, their pollution as a result of discharge into other water ecosystems and monitoring of the areas close to the Caspian Sea was carried out.

Chemical analysis of water samples taken from the Oil Refinery

In this section, the results of the chemical analysis of industrial wastewater samples taken from different areas of the Caspian Sea and the Oil Refinery are given. For this purpose, water samples were taken and analyzed from the catalytic cracking area of the Oil Refinery. Phenol and its derivatives, polycyclic aromatic hydrocarbons (PAH) and heavy metals were determined in water samples.

It is known that industrial waste water contains enough oil products. Industrial waste water and rainwater collected in the technological facilities and commodity parks of the Oil Refinery named after H. Aliyev undergo mechanical cleaning. These waters are then fed into biological treatment plants. Then industrial wastewater is treated in biological treatment facilities (50 thousand m^3/day). Cleaning is carried out in several stages. Thus, waste water is introduced into the first and second stage aeration tanks. Here, waste water is cleaned to a standard level, subjected to biological treatment and only then discharged into the sea. As a result, pollution affects all ecosystems. Pollution of the water layer also causes pollution of the air layer. As mentioned, quite a variety of gases enter the air during the operation of the chemical industry and the petrochemical industry. At this time, serious environmental problems arise as a result of releasing harmful gases such as hydrocarbon mixtures - C_xH_y, then CO_2, N_xO_y, SO_2 into the air.

The gases separated from the process are sent to the incinerator for burning at a temperature of 800-850^{0}C.

Then (medium pressure steam) gases are discharged into the atmosphere through a flue pipe at a temperature of 280^{0}C.

Oil products form an emulsion with water (oil sludge) and seriously pollute water bodies. The phenolic compounds remaining in the waste water become a source of real danger for the living layer of the water ecosystem. As a result, industrial wastewater causes serious damage to the environment in general. During the generation, storage and processing of oil sludges, harmful substances are released into the atmosphere, as well as the deep purification of industrial wastewater becomes difficult, such waters cause serious environmental problems in all ecosystems: atmosphere, hydrosphere, lithosphere layers. Also, industrial waste water discharged into the Caspian Sea after cleaning becomes a source of danger for its flora and fauna.

From this point of view, we took and analyzed waste water samples from the catalytic cracking area of the Oil Refinery. Table 1 below shows the results of the analyses.

Table 1.

Amount of phenol and its derivatives in wastewater taken from the Oil Refinery (in summer months)

Substances (mkg/l)	100	200	Total output
phenol	5.34	5.65	1.44
o-cresol	0.76	0.26	0.16
2-nitrophenol	0.59	0.48	0.08
2,4-dimethylphenol	31.99	8.71	0.20
m,p-cresol	20.59	3.81	0.85
2,6-dichlorophenol	1.14	0.67	1.80
4-chloro-3-methylphenol	0.63	0.43	0.69
2,4,5-TCP	0.48	0.28	0.18
2,4,6-TCP	0.14	0.04	0.25
2,3,4,6-tetrachlorophenol	0.27	0.18	0.002
2-methyl-4,6-dinitrophenol	<0.04	<0.04	<0.04
pentachlorophenol	0.27	0.25	0.06
2-sec-butyl-4,6-dinitrophenol	<0.08	<0.08	<0.08

The results suggest that phenol and its derivatives were not too much. The permissible concentration limit of phenol for the water ecosystem should be 0.1 mg/l. If we take into account that these waters are production waters, then the amount of phenol may be a little high (roughly, between 0.1-1).

PAHs and heavy metals were also determined in these water samples (table 2).

Table 2.

Amount of PAH in wastewater taken from three different points of the Oil Refinery (in summer months)

In water samples taken	Total output	200	100

from an Oil Refinery PAHs, µg/l	µg/l (mkg/l)		
naphthalene	0.08	0.23	20
acenaphthalene	0.02	0.51	15
acenaphthene	0.04	0.33	43
fluorene	0.24	0.81	80
phenenthrene	0.29	4.32	298
anthracene	0.04	0.33	26
flurontene	0.03	3.01	15
pyrene	0.05	13	66
benzo(a)anthracene	0.01	3.5	17
chrysene	0.02	15	41
benzo(b+k)fluoranthene	<0.01	2.2	5.0
benzo(a)pyrene	<0.01	1.3	5.0
indene(1,2,3-cd)pyrene	<0.01	0.37	1.5
benzo (ghi)perylene	<0.01	0.63	1.7
dibenzo(ah)anthracene	0.01	0.57	1.8

The highest pollution level was observed in the 100th tank. Quantitative and qualitative analysis was performed on an HP6890 GC instrument with a ZB-5 (Phenomenex, USA) column GC-MS (Agilent, USA) mass-selective HP5975 detector.

In addition, the amount of heavy metals in the water samples taken from the Oil Refinery was determined (table 3).

Among the heavy metals, cadmium (Cd) (0.001 mg/l (mg/dm^3)) exceeded the permissible concentration limit.

As this metal is toxic in nature, such waters are very harmful to the living world. The amount of lead (Pb) in sea water is 0.0003 mg/l. Like Cd, Pb has exceeded the permissible hardness limit. There may be various reasons for this. Unlike cadmium, lead is more common in minerals distributed throughout the earth. It is found in more than eighty minerals. Cobalt (Co) is present in seawater in amounts of $1.7\cdot10^{-10}$ mg/l. Drinking water should be many times less.

Table 3.

Determination of heavy metals in water samples taken from the Oil Refinery

Heavy metals, mg/l	100	200	Total output

Fe	0,044	0,042	0,043
Zn	0,111	0,067	0,002
Cu	0,022	0,023	0,020
Mn	0,0168	0,102	0,036
Pb	0,020	0,014	0,007
Cd	0,005	0,003	0,006
Cr	0,002	0,001	0,001
Co	0,007	0,010	0,008
Ag	0,006	0,008	0,006

Also water samples were taken from different areas of the Caspian Sea and analyzed. Phenolic compounds and polycyclic aromatic hydrocarbons (PAHs) were determined in seawater samples (table 4 and table5). Thus, in order to check the degree of contamination of water samples, were taken and analyzed. Phenol is more soluble in water. However, polycyclic aromatic hydrocarbons are hydrophobic and tarnish and sink to the bottom of the water. There is enough information about pyrogenic and petrogenic pollution of the Caspian Sea. For the purpose of ecological assessment of the environment, monitoring of water samples taken from several areas near the Caspian Sea was carried out; the chemical composition of the sea waters of Shikhov, Sahil, Guneshli, and other areas was analyzed.

It was noted that the waste water of the Oil Refinery is discharged into the Caspian Sea after partial treatment.

In this case, the increase in the amount of toxic substances in sea water becomes an undeniable fact.

It should be noted that water samples from some areas were taken and studied many times.

Table 4 shows the results of chemical analyzes of water samples taken from some areas.

Table 4.

Amount of phenolic compounds in water samples taken from four different areas of the Caspian Sea

Phenol, mkg/l	**Sahil**	**Shikov**	**Boulevard**	**Guneshli**	**Permis. limit**
phenol	0.14	0.10	0.14	0.12	0.01
o-kresol	0.06	0.02	0.03	0.02	0.01

2-nitrophenol	0.16	<0.04	0.04	0.04	0.01
2,4-dimethilphenol	0.15	0.02	0.04	0.03	0.01
2,4-diclorophenol	<0.02	<0.02	<0.02	<0.02	0.01
2,6-diclorophenol	0.11	0.02	0.04	0.12	0.01
4-cloro-3- methilphenol	0.21	<0.04	0.05	0.05	0.01
2,4,5-TCP	0.09	<0.04	<0.04	0.08	0.01
2,4,6-TCP	0.10	<0.04	<0.04	0.09	0.01
2,3,4,6-tetraclorophenol	0.09	<0.04	<0.04	0.08	0.01
pentaclorophenol	0.14	<0.04	<0.04	0.12	0.01

Table 5.

Amount of PAHs in water samples taken from four different areas of the Caspian Sea

PAHs, mkg/l	**Guneshli**	**Hovsan**	**Shikhov**	**Boulevard**
Naphtalene	0.09	0.19	0.07	0.04
Acenaphthylene	<0.01	<0.01	<0.01	<0.01
Acenaphtene	0.01	0.01	<0.01	0.05
Fluoren	0.04	0.07	0.04	0.07
Phenanthrene	0.09	0.17	0.06	0.17
Antrcene	0.01	0.01	<0.01	0.01
Fluoranthene	0.01	0.01	<0.01	0.01
Pirene	0.01	0.01	<0.01	0.01
Benzo (a) anthracene	<0.01	0.00	<0.01	0.00
Chryzen	0.02	0.01	<0.01	0.01
Benzo (b + j+ k) fluoranthene	0.01	0.03	0.03	0.03
Benzo (a) pyrene	0.01	0.01	<0.01	0.01
İndeno	<0.01	<0.01	<0.01	<0.01
(1,2,3-cd) pyrene				
Benzo perylene	<0.01	<0.01	<0.01	<0.01
Dibenzo(ah)a nthracene	<0.01	<0.01	<0.01	<0.01

Polycyclic aromatic hydrocarbons were also determined in water samples. In some water samples, the permissible concentrations of the determined substances have been exceeded.

All compounds of organic origin increase the level of water pollution either completely or partially by their presence in water. Based on the results of the above analysis, it should be noted that industrial waste water is more dangerous in this respect. They cause excessive pollution of sea and river water.

It should be noted that the amount of polycyclic aromatic hydrocarbons in water samples varies depending on the temperature factor, degree of pollution and other factors. In general, since the water system is a dynamic system, the indicators of the samples can change frequently. However, in cold and hot months, changes in the amount of polycyclic aromatic hydrocarbons and phenolic organic compounds in water samples occur at certain intervals. The amount of polycyclic aromatic hydrocarbons in the examined water samples exceeded the norm (especially in the case of naphthalene). This is due to the fact that the cyclization of hydrocarbons occurs mainly in the catalytic cracking and reforming processes, and in the reforming process mainly aromatization occurs.

Air and water ecosystems were taken as the main object of study in the work under review. The main direction of research was to study the factors influencing the pollution of both environments. Currently, the problem of air pollution and water ecosystems is the most important of the serious global ecological problems.

Against the background of air pollution, the greenhouse effect, against the background of the increasing greenhouse effect, the reduction of fresh water resources due to the melting of glaciers and the mixing of fresh water with dirty water, pollution of ecosystem waters, the need for fresh water is growing every day.

To this end, scientific research was carried out in the direction of taking serious steps to solve problems arising in the air and water environments in the dissertation work under consideration. As is known, the ecosystems of the biosphere are closely connected with each other, and pollution of one ecosystem leads to pollution of other ecosystems.

On the other hand, the oil industry, which is important for Azerbaijan, causes pollution of both air and water ecosystems.True, pollution does not bypass the soil ecosystem, but since the soil layer is less dynamic than the air and water ecosystems, pollution is more pronounced in these two systems.

Since almost 85% of the oil in the Refinery is used to obtain the fuel used in the automotive industry, the oil industry is very closely related to the automotive industry. Air damage caused by automobile traffic (especially in Baku city) is one of the most prominent negative effects today. Therefore, many of the smoke gases produced during the operation of car engines and fuel combustion are directly involved in the formation of greenhouse gases, and some of them cause second types of pollution. At this time, it is a separate issue that the additives added to the fuel meet environmental standards and do not have a toxic effect, and it is very important from an environmental point of view. At the same time, it is very important from the environmental point of view that the additives added to the fuel have a minimum level of smoke reduction. As a result, it is very important from the environmental point of view that the smoke gases emitted from motor vehicles do not have a negative effect.

On the other hand, as a result of the chemical processes occurring in the oil refining industry, the introduction of phenol-type compounds into the air, along with many organic and inorganic compounds, leads to serious environmental problems. Since phenol is a toxic substance, its presence in air and water is very dangerous. In particular, it is worth noting here the negative impact of the waste water of the petrochemical industry on the flora and fauna of the water ecosystem.

Later, the purification of toxic phenol from waste water using nano technological methods will be considered. In this case, we will talk about the perspective of methods of purification of phenolic compounds from waste water using nano approaches.

For this purpose, TiO_2 nanoparticles with a rutile phase with a size between 10-30 nm were used in the research.

Investigation of photochemical degradation of phenol in the presence of TiO_2 nanoparticles from wastewater

In this section, the photo catalytic properties of TiO_2 nanoparticles were investigated. The light absorption properties of TiO_2 nanoparticles have been studied and due to this property, they have been widely used in photo catalytic reactions. Using different systems, photo catalytic reactions of 10-30 nm TiO_2 nanoparticles under ultraviolet radiation were carried out. Photochemical decomposition of phenol with 99% yield was achieved. TiO_2 with photo catalytic properties is widely used in chemical reactions; it is obtained in different ways. Its recombination occurs during chemical reactions and its photo catalytic properties are weakened. TiO_2 nanoparticles are widely used for the solution of this problem: formation of nanostructures, lack of oxygen (due to electro acceptor), chemical alloying, surface sensitization, use of nano composites.

Until now, the decomposition of toxic compounds of organic origin in the water environment was carried out by the method of deposition of precious metals such as silver, gold, and platinum on the surface of TiO_2, based on the increase of its photo catalytic efficiency. These reactions considered are heterogeneous photo catalysis reactions. Heterogeneous photo catalysis is a transfer oxidation process. On the basis of this process, large-scale decomposition or destruction of pollutants in the air and water environment took place. So far, photo catalytic oxidation or mineralization of phenol has been carried out in the presence of "Degussa P25" (a TiO_2 suspension consisting of 80% anatase and 20% rutile phase). Reactions with titanium 4-oxide in the anatase form are often reported in the literature. It is considered that using its mixed form (together with anatase) is more efficient. TiO_2 modification with anatase form with a size of 42.39 nm was used during the research. Based on the XRD analysis, it was determined that the tetragonal modification has an anatase form. The curves obtained from the analysis of TiO_2 with anatase form completely coincided with the bibliographic data of the XRD device.

We used rutile phase TiO_2 nanoparticles. This modification is more resistant to high temperature. As we know, the most common rutile phase titanium 4-oxide is found in nature, it is the most common mineral on earth. From this point of view, from the economic point of view, rutile phase titanium 4-oxide is efficient and easy to obtain, so it is more appropriate to use it in reactions. Also, from an environmental point of view, this substance is non-toxic. Therefore, it is appropriate to use it in solving environmental problems. Therefore, TiO_2 is currently a very demanding material in the world. Rutile-phase TiO_2

modification has not been widely used in photo catalytic reactions, there is almost no information about it.

The reaction of TiO_2 with Degussa mixture took place under completely different conditions. Photodecomposition was carried out in the presence of two high-pressure Hg lamps: 254 nm (15W) and 365 nm (400W). Effects of mixing speed, initial concentration of phenol, amount of catalyst, pH of suspension and medium, light intensity and other factors on the decomposition process were also studied. These parameters were studied to find the optimal conditions for rapid and complete decomposition of phenol. Kinetic studies were carried out at a temperature of 32°C when the concentration of phenol was 2.5-25 mg/l. The process was carried out in a spiral reactor in the presence of a constant light flood. It should be noted that the effectiveness of the process depends greatly on the conduct of the experiment. In the reaction, TiO_2 was taken in the concentration range of 0.1-1 g/l, and the pH of the suspension was between 3-9. In the process, the dependence between millivolt (mV) and the pH of the medium was also studied. Among the heavy metals, cadmium (0.001 mg/l (mg/dm^3)) has exceeded the maximum limit. Since this metal is toxic, such waters are harmful to living creatures. On the basis of the study of TiO_2 nanoparticles and ultraviolet radiation, photochemical decomposition reactions of phenol were carried out.

Complete purification of phenol from water remains a global environmental problem. Until now, various physico-chemical and biological methods have been used for cleaning purposes. When using sorbents, when using chemical reagents, these substances remain in water and there are difficulties in their cleaning. Therefore, methods should be developed that use a small amount of chemical reagents and are environmentally effective. In this regard, the purification of phenol from waste water was carried out using TiO_2 nanoparticles and positive results were obtained from the environmental point of view. For this purpose, TiO_2 nanoparticles with rutile phase were used in all conducted photochemical reactions.

Information on the participation of TiO_2 nanoparticles with rutile phase has not been found in the literature, the work done by us is new in this respect. However, there is information in the literature that TiO_2

with rutile phase is a very good photo catalyst, as well as having an energy capacity. Based on this feature, it is used in photo catalytic reactions based on sunlight. Therefore, the use of TiO_2 in photochemical reactions has been expanding recently.

There is a lot of information about the photo catalytic properties of TiO_2 nanoparticles. Heterogeneous catalysis reactions mainly take place with TiO_2. From this point of view, phenol solutions of different concentrations were taken and researches were conducted on the basis of them in laboratory conditions.

In our case, first of all, phenol solutions of different concentrations were prepared and based on them, photochemical reactions were observed. 0.05 grams of TiO_2 nanoparticles were used in the reactions. It should be noted that earlier reactions were carried out with very solid phenol solutions. For this purpose, phenol solutions with concentrations of 5 and 10 g/l were taken and their reactions with TiO_2 nanoparticles were carried out in the presence of ultraviolet radiation. The purpose of taking phenol solutions at different concentrations was to determine at which concentration TiO_2 nanoparticles would have an effective effect on the phenol solution. At that time, the highly sensitive "Varian Cary 50" spectrophotometer, the mixture obtained after the photochemical reaction of high concentration phenol solutions gave signals outside the scale of the device. Obtaining a high error means that it is necessary to increase the concentration of TiO_2 nanoparticles in order for the photochemical reaction to proceed in phenol solutions at high concentrations. In this case, it is impossible to measure the solution obtained in the form of a suspension in a sensitive spectrophotometer. Almost no photochemical degradation occurred between 10 g/l phenol solution and 0.05 g of TiO_2 nanoparticles; at this time, only 0.01% phenol photochemical decomposition occurred. Later, studies were continued on the basis of 5 g/l phenol solution.

At this time, the photochemical decomposition of phenol in the presence of TiO_2 nanoparticles was very low. In the process, after photochemical degradation of 5 g/l phenol solution, 92% phenol remained in the solution, which means that only 8% of phenol underwent photochemical degradation. Since TiO_2 nanoparticles aggregate in solid solutions, dissociation or decomposition is poor. However, in the presence of TiO_2 nanoparticles in solid phenol solutions, photochemical decomposition was more effective. For this purpose, 1 mg/l phenol solution was used.

The photochemical decomposition reactions of phenol based on the study of TiO_2 nanoparticles and ultraviolet radiation were studied. Photochemical decomposition of phenol-based on ultraviolet radiation in a 1mg/l phenol+ TiO_2 system was considered. A phenol solution of 1 mg/l was used for the purification of phenol from aqueous solutions. 99% photochemical dissociation of this solution took place using rutile phase TiO_2 nanoparticles in the presence of ultraviolet radiation (table 6). Compositional analyses of TiO_2 nanoparticles used in the process were carried out.

Table 6.

Results of reaction mixture analysis after photochemical process in 1 mg/l phenol+TiO_2 mixture

Compounds	**discount rate (mkg/l)**
phenol	10,0
o-kresol	4,8
m+p-methilphenol	4,9
2-nitrophenol	0,5
2,4-dimethilphenol	2,5
2,6-diclorophenol	1,2
4-cloro-3-methilphenol	0,9
2,4,5-TCP	1,2
2,4,6-TCP	1,7
2,3,4,6-tetraclorophenol	0,0
pentaclorophenol	0,0

It should be noted that when the same reaction was carried out for five hours instead of one hour, the amount of phenol derivatives shown in table 6 decreased sharply. This is explained by the fact that the decomposition of substances in the reaction mixture depends linearly on the time of the photochemical process. That is, the longer the process, the greater the breakdown products.

After the photochemical process, the reduction of phenol remaining in the solution was observed from 1 mg to 10 µg, which means 99% decomposition of phenol. Compositional analyzes of TiO_2

nanoparticles used in the process were carried out.

The photochemical reactions of 2 mg/l phenol solution in the presence of graphene oxide and TiO_2 nanoparticles ($GO+TiO_2$), as well as Al_2O_3 nanoparticles were considered. For this purpose, 5 ml of the solution obtained after complete mixing of 0.05 g of graphene oxide (GO) nanoparticles and 0.05 g of TiO_2 nanoparticles in 10 ml of distilled water was taken and added to 20 ml of 2 mg/l phenol solution (25 ml in total).

Initially, $GO+TiO_2$ system was used for photochemical decomposition of phenol. This mixture was irradiated under UV irradiation for one hour. The photochemical decomposition of phenol in the considered process was 40.8%.

As a second system, a 5 ml solution of 0.05 grams of Al_2O_3 nanoparticles dissolved in water was prepared and added to a total volume of 20 ml of 2 mg/l phenol solution. Unlike the reaction with TiO_2 nanoparticles, no photochemical reaction occurred in the reaction in the presence of Al_2O_3 nanoparticles and ultraviolet radiation. During the photochemical reaction in the presence of ultraviolet rays, Al_2O_3 nanoparticles were observed to sink to the bottom of the reaction flask from the first moments of the process. Thus, it can be said that the process is not going on here. This is a manifestation of Al_2O_3 nanoparticles not having photocatalytic properties. SEM analysis of the TiO_2 nanoparticles in the process was carried out on a JEOL JSM-7600F (15kV voltage, SEI mode) device, and the result of the analysis is shown below (figure 3).

The size of TiO_2 nanoparticles was between 10-30 nm. The results were confirmed by XRD analysis (figure 4).

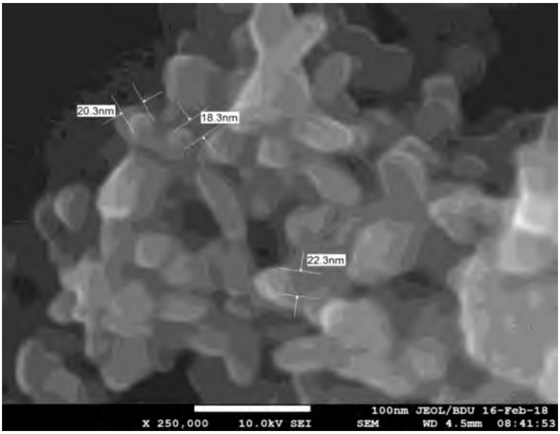


Figure 3. SEM analysis of TiO_2 nanoparticles

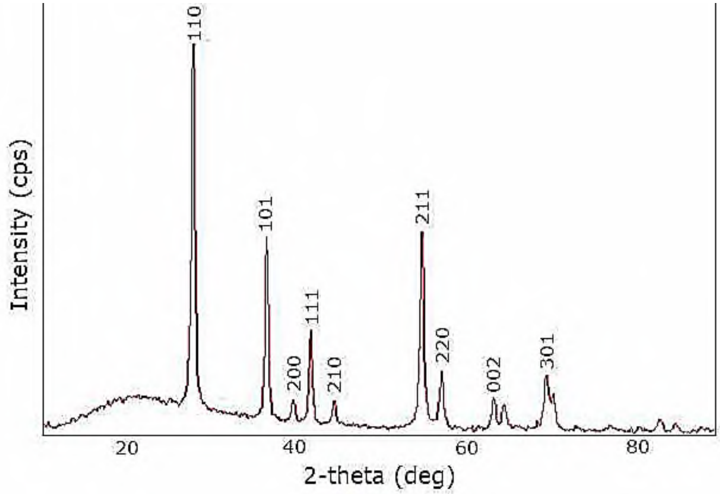


Figure 4. XRD analysis of rutile phase TiO_2 nanoparticles

The crystallinity and purity of TiO_2 nanoparticles with rutile phase were determined by the XRD method on a Mini Flex 600 X-ray diffraction measuring device. X- ray structural analysis graphs of the investigated nano composite materials were recorded on a Rigaku Mini Flex 600 powder diffract meter. An X-ray tube with a copper anode (Cu-Kα radiation, 30 kV and mA) was used to take diffraction spectra at room temperature. These spectra were obtained in the $2\theta =$

20°-80° discrete increment mode $\Delta 2\theta = 0.05°$ and the exposure time was τ=5 seconds.

Determination of the crystallinity and purity of TiO_2 nanoparticles by the XRD method was carried out on a MiniFlex 600 X-ray diffraction measuring device. Repeatedly, XRD analysis was performed for TiO_2 nanoparticles.

The XRD spectra of the TiO_2 nanoparticles are shown below. All the peaks were probed sensitively and the TiO_2 nanoparticles corresponded to the rutile phase. According to the Scherer method, according to the diffraction point (101), the average size of TiO_2 was 10.3, and the specific surface area of the crystals was 159.6 m^2/g. Signals for TiO_2 nanoparticles had characteristic peaks at 27.90° (110), 36.01°(101), 41.58°(111), 54.71°(211).

For the process, 20 ml of 1 mg/l phenol solution was taken, 5 ml of solution containing 0.05 mg of white TiO_2 nanoparticles (25 ml in total) was added, and photochemical dissociation of this solution was carried out in the presence of UV radiation. The process lasted for an hour. The photolysis product was quantitatively analyzed by mass chromatography and the phenol degradation was 99% (figure 5).

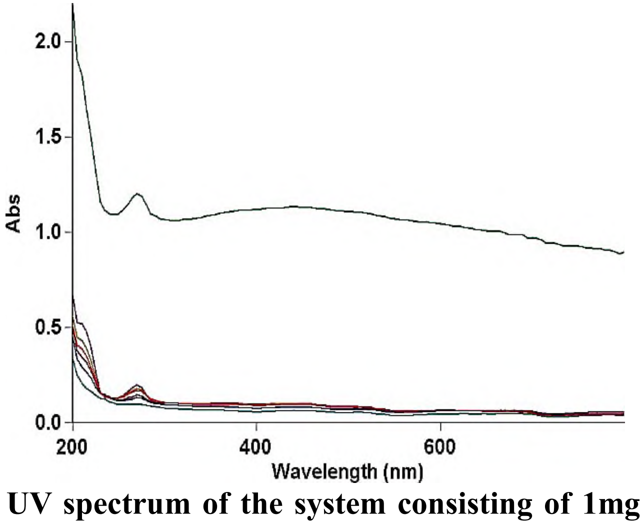


Figure 5. UV spectrum of the system consisting of 1mg/l phenol solution and TiO_2 nanoparticles after the photochemical process

-green line- the curve drawn before the photochemical reaction of the phenol solution;

-blue line is a curve drawn 1 hour after the photochemical reaction. As can be seen from figure 5 the concentration of phenol decreased sharply from the green line to the blue line. Thus, while a sharp swelling was observed in the green curve in the 270 nm range typical for phenol, this swelling was not observed in the blue curve as time passed. This is explained by a sharp decrease in the amount of phenol in the reaction mixture.

The general appearance of the chromatogram of the studied reaction mixture after the process is shown in figure 6. In this way, according to table 6, the names of each of the substances in the reaction mixture are listed.

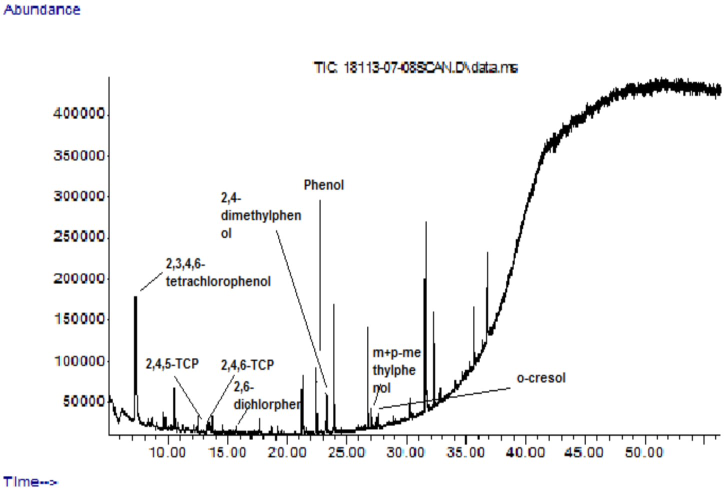


Figure 6. General view of the mixture chromatography after the 1mg/l phenol solution+ TiO$_2$ reaction

Molecular spectra (MS) of some of the substances obtained after photochemical degradation are shown. Molecular spectra provide information on the molecular mass of the substances present in the reaction mixture after photochemical decomposition (figure 7).

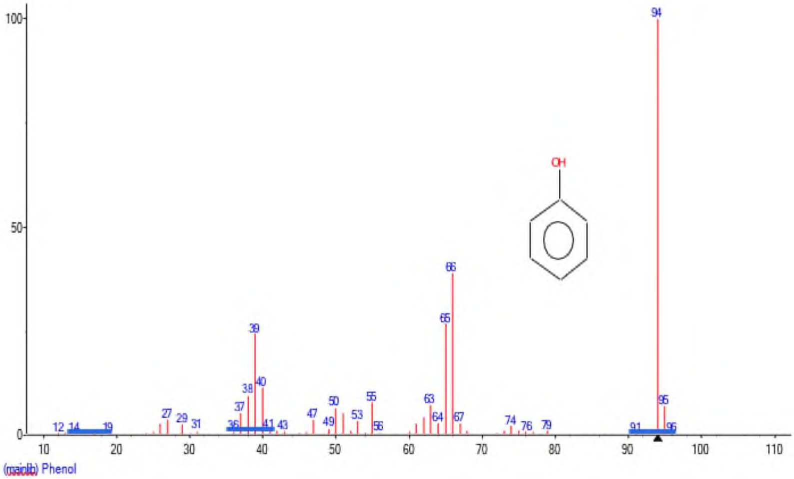
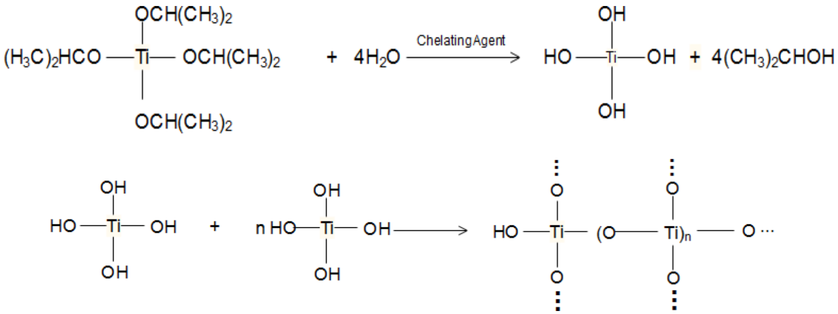


Figure 7. Molecular spectrum of phenol

TiO_2 nanoparticles used in the process were synthesized according to the sol-gel method. TiO_2 nanoparticles (IV) used in the process were synthesized according to the sol-gel method of titanium isopropoxide. Process (IV) proceeded with the formation of $Ti(OH)_4$ based on the hydrolysis of titanium isopropoxide. Ti-O-Ti bond breaking occurred due to low hydrolysis rate and as a result nanoparticles were formed due to $Ti\ (OH)_4$ decomposition. TiO_2 nanoparticles obtained from the reaction were used for conducting a series of photochemical reactions. A small amount of TiO_2 was used in each process. The course of the reaction is shown below.



The same process was carried out in the presence of nitrogenfixing agents (methyl3-aminocrotonate). For the process, 20 ml of 1 mg/l phenol solution was taken, 0.05 mg of white TiO_2 nanoparticles and 0.05 mg of methyl 3-aminocrotonate were added to it. In the presence of 10-30 nm TiO_2 nanoparticles and methyl3-aminocrotonate, the photochemical dissociation of 1 mg/l phenol was 60% (table 7), and in the presence of 10-20 nm TiO_2 it was up to 80%. At this time, the photolysis process extended from the ultraviolet field to the visible field, which ultimately increased the practical importance of the considered work.

Table 7.

Results of reaction mixture analysis after photochemical process in 1 mg/l phenol+methyl3-aminocrotonate+TiO_2 mixture

Substances	Rate (mkg/l)
phenol	0,40
o-kresol	0,62
m+p-methilphenol	0,54
2-nitrophenol	0,20
2,4-dimethilphenol	0,90
2,6-diclorophenol	0,48
4-cloro-3-methilphenol	0,36
2,4,5-TCP	0,48
2,4,6-TCP	0,66
2,3,4,6-tetraclorphenol	0,00
pentaclorophenol	0,00

It is assumed that the oxidation of phenol in the presence of N+ TiO_2 nanoparticles and UV radiation in the process of photochemical dissociation proceeds as follows:

TiO_2+N organic matter+H_2O+hv→ TiO_2-N(e-+ h+)
Phenol+$OH^{\cdot}$ → oxidation products (visible area)
Phenol + (e-) → oxidation products (visible area)
Phenol +(h+) → oxidation products (visible area)

In the process, the abundance of nitrogen atoms ensures that the photochemical decomposition passes from the UV area to the visible area due to the absorption of sunlight. From this point of view, it is very important to develop methods of maximum purification of waste water and to eliminate toxic substances from it. The main difference of the research work presented by us from other scientific works is that the synthesized TiO_2 nanoparticles have a rutile phase. The rutile phase is more common in nature, easy to obtain and non-toxic. The advantage of the process is that by using a simpler method, the photolysis reaction took one hour in the presence of UV radiation and 99% phenol decomposition was achieved. As already mentioned, the electronic configurations of carbon, nitrogen and oxygen elements are considered to be close to each other, and it is theoretically interesting how the photo catalytic property of TiO_2 changes in carbon+nitrogen systems.

There are scientific studies on reactions carried out in carbon systems. It should be noted that there are more scientific studies with nitrogenous systems than with carbonaceous systems in the literature.

Photochemical decomposition reactions of phenol using several organic compounds containing both carbon and nitrogen and TiO_2 nanoparticles were studied by us. As a continuation of the reactions taking place in the phenol+carbon and nitrogen compounds+TiO_2 system, the non-toxicity of the newly synthesized organic substance ethyl-3,3,5,5-tetracyano-2-hydroxy-2-methyl-4,6diphenyl cyclohexane carboxylate and taking into account the possibilities of its use in the preparation of medicinal preparations, it was used in the course of the photochemical reaction. The synthesized new compound was confirmed by X-ray structure analysis. The photochemical reaction with this substance was carried out in the same way as in the reaction with methyl3-aminocrotonate. The process lasted for an hour. At this time, the photochemical decomposition of phenol was 52%. It is believed that the complex structure and nature of the substance affected the photochemical decomposition of phenol in the reaction.

TiO_2 with rutile phase is more common in nature, easy to obtain and non-toxic. As already mentioned, since the electronic configurations of carbon, nitrogen and oxygen elements are consecutive and considered close to each other, how the photo catalytic property of TiO_2 changes in carbon+nitrogen systems has become of interest.

In the literature, there are scientific studies on photochemical reactions carried out in carbonaceous systems. However, it should be noted that there are more scientific studies with nitrogen systems than with carbon systems. In this regard, photochemical reactions in both systems were considered.

The reaction mixture consisting of phenol solution, methyl3-aminocrotonate and TiO_2 nanoparticles was irradiated in the presence of ultraviolet (UV) radiation for one hour and the reaction mixture was subjected to photochemical decomposition. After the photochemical process, the wavelength dependence of the adsorption coefficient of the reaction solution in the UV irradiating device was measured. The photochemical degradation of phenol after the process was studied and was 60%.

At this time, it was possible to extend the process of photochemical decomposition of phenol from the ultraviolet radiation area to the visible radiation area by using compounds that retain nitrogen and carbon. However, these reactions took place better in the presence of nitrogen-containing compounds. In this regard, nitrogen-retaining compounds were used; the course of the process in the presence of methyl 3-aminocrotonate is shown below.

A mixture of 0.05 grams of TiO_2 nanoparticles dissolved in 10 ml of distilled water was prepared for the purpose of carrying out the reaction in the phenol+ methyl3-aminocrotonate+ TiO_2 system. 5 ml of this mixture was taken and added to 20 ml of phenol solution (25 ml in total) and then 0.05 g of methyl 3-aminocrotonate was added. The reaction mixture was carried out in the presence of ultraviolet (UV) radiation for one hour and the reaction mixture was subjected to photochemical decomposition. After the photochemical process, the wavelength dependence of the adsorption coefficient of the reaction solution in the UV irradiating device was measured. The photochemical degradation of phenol after the process was studied and was 60%. It should be noted that the photochemical reactions in cases where the sizes of TiO_2 nanoparticles are between 10-20 nm and 10-30 nm (sometimes 10-32 nm) were also considered separately. In the first case, the photochemical decomposition in the process was 80%, and in the second case it was 60%. From this, it can be concluded that the photolytic properties of TiO_2 nanoparticles are more effective when they are smaller in size. This is explained by the fact that the number of active collisions is high and the reaction is more intense. On the other hand, when photochemical decomposition reactions occur in carbon and nitrogen storage systems based on UV radiation, it extends into the visible area. This increases the practical importance of the process and allows such reactions to be widely used in practice based on visible light rather than UV radiation. In our case, the TiO_2 photo catalyst was investigated by X-ray diffraction (XRD). In addition, there are scientific studies on the study of various photo catalysts by X-ray photoelectron spectroscopy (XPS), gravimetric-differential thermal analysis (TG-DTA), UV- visible (UV-Vis) and reflection spectrum method (UV-Vis-DRS) in the literature. The photo catalytic activity of the considered nitrogenous compounds was confirmed by excitation under UV or solar radiation. When these substances are doped with TiO_2, they absorb strong solar rays due to the decrease of oxygen and the increase of nitrogen atoms in the molecule, due to the closeness of the electronic structures (2pe-) in the molecule.

Based on this, photo catalytic excitation in phenol + methyl 3-aminocrotonate +TiO_2 systems can pass from UV radiation to the visible phase (figure 8). Below is a comparative characterization of the photochemical radiation for the phenol+methyl3-aminocrotonate+TiO_2 system.

According to the comparison of the curves obtained after the photochemical decomposition process, the bumps characteristic of phenol in the 270 nm area gradually decrease in certain time limits, and this indicates the gradual photochemical decomposition of phenol. Quantitative analysis of phenol based on mass chromatography after photochemical decomposition was performed and the results were confirmed. The pH of the medium was also determined during the course of the photochemical reaction. The pH change of 1 mg/l phenol solution was determined by "PHS-25" device.

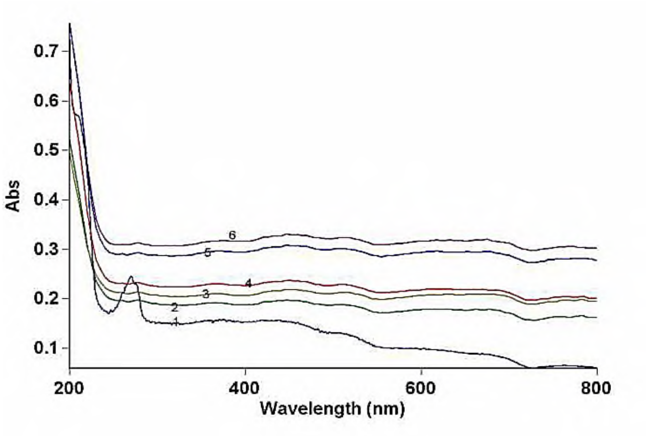


Figure 8. Comparison of spectra based on photochemical radiation for phenol + methyl 3-aminocrotonate+TiO_2 system
curve 1 - before the photochemical process;
curve 2 - in the 60th minute of the photochemical process;
curve 3 - in the 55th minute of the photochemical process;
curve 4 - in the 50th minute of the photochemical process;
curve 5 in the 45th minute of the photochemical process;
curve 6 - taken at the 40th minute of the photochemical process.

It was determined that the decomposition of TiO_2+ phenol+methyl3-aminocrotonate solution proceeds better in an acidic environment. The most optimal condition for the process was pH=4.

Figure 9 shows the dependence of the photochemical dissociation of the phenol solution on the pH of the medium.

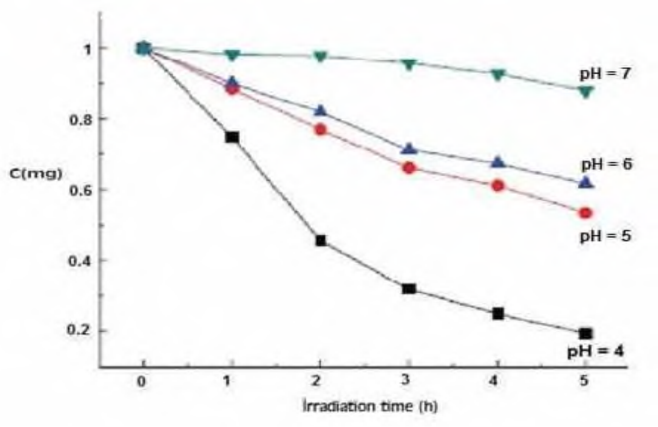


Figure 9. Dependence of photochemical dissociation on the pH of the medium in the 1 mg/l phenol+TiO_2+methyl3- aminocrotonate system

It is believed that in an alkaline medium, phenol changes its structure and becomes a tautomer, and in this case, the phenol molecule becomes difficult to dissolve. However, in an acidic environment, it is easier to detach this functional group from the benzene nucleus, which is connected to the hydroxyl group, and as a result, the phenol molecule breaks down. It should be noted that the photo catalytic properties of TiO_2 nanoparticles with either anatase or rutile phase are clearly more active in an acidic environment.

The light absorption and light emission of nanoparticles with the rutile phase are shown in the following figures (figure 10 and figure 11).

It would be sufficient to show one of the spectra taken on a “Specord 250” spectrophotometer, but both the absorption and emission spectra of TiO_2 nanoparticles with a rutile phase are shown. It can be seen from the images that after ultraviolet irradiation of TiO_2 nanoparticles, the highest peaks were obtained for TiO_2 at wavelengths of 300-350 nm. Starting from this wavelength (350 nm), the emission of the UV spectrum increases dramatically.

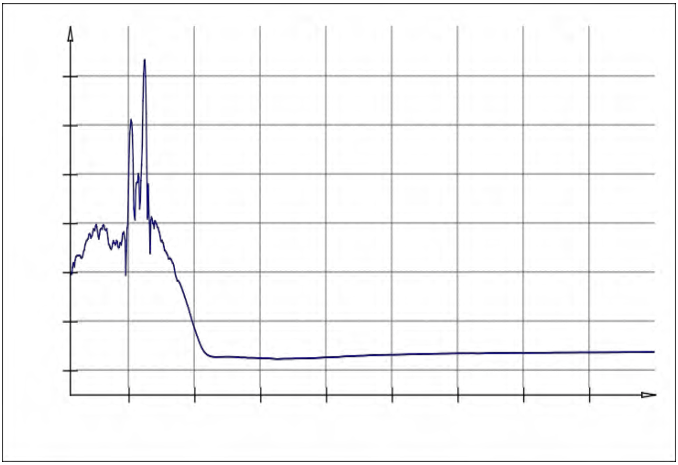


Figure 10. Light absorption of TiO_2 nanoparticles with rutile phase

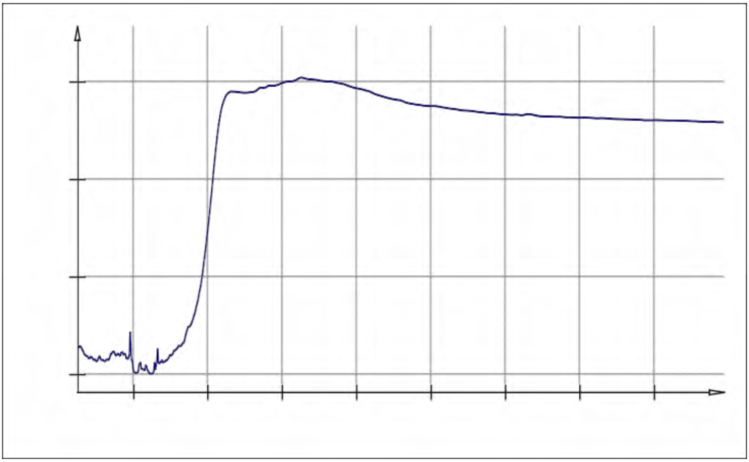


Figure 11. Light emission of TiO_2 nanoparticles with rutile phase

Quantitative analysis of the dissociation of phenol in the process was carried out on a high-performance Agilent 5975 mass-selective detector equipped with a 6890N gas chromatograph (figure 12).

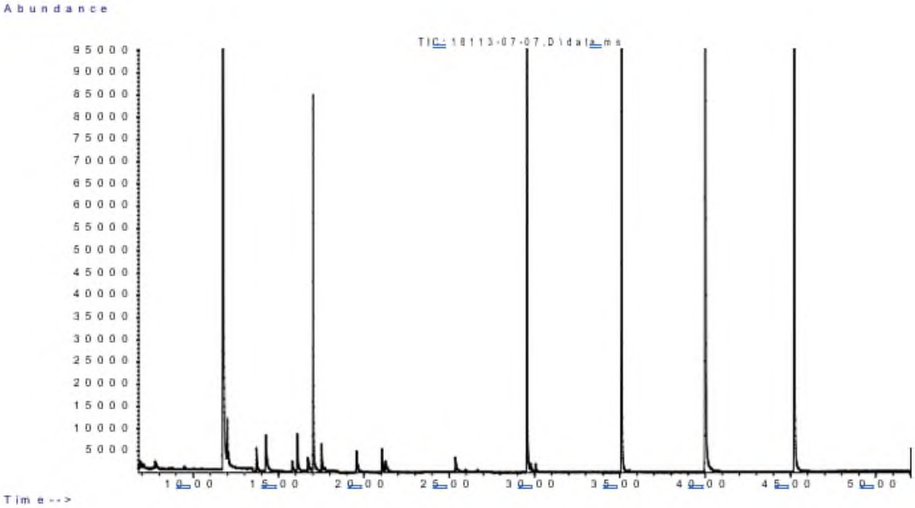


Figure 12. General view of the mixture chromatography after the 1mg/l phenol solution+ methyl3-aminocrotonate+TiO_2 reaction

In addition, the photochemical decomposition of phenol in the presence of TiO_2 nanoparticles was also studied in the seawater sample.

The photo catalytic decomposition of phenol in seawater taken from Shikhov and Boulevard areas of the Caspian Sea was considered. The process was studied as above for one hour. It is known that the composition of seawater is multi-component and rich in organic components, so it is considered that longer time is needed for the complete decomposition of phenol. However, since it is a comparative study, the process was carried out within one hour, as in other processes. The curves obtained from the photochemical process were as follows (figure 13).

An overview of the chromatogram of the seawater sample is shown in figure 14.

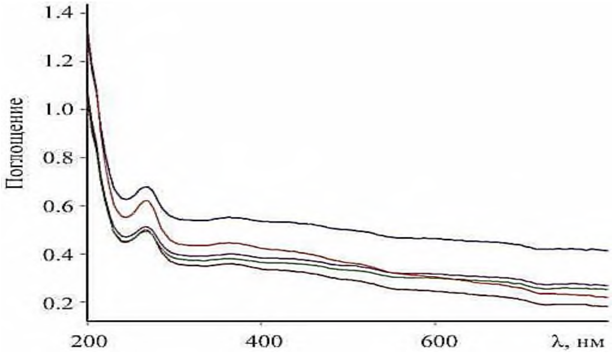


Figure 13. Curves obtained on a “Varian Cary 50” after photochemical processing for a seawater sample

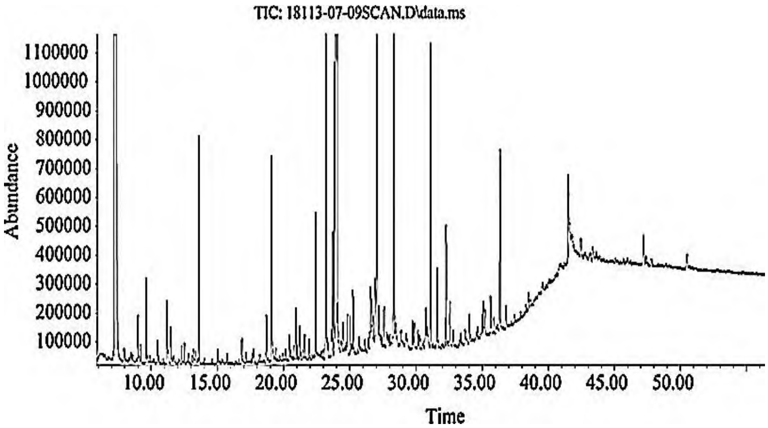


Figure 14. General view of seawater sample chromatogram

As can be seen from the received spectrum, the signals received at different times indicate the presence of many substances in the seawater sample. It was found that the photochemical decomposition of phenol in sea water is 38-40% within one hour. Many factors influence the low-yield degradation of phenol in seawater. Temperature, pH factor and, most importantly, the variety of substances present there and multi-component environment are one of the main factors here. Since there are many toxic organic substances in seawater, it is necessary to select more optimal conditions for the photochemical reaction to proceed.

Investigation of the adsorption of phenol-contaminated waters in the presence of TiO_2 nanoparticles

In this section, the adsorption properties of TiO_2 nanoparticles with rutile phase were investigated. For the purpose of comparison, the adsorption of phenol solution in other systems was considered. First, the adsorption of phenol in the phenol+graphene oxide (GO) system was considered.

It is known from the literature that TiO_2 nanoparticles with anatase form do not show adsorption capacity. In this regard, in addition to the study of the photo catalytic properties of TiO_2 nanoparticles with a rutile phase, we also studied the adsorption capacity of nanoparticles. In addition to the purification of phenolic organic substances by photo catalytic method, the purification of phenol from wastewater by adsorption method was also investigated. For this, the adsorption of phenol in different systems was studied. Adsorption processes in the presence of TiO_2 nanoparticles were also conducted and compared.

One of the widely used methods in wastewater treatment is adsorption. Depending on the nature of the absorbed adsorbent, the efficiency of the adsorption process can increase or decrease. It is known that graphene oxide (GO) is a very good adsorbent. In addition, activated carbon (C) is also known to have adsorption capacity. Taking into account the adsorption properties of both substances (GO and C), the adsorption of phenol solution in the presence of these substances was considered for the purpose of comparison. Then, the adsorption of phenol solution in the presence of TiO_2 nanoparticles was studied and compared with the previous two systems.

GO-graphene oxide is the oxidation product of graphite, which is an allotropic form of carbon. Its molecule has various functional groups with an active center. Therefore, GO with active centers is a very good adsorbent. Graphene oxide is a cheap raw material and is stable. Many studies show that GO membrane has very good ion and molecular selectivity properties and water permeability. In this regard, we have used graphene oxide to remove phenol from wastewater. GO is obtained by oxidation of carbon (graphite). In the presence of water and under high pressure, the lattice of graphene oxide expands. Graphene oxide is marketed as a raw material. But it takes a long time to get it in laboratory conditions.

Graphene oxide (GO) consists of functional groups, and its layered structure makes it exhibit stronger adsorbent properties based on these functional groups.

Graphene oxide is a blackish-gray solid. Due to excessive oxidation, the dark yellow color can pass; in this case, the C:O ratio in the substance varies between 2.1-2.9. Many structures have been given for graphene oxide, it has a complex amorphous structure. At the same time, there are no special analytical methods to characterize such structures. Therefore, different structures of graphene oxide have been given by different scientists at different times. According to many scientists, graphene oxide forms a single layer of graphite oxide, that is, graphene oxide is a mono-molecule of graphite. According to other scientists, graphene is composed of oxide layers. Due to the irregular distribution of the layers, it has not been possible to give the exact structure until now. The thickness of graphene oxide layers varied between 0.9-1.3 nm. According to X-ray photoelectron spectroscopy, the structure analysis of graphene oxide was carried out and 284.8 eB for carbon atoms that do not contain oxygen atoms in the molecule, 286.2 eB for O-C, 287.8 eB for C=O and 289.0 eB for O=C=O were determined. has been done.

In this case, the adsorption of phenol in the phenol+GO system was investigated.

The process was carried out for two hours at 25^0C at room temperature. Adsorption went well in this system and eventually no signals were obtained in the 270 nm region corresponding to phenol. The progress of the adsorption process was studied in a spectrophotometer. Based on the curves drawn after the adsorption of the solution at room temperature for two hours, it can be said that no corresponding relief was observed in the spectrum corresponding to phenol (in the 270 nm region), which indicates complete adsorption. The process was repeated. It should be noted that the adsorption process weakened as the concentration of phenol in the solution increased, but the process accelerated as the amount of graphene oxide increased (0.02; 0.03; 0.05 g). Adsorption progress is definitely influenced by temperature, amount of adsorbent and other factors, so these parameters were kept constant in all systems.

Below, samples were taken from the solution at 60, 100 and 120 minutes and the curves drawn and obtained in the spectrophotometer were compared (figure 15). In the considered process, the adsorption is complete.

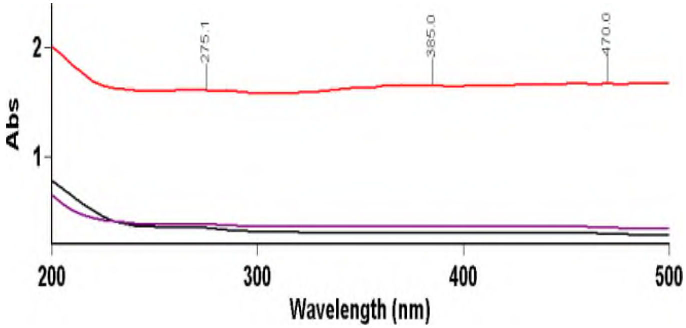


Figure 15. Comparison of curves obtained at 60, 100 and 120 minutes

Black line - 60's, purple line - 100th, and the red line is the curves drawn at 120 minutes.

Below is the curve obtained after adsorption of a mixture of 1 mg/l phenol solution with graphene oxide (figure 16).

The adsorption of phenol in the phenol+C system was also studied (figure 17). The process was carried out in the same way as in the previous system. The conditions were taken the same and the adsorption went well. This can be seen from the curves drawn in the spectrophotometer.

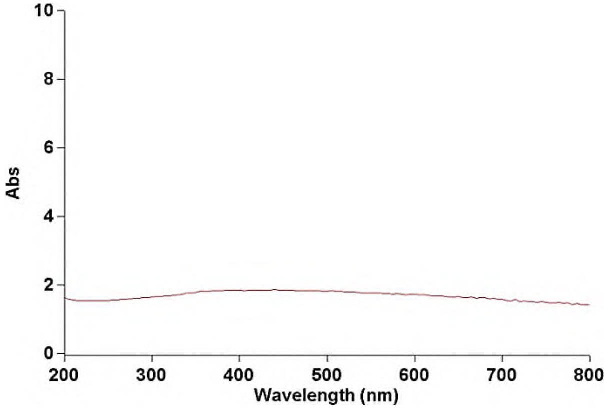


Figure 16. UV curve of a mixture of 1 mg/l phenol solution with graphene oxide after the process

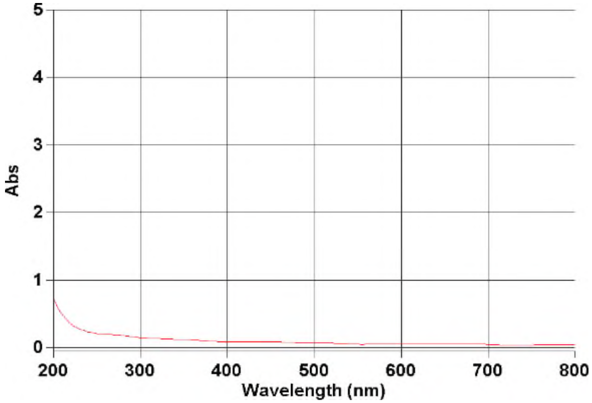


Figure 17. UV curve of the mixture of 1mg/l phenol solution with activated carbon after the process

Adsorption properties of TiO_2 nanoparticles with rutile phase were investigated by us. It is known that TiO_2 nanoparticles with rutile phase have very good photo catalytic properties by absorbing more light due to their crystal lattice. To what extent it has adsorbent properties was determined based on the conducted research. Thus, the use of TiO_2 nanoparticles with photo catalytic properties as adsorbent has many advantages. These advantages include the following:

1. TiO_2 is chemically and thermally stable;
2. On the other hand, TiO_2, which has a photo catalytic effect, is widely used in cleaning toxic substances from various materials.

When increasing the concentration of phenol, measurements in the device become difficult, so phenol solution in small concentrations was taken for the process. As in the previous two systems, the same solution was taken and the process was carried out under the same conditions. It was measured in a spectrophotometer before complete mixing with a stirrer, i.e. before adsorption. After two hours, that is, after adsorption, the white suspension of the mixture consisting of 20 ml of 1 mg/l phenol solution and 0.05 grams of TiO_2 was filtered through filter paper and placed in a standard cuvette, and the signal characterizing the presence of phenol after the adsorption process was recorded in a spectrophotometer "Varian Cary 50" has been observed. It is known that if the adsorption process had gone completely, the signal corresponding to phenol should not have been obtained. This fact indicates that the adsorption process is not neglected in the previous two systems.

In figure 18 below, the red line is drawn at 60 minutes and the blue line is at 120 minutes, but there is no sharp difference between the two curves. This indicates that the process is not working.

Thus, the adsorption of phenol in the phenol+TiO_2 system was studied. It was determined that in the phenol+ TiO_2 system, unlike the previous two systems, the adsorption of phenol occurs weakly.

The following figure 19 shows the comparison of the adsorption curves obtained during the adsorption process (every 25 minutes). In the process, it was observed that the curves at the wavelength corresponding to phenol (240-270 nm) were obtained along the horizontal line.

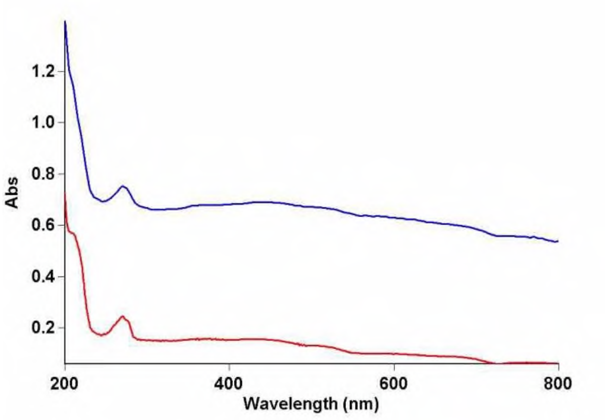


Figure 18. Comparison of adsorption curves drawn at 60 and 120 minutes in the phenol+ TiO_2 system

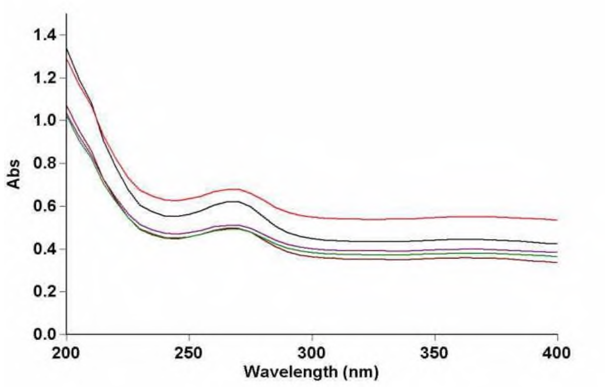


Figure 19. Comparison of the curves obtained during the adsorption of phenol in the presence of TiO_2

In the first moments of the process (red line), this is more pronounced, but gradually, even if a slight decrease occurs(oak line), which indicates that the adsorption is very slightly (figure 19).

The general table 8 for the adsorption process in all three systems was as follows.

Table 8.

Results of adsorption in GO, C and TiO_2 systems

substances	mass(gr)	time	adsorption ability
GO	0.05	2 hour	+
C	0.05	2 hour	+
TiO_2	0.05	2 hour	-

As we know, many factors affect the adsorption process: temperature, time, concentration of substances and other factors.

Although the adsorption capacity of TiO_2 nanoparticles is very small, the process has also been studied in other mediums. For this purpose, the temperature was increased and the process was monitored for a longer period of time (3 hours). No changes were observed at this time either. When the amount of TiO_2 nanoparticles was increased (twice), accumulation of spherical TiO_2 nanoparticles was observed at the bottom of the flask. At this time, when we tried to monitor the progress of the process by increasing the temperature by 10^0C, no changes were observed. Therefore, the temperature factor does not have a positive effect on the adsorption process. No change was observed by prolonging the process time. Therefore, the most optimal condition for testing the adsorption capacity of TiO_2 nanoparticles was to conduct the process at room temperature.

Thus, TiO_2 nanoparticles with a rutile phase are poor adsorbents for their oxide, but very good photo catalysts.

CONCLUSION

1.Based on the conducted research, new perspective directions were proposed and developed in solving the problems of atmospheric air and water ecosystem pollution[2] [4,16,17,21].

2.Using the DEAN/H_2SO_4 (1:2) system, chemical reactions of ferrocene and cymantrene with cyclic ketones were carried out, similar to aliphatic ketones, and it was found that these compounds are 1.5-3 times more effective than ferrocene and simantrene, because fuel additives [1, 2, 3, 6, 7, 9, 10, 12].

3.Thioether derivatives of organometallic compounds were synthesized. Thioether derivatives of organometallic compounds were used in demercaptanization of oil [8].

4.Barium salts of carbinols obtained on the basis of organometallic compounds have smoke reducing properties. It has been studied that the considered compounds have 1-1.5 times more smoke-reducing effect than existing smoke reducers in diesel fuels, and 0.4-0.8 times more than ferrocene and cymantrene [5].

5. Industrial wastewater was taken from the catalytic cracking area of the Oil Refinery, phenolic compounds, polycyclic aromatic hydrocarbons and heavy metals were determined in the water samples [11,13,15, 26, 32, 37,40, 42, 43,47].

6.Phenolic compounds, polycyclic aromatic hydrocarbons and heavy metals were purposefully determined in water samples taken from different areas of the Caspian Sea [14,18,19, 20, 27, 31, 33, 34, 41,46].

7.Photochemical reactions with TiO_2 nanoparticles having rutile phase were studied in various systems [28, 29].

8.99% photochemical decomposition of phenol was achieved in the presence of TiO_2 nanoparticles [16, 22, 23, 24, 25, 38, 44].

9.By using methyl3-aminocrotonate, it was possible to extend the photochemical decomposition from the UV radiation area to the

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visible area. Photochemical decomposition of phenol in the presence of TiO_2 nanoparticles with sizes of 10-30 nm in the process was 60-80% [35,36,45,48].

10.Based on the conducted reactions, the influence of the pH of the reaction medium on the photochemical decomposition of phenol was studied and it was determined that the process goes better in an acidic medium (pH=4) [49,50].

11.It was determined that adsorption did not occur in the phenol and nano-TiO_2 system for two hours at a temperature of 25^0C [30].

12.Logistic and exponential models of processes involving TiO_2 nanoparticles with rutile phase have been developed [39].

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