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ABSTRACT

of the dissertation for the degree of Doctor of Philosophy

EFFECT OF NANO TiO_2 ON PHOTOCATALYTIC CONVERSION PROCESSES OF AQUEOUS SOLUTIONS OF TOXIC COMPOUNDS

Speciality: 3305.05 – Engineering-communication systems

Field of science: Technique

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GENERAL DESCRIPTION OF WORK

Actuality of the topic and degree of development of the topic. Wastewater generated as a result of the activities of industrial sectors causes serious damage to the environment. Proper treatment and processing of this waste, as well as the protection of natural water sources and ensuring the sustainability of the ecosystem, are of great importance in the field of engineering and communication systems and water management. Also, the development of new technologies in this field serves to save resources and protect the environment by ensuring the reuse of water. Safe, high-quality management and treatment of wastewater in accordance with epidemiology, toxicology, and ecological criteria is one of the serious problems of our time. When solving this problem, using alternative energy sources (solar, wind energy) as an energy source can make the technologies economically profitable. The use of energy obtained from alternative energy sources corresponds to the "Green energy" concept, which is relevant for our republic. Eliminating the negative impact of waste water on the environment and human health poses the development of new effective methods for their treatment as an urgent scientific issue. Issues related to the improvement of the ecological situation in the Republic of Azerbaijan, including waste management, are included in the "Comprehensive Action Plan for the Improvement of the Ecological Situation in the Republic of Azerbaijan for 2006-2010" approved by the President of the Republic of Azerbaijan on September 28, 2006 (Decree No. 1697) works are continued in the directions that have been reflected in the plan. The preparation of proposals for the use of iodine-bromine production from formation water released during oil production is included in the plan of actions[1]. SOCAR's Environmental Policy document was approved in 2008, and one of the priority areas was mentioned as conducting scientific research for groundwater treatment. In SOCAR's sustainable development reports, the amount of groundwater formed in the territory of the republic during the years 2000-2022 and the currently used cleaning methods are shown.

[1] Environmental Policy of the State Oil Company of the Republic of Azerbaijan:/ - Baku: – 2008. -30 p.

At present, the amount of produced water in the oil industry is 20.24 mln/m^3. [2]

Despite the existence of traditional methods for cleaning waste water of various origins from toxic waste, currently for this purpose physical factors - ionizing (γ-quanta, X-rays, accelerated electrons, neutrons, protons, α-particles, high-energy ions, etc.) radiation, electric discharges and technologies based on the application of modern oxidation processes (MOP) are being developed. These technologies have a number of advantages: they do not require additional reagents and special conditions (temperature, pressure), regeneration of the used materials is not required, and they are one-step and carried out at normal temperature and pressure.

Among these technologies, photochemical processes involve the use of industrially produced ultraviolet (UV) lamps as an energy source. This is due to the possibility of using solar energy during the use of these technologies, the absence of risks for the environment, technical simplicity of use, the presence of experience in the industrial application of UV lamps, the lack of radiation safety, the initial capital investment is small and, as a result, the economic efficiency is acceptable. Photochemical methods make it possible to expand their absorption range and use the radiation energy in the visible light range by modifying a number of semiconductors with an absorption spectrum in the UV radiation region, TiO_2, ZnO, Fe_2O_3, CdS, ZnS.

In "Azerbaijan 2030: National Priorities for socio-economic development", the issue of expanding the production of "green energy" in our country was also given an important place. The goal is to increase the share of renewable energy in the total energy production capacity from the current 17.3 % to 24 % in 2025 and 30 % in 2030. The use of energy obtained from alternative energy sources for various purposes, including solving environmental problems, is an urgent scientific issue.

Since nano TiO_2 is resistant to photochemical corrosion, various types of wastewater treatment with its presence are currently

[2] SOCAR annual reports 2015-2021. https://www.socar.az/az/page/illik-hesabatlar

being widely studied.

During the application of photochemical technologies, the quality indicators of the parameters characterizing the purification process and the initial composition of formation waters, the spectrum of components play a decisive role. The reason for this is that the rate of reaction of the active particles formed during the photochemical act with the toxic component molecules depends on the type of molecules and the rate constant of the corresponding reactions. Using data from existing literature materials for kinetic analysis may give inaccurate results for evaluating the effectiveness of the particular process under consideration. For this reason, the comprehensive study of reservoir waters and the development of effective catalytic systems in the oil and gas industry of Azerbaijan is an important scientific issue.

The importance of the study consists of several main aspects:

1. Environmental Protection: The removal of toxic compounds from aquatic environments is vital to environmental protection. Photocatalytic processes allow the complete neutralization of pollutants, which improves the quality of water resources.

2. Human Health: Demand for clean water resources continues to grow. Effective removal of toxic compounds is essential to protect human health. This thesis can make an important contribution to the development of water treatment technologies.

3. Technological Innovation: The use of nano TiO_2 plays an important role in the development of new technologies. This research may contribute to the development of new methods and materials to increase the efficiency of photocatalytic processes.

The dissertation focuses on the innovative technology of using renewable energy sources in groundwater treatment. This research area addresses the urgent need for sustainable solutions in wastewater treatment, especially in industries such as oil and gas production where large volumes of groundwater are generated. By incorporating renewable energy technologies such as solar, wind or hydropower into cleanup processes, the dissertation aims to explore the feasibility, efficiency and environmental benefits of these approaches. The study examines the technical aspects of integrating renewable energy systems with water treatment plants, evaluating their performance in terms of water quality improvement, energy efficiency and overall economic efficiency.

The object and subject of the research. Taking into account the above, the research object of the dissertation is the determination of the composition of various types of industrial wastewater and the determination of the activity of nano TiO_2 of various sizes in the cleaning process. For this purpose, it is necessary to develop the design of a cleaning device equipped with UV lamps inside, to verify the reliability and effectiveness of the cleaning technology on the model, and to specify the technological parameters of the cleaning device operation in industrial conditions.

The subject of the study is the assessment of the kinetic regularities of the transformations of toxic compounds during the photolysis of the systems under consideration and the technical parameters necessary for the purification of produced water by the photocatalytic method.

Aims and objectives of the research. The aim of the work is to synthesize and modify nano TiO_2 catalysts using various methods to increase the efficiency of the photochemical treatment of wastewater, study their photocatalytic properties, study the kinetic regularities of the photochemical treatment of strata waters, and evaluate the possibilities of applying the treatment technology using solar energy. At the same time, the main objectives of the research are to investigate the technological and economic indicators of the selected method, to determine whether it is economically feasible, environmentally friendly, and technologically feasible.

For this purpose, the following issues were resolved.

- Synthesis of nano TiO_2 samples modified by various methods and determination of their characteristic parameters;
- Investigation of the catalytic activity of modified nano TiO_2 in model systems;
- Comprehensive study of the initial composition of reservoir waters;
- Determination of photochemical yield and dependence of the concentration of gas products formed in the process of photochemical

degradation of formation waters in the homogeneous phase on the irradiation time;

-Investigation of the dependence of the liquid products produced in the process of photochemical cleaning of formation waters in the homogeneous phase on the irradiation time by UV and GS-MS spectroscopy methods;

- Investigation of the used TiO_2 catalyst at different irradiation times by the IR spectroscopy method;

- Determination of photochemical yield and dependence of the concentration of gas products generated in the process of photocatalytic degradation of formation waters in the heterogeneous phase on the irradiation time;

- Investigation of the dependence of the liquid products formed in the process of photocatalytic cleaning of formation waters in the heterogeneous phase on the irradiation time by UV and GS-MS spectroscopy methods;

- Evaluation of technical and economic parameters of photocatalytic technologies;

Research methods. International standard methods and modern physicochemical methods - IR, UV spectoscopy, Gas chromatography and GS-MS chromatographic analysis methods were used in the research to determine the physicochemical parameters, SEM, TEM, REM, NANOSIZER devices were used to study the morphological and surface properties of the catalyst.

The main provisions of the defense are as follows:

1. Determined parameters of the effect of nano TiO_2 synthesized by various methods and modification methods on the conversion processes of photocatalytic toxic components (SEM, TEM, REM, NANOSIZER);

2. Kinetic regularities and parameters of the photocatalytic conversion process of wastewater taken as a model system (effective rate constants and COD);

3. Comprehensive study of the initial composition of reservoir waters - physical-chemical parameters, spectroscopic methods and chromatographic analysis results;

4. Time dependence of the concentration of the liquid (aliphatic

and aromatic compounds) and gaseous phase products (H_2, CO_2, C_1-C_9 hydrocarbons) formed during the photolytic processes of produced waters, as well as in the presence of nano TiO_2 (quantum yields, effective rate constant);

5. Technical and economic indicators of the photocatalytic conversion process of produced water;

Scientific innovation of research. Initially, the composition of industrial wastewater (wastewater generated during the production of olive oil and methanol and produced water generated during oil and gas extraction) was analyzed in a complex manner and it was determined that the number of organic substances in the composition of this type of water is the majority. The catalyst used for the photocatalytic method chosen as the purification method was selected, the photocatalytic properties of nano TiO_2 modified by various methods were studied in a comparative manner and it was shown that magnetic TiO_2 has the highest activity in the decomposition process of methyl blue from powder, sol-gel, N-TiO_2, magnetic TiO_2 nanooxides. For the first time, the kinetic characteristics of the process of purification of produced water from toxic waste were studied in a complex manner, and the quantum yields of the transformation processes of the products formed in the gas and liquid phases formed in the photolysis process were determined. The principal scheme of the device, equipped with an alternative energy source, reflecting the purification technology, was drawn up.

Theoretical and practical significance of research. The results obtained in the dissertation can be a theoretical basis for the selection of catalysts for photocatalytic processes (type of modification, used light source, distribution and sizes of nanoparticles in the catalyst). The obtained results also show that nano TiO_2-based photocatalytic processes are promising for the treatment of various wastewaters.

Approbation and application. The main materials of the dissertation were reported and discussed at the following scientific conferences:

1. "International Scientific and Practical Conference on Ecological

Issues in Engineering Systems and Installations. December 10-11, 2019, Baku."

2. International Conference Modern Trends in Physics. Dedicated to the 100th anniversary of Baku State University. 01-03 May (2019), Baku.
3. "XXIII National Scientific Conference of PhD Students and Young Researchers. Conference dedicated to the 650th anniversary of the great Azerbaijani poet Imadeddin Nesimi. Azerbaijan University of Architecture and Construction, December 3-4, 2019."
4. Environmental Remediation Conference. İnnovative centre to support a postgraduate 3rd cycle Advanced Course to face environmental emergency in Azerbaijan /İTACA. Modern Scientific Technology İnternational Scientific Conference. 26-27 May (2022) Granada, Spain.
5. Modern Scientific Technology. Stockholm, Sweden. October 13-14, (2022) №1.
6. "SOCAR, Baku Higher Oil School, 4th International Scientific Conference on Oil and Gas Geology and Engineering for Students and Young Researchers, dedicated to the 100th anniversary of the National Leader of the Azerbaijani People, Heydar Aliyev."
7. "Conference on 'Innovative Technologies in Water Management and Engineering Communication Systems.' April 12-13, 2023, Baku."
8. "Conference on 'Innovative Technologies in Water Management and Engineering Communication Systems.' June 8-9, 2023."
9. "Scientific-Technical Conference dedicated to the 100th anniversary of the birth of National Leader Heydar Aliyev. Baku, June 8-9, 2023."
10. "Azerbaijan State Oil and Industry University. National Scientific Conference for PhD Students and Young Researchers dedicated to the 100th anniversary of National Leader Heydar Aliyev. Baku, May 3-4, 2023."

Published scientific works. The results of the dissertation work were published in scientific works. 10 of them are articles (3 articles in foreign scientific journals indexed in international databases, 7 articles - in republican journals included in the list of SAC), and

10 are theses of reports published in international and republican conferences. The printed works fully reflect the essence of the dissertation.

The name of the organization where the dissertation work was performed. The dissertation was completed at the "Nature and waste water treatment" laboratory of the Azerbaijan University of Architecture and Construction, at the "Chemical Engineering Materials Environment" laboratory of La Sapienza University, Rome, Italy.

Personal involvement of the author. Conducting experimental studies, processing the obtained results and preparing the materials for printing in the dissertation work were mainly carried out by the author. The author's share in the scientific works he co-authored was decisive.

The total volume of the dissertation is expressed in characters, with the volume of each structural section of the dissertation indicated separately. The dissertation is written in accordance with the requirements set by the Higher Attestation Commission under the President of the Republic of Azerbaijan. The dissertation consists of an introduction, 4 chapters, a conclusion, an appendix and a list of references.

The dissertation consists of an introduction (26356 characters), four chapters (Chapter I-53842, II-13892, III-27954, IV-55770 characters) and conclusions. The dissertation consists of 174 pages on a standard A4 sheet. The work contains 23 figures, 37 graphs, 44 tables and a list of references with 174 names.

MAIN CONTENT OF WORK

The introduction outlines the overall context of the problem, highlighting the importance and relevance of the dissertation topic. It defines the research goals and objectives while emphasizing the scientific novelty and practical significance of the study. Additionally, it presents the key findings and main arguments that will be defended**.**

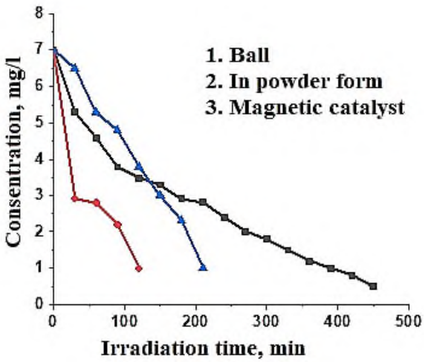
In Chapter I, the available literature data on the topic of the dissertation was analyzed, it was determined that the process of photocatalytic cleaning of toxic waste with the presence of a number of nano oxides, especially nano TiO_2, was studied. As a result of the study of the degradation processes of methyl blue, produced water and oil sludge under the influence of UV rays with the presence of Nano TiO_2, the research works were analyzed and the obtained results were discussed. It has been shown that the parameters characterizing the process have not been widely studied in the considered works. This does not allow determining the energy output of the cleaning process and the kinetic parameters of the reactions occurring in the conversion processes, for example, the kinetic rate constant.

In Chapter II, the methods used in the research work and the rules for conducting analyzes are given. International standard methods, spectroscopic and chromatographic methods and Nanosizer, SEM, TEM and REM methods were used for structural analysis.

In Chapter III, synthesis methods of TiO_2 catalyst samples modified by various methods were given, and their photocatalytic properties in different wastewater environments were studied. Initially, the synthesized nano TiO_2 was used in the process of photolysis of aqueous solution of model methyl blue, waste water produced during the production of olive oil and methanol.

Firstly methyl blue was used as standard solution. A 7 mg/L solution of analytically pure methylene blue (Methylene blue (methylthioninium chloride), a cationic dye with a chemical reagent brand Alfa Aesar) was prepared. The process was carried out using TiO_2 impregnated on glass spheres, magnetic TiO_2 and synthesized

TiO_2[3].



Graph 1. Graph of the decomposition of methyl blue using catalysts prepared by various methods

Based on the obtained results, the effective rate constants of the decomposition reaction of methyl blue during the photolysis process with the presence of the TiO_2 nano catalyst synthesized by different methods were compared and shown in the table below.

Table 1

Effective rate constants of the decomposition rate of methyl blue during the photolysis process

Synthesis method of TiO_2 oxide	Effective speed constant, 1/min
Zol-Gel method TiO_2 impregnated on glass spheres (in reactor)	0,00498
TiO_2 synthesized by magnetic method (in a chemical beaker)	0,01552
Powdered synthesized TiO_2 (in reactor)	0,00684

As can be seen from the table, the highest effective rate constant is observed in the photolysis process of TiO_2 synthesized by the magnetic method of methyl blue.

[3]Ibrahimova, S., Aliyev, F.G., Stoller, M. and Chanese, A. Optimal Configuration of a Photocatalytic Lab-Reactor by Using Immobilized Nanostructured TiO_2. Chemical Engineering Transactions, - 2016, -p.199-204.

The mathematical model used to determine the first-order kinetics of photocatalytic reactions is as follows:

1. First-order kinetic reaction equation.

Photocatalytic reactions are usually described by first-order reactions. The kinetic equation for first-order reactions is as follows:

$$\ln\left(\frac{C_0}{C}\right) = kt \tag{1}$$

Here C_0 – initial concentration, mg/l

C – concentration at a certain moment, mg/l

k – reaction rate constant, min^{-1}

t – time, min.

From the given graph, we can determine the constants using the equation:

$$\ln\left(\frac{C_0}{C}\right) = 0{,}005t \tag{2}$$

In this case, the mathematical model of the process will be as follows

$$C = C_0 e^{-kt} \tag{3}$$

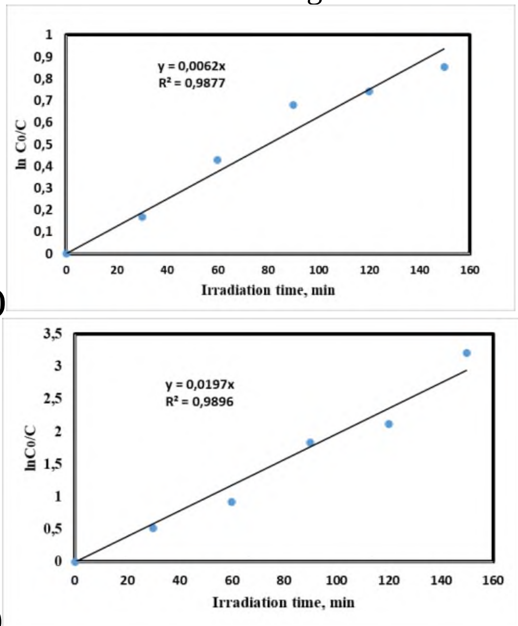
Here, k=0,005 min^{-1}.

If the initial concentration is C_0=7 mg/l and the irradiation time is 200 minutes, to calculate the new concentration: The general form of the mathematical model will be:

$$C = 7e^{-0{,}005\cdot 200} = 7e^{-1} = 7 \cdot 0{,}3679 \approx 2{,}6\, mg/l \tag{4}$$

That is, after 200 minutes of irradiation, the concentration of methyl blue will be about 2,6 mg/l.

As a preliminary treatment, the wastewater was spun through an Avanti J-20XP centrifuge to settle the solid residues from the pressed olives during the olive oil production process. One liter of waste water was filled in each container of the centrifuge and spun at 7500 rpm for two hours. The liquid phase was filtered from the bowls of the centrifuge and made ready for the degradation process. The COD parameter was used to study the kinetic dependence of the degradation process. In the experiments, the photolysis process was carried out using UV and visible light sources. Characteristic properties of the degradation process - absorption (Abs) and the dependence of the degree of conversion on the irradiation time were studied. The dependence of the $\ln C_0/C$ parameter on the irradiation time was studied by using the first-order reaction equation to determine the effective rate constant of the corresponding processes, and the rate constant was determined from the linear dependences. The obtained results are shown in the figure below.



a) b)

Graph 2. a) UV irradiation b) Incandescent lamp photolytic decomposition reaction rate versus time graph

It was determined that the use of incandescent lamps in the considered area causes a greater increase in the rate of degradation. The effective rate constant during UV radiation is k=0,00625 (1/min), the effective rate constant during incandescent lamp radiation is k=0,0197 (1/min). The mathematical model of the research result will be as follows:

The given graph shows the change in the concentration of pollutants as a result of the photocatalytic oxidation process of olive oil wastewater. The equation shown and the value of R^2 describe the kinetics of a first-order reaction. If we determine the constant from the equation given in the graph

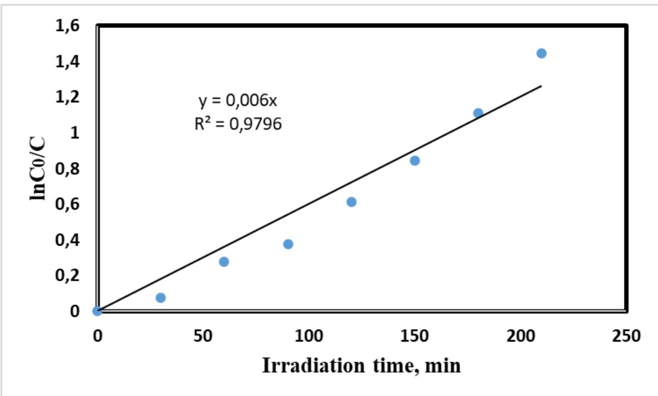
$$ln\frac{C_0}{C} = 0{,}0197t \quad (5)$$

Using this model, it is possible to calculate the concentration of water at any time instant (t). For example, if the initial concentration is C_0=1mg/l and the exposure time is 100 minutes, to calculate the new concentration:

$$C = 1 \cdot e^{-0{,}0197\cdot 100} = 1 \cdot e^{-1{,}97} \approx 0{,}14\, mg/l \quad (6)$$

That is, after 100 minutes of irradiation, the concentration of the pollutant will be about 0,14 mg/l.

TiO_2 nanoparticles with a size of 66 nm were used for the neutralization of the liquid waste of the methanol plant. The physical parameters of the synthesized TiO_2 nanoparticles were analyzed by X-ray diffraction Miniflex 600 and JEOL JSM 6610-LV instruments for SEM analysis. Initially, the amount of COD in the water sample was 350 mg/L. The samples were irradiated for 1-210 min. The dependence of the conversion rate of methanol on the irradiation time is given in graph 3.



Graph 3. Graph of the lnC0/C=kt equation for the first order decomposition reaction calculated based on the kinetic curve

It has been shown that as the irradiation time increases, the amount of COD decreases sharply, which indicates the decomposition of organic substances in the waste water. As a result of photolysis, the degree of degradation of organic substances is 86% (210 min). The effective rate constant during UV irradiation was k=0,00685 1/min[4].

In Chapter IV, kinetic regularities of formation and physico-chemical parameters of products formed in the gas phase and liquid phase during photolysis of produced were studied.

In the research work, formation water taken from oil and gas production wells working under the oil and gas production department of Garadagh region of the Republic of Azerbaijan was used.

Ampoules made of optical quartz with a volume of V=35 ml were cleaned both by chemical methods and with distilled water, thermally processed at a temperature of T=873K, for a period of t=72 hours. After cooling down the ampoule, 30 ml of formation water and an iron grate were placed inside it for equal distribution of oil products by using a magnetic stirrer during irradiation. Then, air was expelled inside the sample at a pressure of 10^{-1} Pa through a vacuum-adsorption device and the ampoule was closed. The ampoules were placed on a tripod on a magnetic stirrer at a distance of 10 cm from the UV lamp. The magnetic stirrer was operated continuously during the irradiation period. During the irradiation process, the temperature was controlled by means of a UV lamp and an ampoule fan. The model of the research facility is depicted in figure 1.

[4]Aliyev, F.G., Hasanova, S.A. Synthesis of titanium dioxide nanoparticles and application to the catalytic removal of methanol from water. Mühəndis sistem və qurğularında ekologiya məsələləri mövzusunda beynelxalq elmi-praktiki konfrans. – Bakı, -2019, p. 267-271

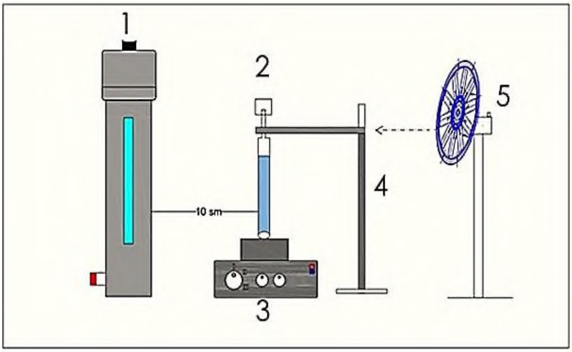


Figure 1. Schematic of the irradiation process through a UV lamp: 1-UV lamp, 2-quartz ampoule with a volume of 30 ml, 3-magnetic stirrer, 4-stand, 5-fan

Initially, the dynamics of the solution's pH index, electrical conductivity, salinity, and the density of suspended particles depending on different irradiation times were studied[5,6].

Table 2

Dependence of pH indicator, electrical conductivity, salinity and concentrations of suspended particles on irradiation time ($\phi=7,5\cdot10^{15}$ quanta/sec)

Irradiation time, min	pH	Electrical conductivity, mS	Salinity, mg/l	TDS, g/l
0	7.45	29,53	7900	20,13
30	9.6	10,09	8000	14,18
60	9.4	14,28	8100	9,75
120	9.8	14,20	8100	9,69
240	9.7	13,89	8100	9,87
480	9.1	14,11	7900	9,70

[5]Hasanova, S.A., Aliyev, F.G., Gurbanov M.A. Study of photochemical transformations of toxic components of polluted water. Baku Higher Oil School, IV International Scientific Conference of Oil and Gas Geology and EngineeringBaku: SOCAR, -2023. -p.435-437.

[6]Hasanova, S.A., Jafarov, Y.D. Chromatographic determination of gases formed from the decomposition of formed water under the influence of ultraviolet rays // Republican Scientific Conference. – Baku: - 2023, -p.124-127

As can be seen from the table, the pH of the samples taken as a result of UV radiation increases, while other parameters decrease. Electrical conductivity decreases by about 2 times, salinity by about 2 times, and TDS by about 2 times during the considered irradiation time interval. UV spectra of the irradiated samples were taken and the obtained results are shown in the figure below.

As liquid products in the photolysis process, aliphatic (normal, iso, cyclic and unsaturated hydrocarbons) (C_9-C_{18}) (normal, iso, cyclic and unsaturated hydrocarbons) and aliphatic (C_{19}-C_{36}), aromatic and PAHs (Fluoranthene, Benz(b+k)fluoranthene Naphthalene, 2-Methylnaphthalene, Acenaphthylene, Acenaphthene, Fluorene, Phenanthrene, Anthracene, Pyrene, Benz[a]anthracenes, Chrysenes, Benzo[a]pyrene, Indole, Pyrene+Dibenzo anthracene, Benzopyrene) concentration by chromatographic method were determined and the dependence of their thickness on the irradiation time was studied.

Only 2-methylnaphthalene and acenaphthalene concentrations of polycyclic aromatic compounds in irradiated samples were determined because they were higher than the sensitivity level of the analysis. Concentrations of other polycyclic aromatic hydrocarbons were not evaluated because they were less than the sensitivity of the assay. The same picture is observed for aliphatic hydrocarbons. Based on the grading curves, the concentrations of the corresponding products were determined. The obtained results are given in the table below[7].

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[7]Hasanova, S.A. F.G. Aliyev, M.A. Gurbanov, Y.D. Jafarov. Study of the chemical processes occurring in the gas phase as a result of photolysis of produced waters under the ultraviolet rays' influence. PPOR, - Baku: -2023. №4. -p. 260-267.

Table 3

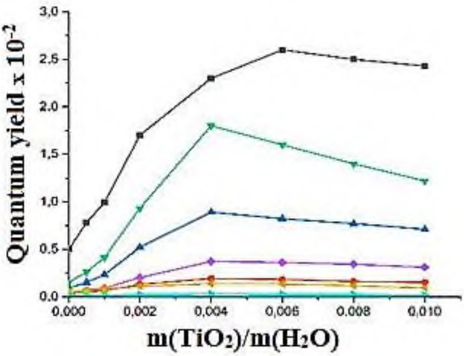
Dependence of concentration of liquid products on irradiation time, mg/l

Irradiation time	Aliphatic C_9-C_{18}	Aliphatic C_{19} –C_{36}	Aromatic C_{11}-C_{22}	Total hydrocarbons
Initial	1,550	2,793	8,647	12,991
30 min	2,413	1,878	5,963	10,254
120 min	3,284	1,650	3,519	8,453
480 min	3,682	1,550	1,850	7,082

During the photolysis of the heterogeneous phase, the kinetics of formation of gaseous products of photolysis of reservoir water with different amounts (0,015-0,09 g) of nano-TiO_2 added in the first stage was studied. Ampoules made of quartz material (6 pieces) were washed 3-4 times with distilled water and kept at a temperature of 350-400 ^{0}C. 0,015 g, 0,03 g, 0,06 g and 0,09 g of 21 nm TiO_2 were added to the ampoules, respectively.

After heating the ampoule again under the above conditions, 30 ml of sample water is added to it. The samples were irradiated and obtained at different hours, so that a weak change of pH, electrical conductivity, salinity and MHM parameter depending on the irradiation time is observed. The obtained kinetic curves show that the thickness increases non-linearly as a function of time in the considered irradiation time interval. It was determined that as the amount of TiO_2 increases, the quantum yield of hydrogen and C_1-C_5 increases and saturation is observed at large amounts of TiO_2. As the amount of TiO_2 increases from 0,015 g to 0,12 g, the quantum yield of the consumption process of C_6-C_9 increases.

The dependence of the density of gaseous products formed at different values of TiO_2 on the irradiation time was studied. It has been shown that the rate of H_2 formation increases as the amount of TiO_2 introduced into the system increases. From the obtained curves, the quantum yield of H_2 formation was calculated as a function of the TiO_2/H_2O ratio. The rate of initial formation of other gas products CH_4, C_2H_6, C_2H_4, C_3, C_4, C_5 increases depending on the amount of TiO_2 oxide. However, unlike the formation of H_2, the dependence of the quantum yield of other hydrocarbons on the TiO_2/H_2O ratio is characterized by a maximum, and this maximum value is observed at the value of 0,005 of the ratio.



Graph 4. Graph of dependence of the quantum yield of hydrocarbons on TiO_2/H_2O ratio

We can apply mathematical models to describe these changes. For each component, exponential or linear models can be fit, showing how the density varies with irradiation time.

Exponential model for aliphatic C_9-C_{18}:

$$C_{C_9-C_{18}}(t) = C_0 e^{kt} \tag{7}$$

Here: $C_{C_9-C_{18}}(t)$ – concentration of C_9-C_{18} aliphatic hydrocarbons during irradiation time, C_0 - initial concentration (1,55 mg/l), k - reaction rate constant (must be determined), t – irradiation time

It is possible to construct a model for the sum of the total hydrocarbons by determining the quantum yields and rate constants of the reactions by applying similar models for each component. This model can be used to predict concentrations dependent on irradiation time to accurately describe the results. First, let's determine the k values for each component, applying the exponential model.

For aliphatic C_9-C_{18};

$$C_{C_9-C_{18}}(t) = ln(C_0) + kt \tag{8}$$

Start t=0 min; C_0=1,55 mg/l after 30 minutes t=30 min

$$\ln(2{,}413) = \ln(1{,}55) + 30k \tag{9}$$

$$k = 0{,}0147 \tag{10}$$

For aliphatic C_{19}-C_{36};

$$C_{C_{19}-C_{36}}(t) = ln(C_0) + kt \quad (11)$$

Start t=0 min; C_0=2,793 mg/l after 30 minutes t=30 min

$$\ln(1{,}878) = \ln(2{,}793) + 30k \quad (12)$$

$$k = -0{,}0133 \quad (13)$$

It is possible to construct a model for the sum of the total hydrocarbons by determining the quantum yields and rate constants of the reactions by applying similar models for each component. This model can be used to predict concentrations dependent on irradiation time to accurately describe the results.

For aliphatic C_9-C_{18};

$$C_{C_9-C_{18}}(t) = 1{,}55e^{0{,}0147t} \quad (14)$$

Alifatik C_{19}-C_{36}

$$C_{C_{19}-C_{36}}(t) = 2{,}793e^{-0{,}0133t} \quad (15)$$

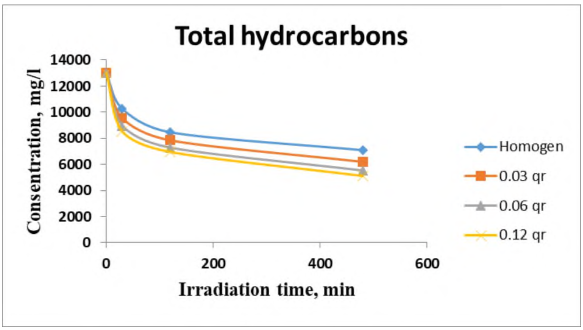
C_{11}-C_{22} from aromatic

$$C_{C_{11}-C_{22}}(t) = 8{,}647e^{-0{,}0123t} \quad (16)$$

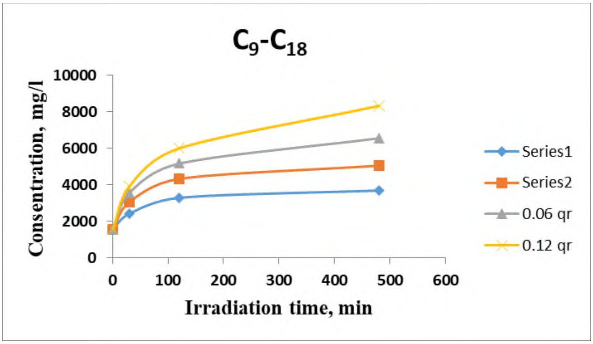
Total Hydrocarbons

$$C_{C_9-C_{36}}(t) = 12{,}991e^{-0{,}0078t} \quad (17)$$

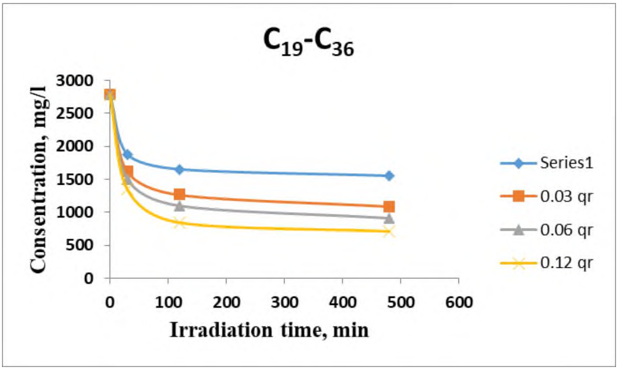
Based on the given data, it is possible to build mathematical models explaining how aliphatic and aromatic hydrocarbons change depending on the irradiation time in the photolysis process by applying exponential and linear models. These models can help to better understand and optimize the process.



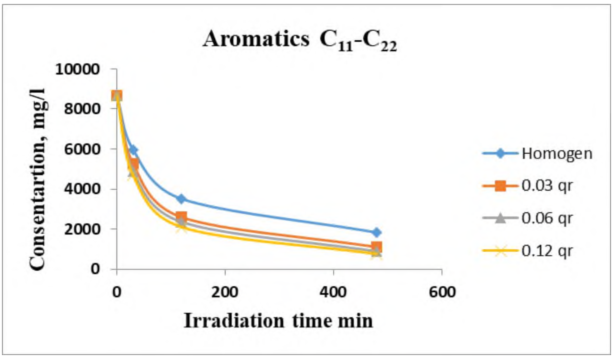
Graph 5. Dependence of the amount of hydrocarbons on the irradiation time



Graph 6. Dependence of the concentration of C_9-C_{18} aliphatic hydrocarbons on the irradiation time



Graph 7. Dependence of the concentration of C_{19}-C_{36} aliphatic hydrocarbons on the irradiation time



Graph 8. Dependence of the concentration of C_{11}-C_{22} aromatic hydrocarbons on the irradiation time

In accordance with the technological process of the wastewater treatment plant, the water collected in the tank is transferred directly to the large-sized grate and pumping station by means of a pump through D1800 mm reinforced concrete pipes (given that the wall thickness of the pipe is 250 mm, the internal diameter is D1300 mm). The image of the reinforced concrete pipe is shown in Figure 2.

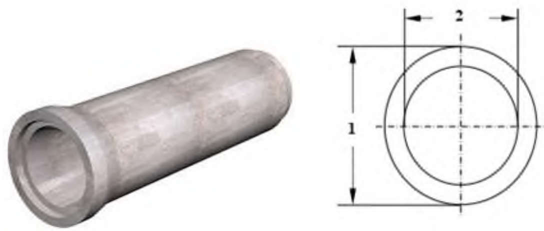


Figure 2. Image and dimensions of a reinforced concrete pipe; 1-D1800 mm, 2-D1300 mm

In the large-sized grate area, easily collected waste materials (sizes over 30 mm) are captured from the wastewater. Then, the wastewater coming out of the grates is transferred to the collection chamber. Pumps are installed in the collection chamber and through these pumps, the wastewater is transferred to the inlet chamber of the small-sized grate and sand trap devices with pressure lines (D700 mm and D400 mm).

The wastewater enters the fine grate chamber from the inlet chamber with its own flow. Here, particles larger than 10 mm in the wastewater are captured and stored.

The sequence diagram (principle diagram) of the production processes is shown in Figure 3.

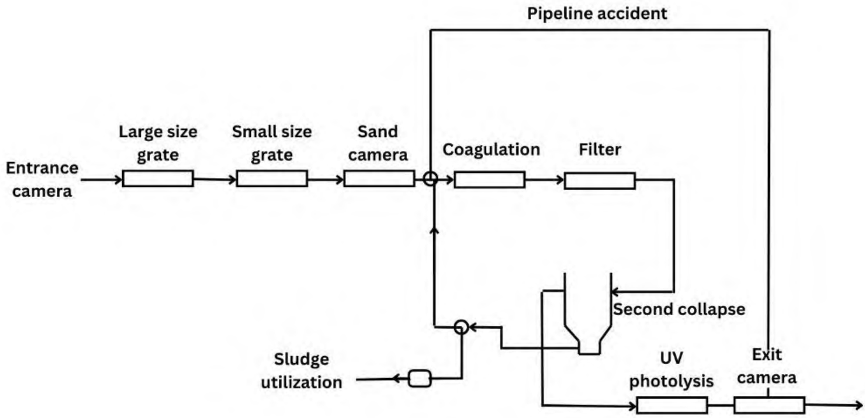


Figure 3. Production process flow chart

As shown in the diagram, the wastewater initially passes through mechanical treatment devices (large and small-sized screens) and enters the next mechanical treatment devices, sand and oil catcher devices. Then, the wastewater is transferred to the flow measurement chamber through 900 mm diameter pipes, and from there to the coagulation and filtration chamber. In order to ensure greater efficiency of the treatment process, it is planned to use a coagulant solution of aluminum sulfate or other composition. After the treatment processes, the wastewater enters the distribution chamber of the clarifiers by its own flow through a pipe with a diameter of 1100 mm. In the distribution chamber, the wastewater is transferred to the clarifiers. In the clarifiers, the activated sludge solids are separated from the mixed liquids and transferred to the disc filter.

The wastewater purified in the disc filter is then transferred to an ultraviolet irradiation chamber for a deeper purification process at the end of the processing processes, where the photocatalytic purification process is carried out.

Based on the results we received, the cost of energy required during the photocatalytic treatment of 1 ton of groundwater is calculated using the following methodology:

When the used 20W mercury lamp is used to irradiate 30 ml of water for 3,5 hours, 20·3,5Vt·hour=70Vt·hour=0,07kVt·hour is consumed from the electric grid, taking into account the 90% purification rate of the groundwater. Then, the amount of electricity used for cleaning 1t of groundwater is $0{,}07kWh\cdot 10^6$ $ml/30ml=2{,}3\cdot 10^3 kWh$. The lamp uses this amount of energy for 3,5 hours in laboratory conditions. To reduce this time, it is necessary to use more powerful mercury lamps. Mercury lamps used on an industrial scale are divided into three groups: low, medium and high pressure. Since medium pressure UV lamps do not require a special cooling system, their use is technically more convenient. For example, 150 W mercury lamps are used on an industrial scale. The power of this lamp is 150/20=7,5 times greater than the power of the lamp used in laboratory conditions. In this case, if 1 lamp is used, the contact time can be 7,5 times less than 3,5 hours to obtain a 90% purification rate in the contact time. That is, it is 0,46 hours or 28 minutes. In order to further reduce the contact time, the number of lamps can be increased according to the construction of the tanks. However, the specific calculation should be calculated according to the construction of industrial tanks intended for industrial scale. In order to reduce the level of photochemical corrosion and surface pollution of mercury lamps, it is necessary to separate these lamps from the water environment with a quartz partition.

In the work under review, some parameters of the photocatalytic purification process of selected wastewaters were calculated according to the following conditions during the use of UV lamps.
The principle scheme of the proposed device is as follows.

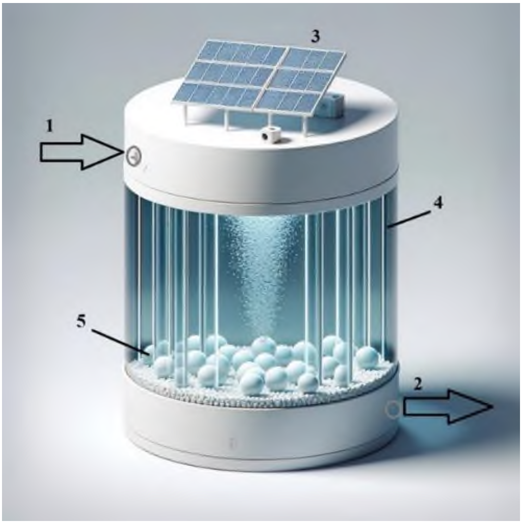


Figure 4. The principle scheme of the cleaning device. 1-Inlet water, 2- Outlet water, 3-Solar panel, 4-UV lamp, 5-N-TiO_2 catalyst

Obtaining the required energy from alternative sources such as solar and wind installations can increase the energy efficiency of the photocatalytic method. Powering these lamps using alternative energy sources (wind and solar installations) instead of grid electricity can increase the economic efficiency of the photocatalytic method as mentioned above.

To calculate the number of solar panels needed for $2,3 \cdot 10^3$ kWh of energy, we need some information:

1. The power of each solar panel (usually measured in watts (W) or kilowatts (kW)).

2. It is necessary to take into account how many hours a year the solar panel will work (working hours vary according to the availability of sunlight and geographical location).

Required Energy- $2,3 \cdot 10^3$ kW/h = 2300000 W/h, the power of solar panels and operating hours may vary, but if we assume the power of a standard solar panel to be 300 W (an average value for annual operating hours may be 1500 hours (this , depends on the geographical location and is an average price) annual energy production is calculated using the following formula:

Annual Energy Production = 300W · 1500 hours = 450000 W · · hours = 450 kW · h (18)

The number of solar panels required can be calculated as follows:

Number of panels needed = 2300000W · hours / 450000 W · · hours = 5 times (19)

After this calculation, you will need 5 solar panels of approximately 300 W each.

The device is equipped with solar panels made of concentrated solar modules installed in a mechanical system that provides the missing heat on cloudy days and in the cold season, and the bottom of the tank is equipped with an electric heater activated by the additional energy collected by the solar panel.

The optimal dimensions of a tank with a volume of 1 ton are calculated as follows:

D= 0,8 m (Radius 0,4 m)

$$V = \pi \cdot (0{,}4^2) \cdot h \quad (20)$$

From here it is found that h≈2 m.

The quantity and size of N-TiO_2-coated quartz spheres under the considered conditions should be determined experimentally. The main condition is that these spheres are evenly distributed in suspension inside the container. This condition is achieved by having a diaphragm mesh in the upper part of the container, the diameter of which is smaller than the diameter of the balls.

The economic evaluation based on technical parameters is as follows:

1. Energy consumption for the treatment process

Energy consumption: 2300 kWh of energy is required to treat 1 ton of produced water.

Electricity cost: If the cost of electricity is assumed to be 1 kWh = 0,1 AZN:

$$2300\text{kWh} \cdot 0{,}1\text{AZN} = 230\text{AZN} \quad (21)$$

This means that the electricity cost required to treat one ton of produced water will be 230 AZN.

2. Cost of one panel

If one solar panel costs 500 AZN:

$$5 \text{ panels} \cdot 500\text{AZN} = 2500\text{AZN} \quad (22)$$

3. Lamp parameters

The length and diameter of the mercury lamp determine the placement method. The diameter of medium-pressure 150 W UV lamps is approximately 40÷60 cm. The jaw lamps can be placed vertically or horizontally. If placed vertically, the depth of the tank should be greater than the length of the lamps. The lamps should be placed at a distance of about 5÷10 cm between them so that they can provide effective lighting and do not overheat.

We can find the number of lamps as follows:

The area of the bottom of the tank:

$$S = \pi R^2 = 3{,}14 \cdot 0{,}4^2 = 0{,}5024\, m^2 \quad (23)$$

The circular area where each lamp is located (with the minimum distance):

$$S = \pi R^2 = 3{,}14 \cdot 0{,}05^2 = 0{,}00785\, m^2 \quad (24)$$

The number of lamps located in the bottom of the tank:

$$n = 0{,}5024/0{,}00785 = 64 \text{ pieces} \quad (25)$$

The average price of a mercury lamp varies depending on the lamp's power, pressure type (low, medium or high pressure), brand and quality. The prices for a medium-pressure 150 W mercury lamp are as follows:

Lamps used in laboratory conditions: 50÷100 AZN.

High-quality lamps intended for industrial use: can 100÷300 AZN.

We can accept an approximate price of 150 AZN. For a more accurate price, the specific model and characteristics of the lamp should be determined.

If n=64 pieces, the total price of the lamps is 64·150 AZN=9600 AZN

4. Tank price: The price of industrial tanks depends on the material and construction. If the approximate price of a stainless steel tank with a volume of 1 m³ is accepted as 1000 AZN, this amount will be added to the total cost.

Total initial cost:

Energy consumption with the electrical network (if used): 230 AZN

Solar panels: 2500 AZN.

Tank: 1000 AZN.

Lamps: 9600 AZN

Other devices (mercury lamps, cooling system, construction): Approximately 2000 AZN.

Annual cost for maintenance and spare parts: Approximately 5% of the initial cost (approximately 275 AZN).

230+2500+1000+9600+2000+275=15605 AZN

As a result of the calculations, it can be noted that 15605 AZN is initially in the photocatalytic cleaning stage required for the treatment of 1 ton of produced water. These calculations are based on technical indicators and may require additional detailed research on an industrial scale.

MAIN RESULTS

1. The research study comprehensively studied the composition of various types of industrial wastewater (olive oil production, methanol production, and produced water generated during oil and gas extraction), and it was determined that organic compounds predominate in the composition of water [1], [5], [9].

2. The methods applied in the process of purification of industrial wastewater contaminated with organic compounds were investigated and a modern purification technology, a physicochemical method, was selected. The morphological structure of nano TiO_2 used as a catalyst was studied, the regularities of the decomposition process were investigated on a model system, and a mathematical model of the purification process was developed [2], [4], [10].

3. Photolysis of produced waters was studied using a UV light source, and it was observed that the quantum yields of gas products varied in the range of $0,5 \cdot 10^{-2}$–$0,04 \cdot 10^{-5}$ molecules/quantum. It was determined that a 3-stage purification process occurred during photolysis, consisting of the decomposition of toxic components, oxidation, and transformation of the resulting products. As a result of UV irradiation, an increase in the pH value of the samples taken, and an approximately 2-fold decrease in the electrical conductivity, salinity, and TDS values were observed [14], [17], [18], [20].

4. When nano TiO_2 is added to the produced water, the quantum yields of gases formed from the photolysis process under the influence of UV rays in the system are $0,07 \cdot 10^{-2}$ –$0,42 \cdot 10^{-5}$ molecules/quantum. An increase in the amount of nano TiO_2 causes the quantum yields of the corresponding processes to increase to a certain value and the formation of a stationary value. The solid residues obtained from the photolysis process were analyzed by the IR spectroscopic method, and it was shown that the intensity of the observed absorption bands increases as the absorbed energy (depending on the irradiation time) increases [14], [17], [18], [20].

5. In the heterogeneous process, the concentration of liquid products increases depending on the irradiation time, while the concentration of C_9-C_{18} increases, while the concentration of C_{19}-C_{36} and aromatic compounds (C_{11}-C_{22}) decreases depending on the irradiation time. Thus, when using 0,12 g of TiO_2, 75% of heavy hydrocarbons and 92% of aromatic compounds were decomposed during the irradiation time. A mathematical model of the scheme reflecting the effectiveness of the purification process was developed [13], [19].

6. A technological scheme of a purification plant based on the use of alternative energy sources based on newly developed technology has been developed and proposed for implementation.

7. The total cost of replacing the energy consumption required in a 1 ton unit with solar panels was calculated to be 15605 AZN in in the photocatalytic cleaning stage. This creates the basis for choosing a technologically feasible and economically more efficient method.

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Claimant's personal contribution in printed works:

[3-4, 8-10, 12] - scientific works were carried out independently by the author.
[1-2, 5-7, 11, 13-20] - in scientific works, the solution of the problem, analysis of the collected data, and conducting experiments were carried out by the author, while the formulation of the problem and the processing of the obtained results were carried out jointly with the co-authors.

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