MINISTRY OF EDUCATION AND SCIENCE OF UKRAINE
NATIONAL AVIATION UNIVERSITY
FACULTY OF ENVIRONMENTAL SAFETY,
ENGINEERING AND TECHNOLOGIES
DEPARTMENT OF ENVIRONMENTAL SCIENCE

APPROVED TO DEFENCE
Head of the Graduate Department
_____________ T.V. Dudar
«_____» ____________ 2021

MASTER THESIS

(EXPLANATORY NOTE)

SPECIALTY 101 “ECOLOGY”,
EDUCATIONAL AND PROFESSIONAL PROGRAM:
“ECOLOGY AND ENVIRONMENT PROTECTION”

Theme: «Photocatalytic treatment of wastewater contaminated with aromatic compounds»

Done by: student of the EK-201 ма group, Alina V. Husieva
(student, group, surname, name, patronymic)

Supervisor: PhD in Eng., Ass.Prof. Marharyta M. Radomska
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KYIV 2021

МІНІСТЕРСТВО ОСВІТИ І НАУКИ УКРАЇНИ
НАЦІОНАЛЬНИЙ АВІАЦІЙНИЙ УНІВЕРСИТЕТ
ФАКУЛЬТЕТ ЕКОЛОГІЧНОЇ БЕЗПЕКИ,
ІНЖЕНЕРІЇ ТА ТЕХНОЛОГІЙ
КАФЕДРА ЕКОЛОГІЇ

ДОПУСТИТИ ДО ЗАХИСТУ
Завідувач випускової кафедри
_____________ Т.В. Дудар
«_____» ____________ 2021 р.

ДИПЛОМНА РОБОТА

(ПОЯСНЮВАЛЬНА ЗАПИСКА)

ВИПУСКНИКА ОСВІТНЬОГО СТУПЕНЯ МАГІСТРА

ЗА СПЕЦІАЛЬНІСТЮ 101 «ЕКОЛОГІЯ»,
ОСВІТНЬО-ПРОФЕСІЙНОЮ ПРОГРАМОЮ
«ЕКОЛОГІЯ ТА ОХОРОНА НАВКОЛИШНЬОГО СЕРЕДОВИЩА»

Тема: «Фотокаталітичне очищення стічних вод від ароматичних сполук»

Виконавець: студентка групи ЕК-201ма, Гусєва Аліна Віталіївна
(студент, група, прізвище, ім'я, по батькові)

Керівник: к.т.н., доц. Радомська Маргарита Миролавівна
(науковий ступінь, вчене звання, прізвище, ім'я, по батькові)

Консультант розділу «Охорона праці»: _____________ Кажан К.І
(підпис) (П.І.Б.)

Нормоконтролер: _____________ Явнюк А.А.
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КИЇВ 2021

NATIONAL AVIATION UNIVERSITY
Faculty of Environmental Safety, Engineering and Technologies
Department of Environmental Science
Specialty, Educational and Professional Program: specialty 101 “Ecology”, Educational and Professional Program: “Ecology and Environment Protection”
(code, name)

APPROVED
Head of the Department
___________ T.V. Dudar
«____» _________ 2021

MASTER THESIS ASSIGNMENT

Alina V. Husieva

1. Theme: «Photocatalytic treatment of wastewater contaminated with aromatic compounds» approved by the Rector on September 15, 2021, № 1872/ст

2. Duration of work: from 15.09.2021 to 15.12.2021

3. Output work (project): calculations of the conversion efficiency of the photocatalytic decomposition of phenol.

4. Content of explanatory note: analysis of the main wastewater pollutants and their impact on the environment and living organisms, investigation technologies for purifying water from organic pollutants, studying photocatalysis as a method of purifying water from organic pollutants, studying the effectiveness of photocatalysts, analyze methods for monitoring the content of organic water pollutants, analysis the possibilities of Ukraine for monitoring of organic pollutants in water.

5. The list of mandatory graphic (illustrated materials): tables, figures.

6. Schedule of thesis fulfillment

№	Task	Term	Advisor's signature
1	Receive themes task, search the literature and legislation	05.09.2021-15.09.2021	
2	Preparing the main part (Chapter I)	16.09.2021-30.09.2021	
3	Preparing the main part (Chapter II)	01.10.2021-15.10.2021	
4	Preparing the main part (Chapter III)	16.10.2021-21.10.2021	
5	Preparing the main part (Chapter IV)	22.10.2021-26.10.2021	
6	Consultation on section V (Occupational safety)	27.10.2021-04.11.2021	
7	Preparation of the main part (Chapter V)	05.11.2021	
8	Formulating conclusions and recommendations of the thesis	21.11.2021-25.11.2021	
9	Making an explanatory note to the previous presentation of the department, consultation with the norms controller	26.11.2021-30.11.2021	
10	Presentation of the work at the department	15.12.2021	
11	Taking into account the comments and recommendations and training to protect	01.12.2021-28.12.2021	
12	Thesis defense at the department	29.12.2021	

7. Consultant(s) of certain chapter(s):

Chapter	Consultant (academic rank, S.N.P)	Date, signature	
		Given by	Accepted by
Labor Precaution	PhD, Associate Professor of the Department of Civil and Industrial Safety, Kazhank K.I		

8. Date of task issue: «15» September 2021

Diploma (project) advisor: _______________ Marharyta M. Radomska
(advisor's signature) (S.N.P.)

Task is taken to perform: _______________ Alina V. Husieva
(graduate's signature) (S.N.P.)

НАЦІОНАЛЬНИЙ АВІАЦІЙНИЙ УНІВЕРСИТЕТ
Факультет екологічної безпеки, інженерії та технологій
Кафедра екології
Спеціальність, освітньо-професійна програма: спеціальність 101 «Екологія», ОПП «Екологія та охорона навколишнього середовища»
(шифр, найменування)

ЗАТВЕРДЖУЮ
Завідувач кафедри
___________Дудар Т.В.
«____» _________ 2021 р.

ЗАВДАННЯ
на виконання дипломної роботи
Гусєвої Аліни Віталіївни

1. Тема роботи «Фотокаталітичне очищення стічних вод від ароматичних сполук» затверджена наказом ректора від «15» вересня 2021 р. №1872/ст.

2. Термін виконання роботи: з 15.09.2021 р. по 15.12.2021 р.

3. Вихідні дані роботи: розрахунки ефективності конверсії фотокаталітичного розкладання фенолу.

4. Зміст пояснювальної записки: аналіз основних забруднювачів стічних вод, їх вплив на навколишнє середовище та живі організми, дослідження технології очищення води від органічних забруднювачів, вивчення фотокаталізу як методу очищення води від органічних забруднювачів, вивчення ефективності фотокаталізаторів, аналіз методів моніторингу вмісту органічних забруднювачів води, аналіз можливостей України для моніторингу органічних забруднювачів в воді.

5. Перелік обов’язкового графічного (ілюстративного) матеріалу: таблиці, рисунки.

6. Календарний план-графік

№ з/п	Завдання	Термін виконання	Підпис керівника
1	Отримання теми завдання, пошук літератури і законодавства	05.09.2021-15.09.2021	
2	Підготовка основної частини (Глава I)	16.09.2021-30.09.2021	
3	Підготовка основної частини (Глава II)	01.10.2021-15.10.2021	
4	Підготовка основної частини (Глава III)	16.10.2021-21.10.2021	
5	Підготовка основної частини (Глава IV)	22.10.2021-26.10.2021	
6	Консультація з розділу V (охорона праці)	27.10.2021-04.11.2021	
7	Підготовка основної частини (Глава V)	05.11.2021	
8	Формулювання висновків та рекомендацій з диплому	21.11.2021-25.11.2021	
9	Зробити пояснювальну записку до попередньої презентації кафедри, консультації з нормоконтролером	26.11.2021-30.11.2021	
10	Презентація праці на кафедрі	15.12.2021	
11	Врахування коментарів та рекомендацій та навчання для захисту	01.12.2021-28.12.2021	
12	Захист диплому на кафедрі	29.12.2021	

7. Консультація з окремого(мих) розділу(ів):

Розділ	Консультант (посада, П.І.Б.)	Дата, підпис	
		Завдання видав	Завдання прийняв
Охорона праці	к.т.н., доцент кафедри промислової та цивільної безпеки ФЕБІТ НАУ, Кажан К.І.		

8. Дата видачі завдання: «15» 09 2021 р.

Керівник дипломної роботи (проекту): ____________ Радомська Маргарита Мирославівна
(підпис керівника) (П.І.Б.)

Завдання прийняв до виконання: _________ Гусєва Аліна Віталіївна
(підпис випускника) (П.І.Б.)

ABSTRACT

Explanatory note to thesis «Photocatalytic treatment of wastewater contaminated with aromatic compounds»: 114 pages, 55 figures, 5 tables, 101 references.

Object of research: organic water pollution, phenol photocatalysis.

Aim of work: assessment of the hazards of organic water pollution, reduction of phenol concentration in waste water using photocatalysis.

Methods of research: literature analysis, experiments with phenol photocatalysis, comparison of photocatalyst efficiency.

Our work on the topic "Photocatalytic treatment of wastewater contaminated with aromatic compounds" is quite important, because water is a vital resource and many factors affect its quality. The release of organic substances into the water, as well as the monitoring of these substances, is an important issue in the field of ecology that requires a solution. Systems for monitoring and combating water pollution by organic matter in Ukraine are underdeveloped and need to be improved.

NATURAL WATERS, WASTEWATERS, ANTHROPOGENIC POLLUTION, AROMATIC SUBSTANCES, EFFECTS OF AROMATIC SUBSTANCES, PHOTOCATALYSIS, PHOTOCATALYSTS, PHENOL, TITANIUM DIOXIDE, LIQUID CHROMATOGRAPHY, HIGH PERFORMANCE LIQUID CHROMATOGRAPHY, TRACKING OF ORGANIC POLLUTANTS, BIOINDICATION, CONTROL OF ORGANIC POLLUTION.

CONTENT

LIST OF SYMBOLIC NOTATIONS AND ABBREVIATIONS

POPs – Persistent organic pollutants;

TDS – Total dissolved solids;

CNTs – Carbon nanotubes;

DBPs – Disinfection by-products

VOCs – Volatile organic compounds

PCBs – Polychlorinated biphenyls

EDCs – Endocrine disruptors

EPPs – Environmental persistent pharmaceutical products

DDT – Dichloro-diphenyl-trichloroethane

PAHs – Polycyclic aromatic compounds

DNA – Deoxyribonucleic acid

BP – Benzopyrene

LC – Liquid chromatography

HPLC – High performance liquid chromatography

UV – Ultraviolet

PAR – Photosynthetically active radiation

UNEP – United Nations Environment Programme

INTRODUCTION

Relevance of the topic. Water is a vital resource and many factors affect its quality. The release of organic substances into the water, as well as the monitoring of these substances, is an important issue in the field of ecology that requires a solution. Systems for monitoring and combating water pollution by organic matter in Ukraine are underdeveloped and need to be improved.

The aim of our work was to determine the applicability of photocatalysis for the degradation of phenol pollution in water.

The main tasks of the work are:

1. To study the literature about organic water pollution sources and impacts on living organisms with accent on aromatic substances, in particular phenol and benzene;
2. To study the methods of phenol content measurement in water and methods of its removal from waters;
3. To conduct experiments with photocatalytic water purification from aromatic phenol and choose the most efficient working conditions;
4. To develop the recommendations on implementation of photocatalytic water purification technology and amendment of environmental water monitoring system in Ukraine.

Object of research – water pollution with organic compounds.

Subject of research – degradation of organic pollutants in water during photocatalytic process.

Methods of research – information search, analysis and synthesis of information, comparative analysis, photocatalysis, chromatography, HPLC.

Practical value. The developed method of water purification from organic compounds can be tested for use on an industrial scale, which will significantly reduce the anthropogenic load on the environment.

Personal contribution of the author – study and analysis of literature, carrying out experiments with photocatalysis of phenol and benzene; selection of methods for the study of organic substances using high-performance liquid-phase chromatography; selection of catalysts for photocatalysis reactions of a solution of organic substances.

Approbation of the results. The content and conclusions of thesis are presented in the discussion in the XV All-Ukrainian scientific-practical conference of young scientists and students "environmental safety of the state", also in the XVI International Scientific and Practical Conference "ACTUAL PROBLEMS OF ECOLOGY", and in the VII International Scientific and Practical Conference "Sustainable Development - XXI Century: Management, Technology, Models (Scientific Readings named after Igor Nedin)"

Publications: based on the results of the work 3 theses were published.

CHAPTER 1

ANTHROPOGENIC POLLUTION OF NATURAL WATERS

Water (chemical formula H_2O) is an inorganic, transparent, tasteless, odorless, and nearly colorless chemical substance, which is the main constituent of Earth's hydrosphere and the fluids of all known living organisms (in which it acts as a solvent). It is vital for all known forms of life, even though it provides no calories or organic nutrients. Its chemical formula H_2O, indicates that each of its molecules contains one oxygen and two hydrogen atoms, connected by covalent bonds. The hydrogen atoms are attached to the oxygen atom at an angle of 104.45°. "Water" is the name of the liquid state of H_2O at standard conditions for temperature and pressure.

A number of natural states of water exist. It forms precipitation in the form of rain and aerosols in the form of fog. Clouds consist of suspended droplets of water and ice, its solid state. When finely divided, crystalline ice may precipitate in the form of snow. The gaseous state of water is steam or water vapor.

Water covers approximately 70.9% of the Earth's surface, mostly in seas and oceans. Small portions of water occur as groundwater (1.7%), in the glaciers and the ice caps of Antarctica and Greenland (1.7%), and in the air as vapor, clouds (consisting of ice and liquid water suspended in air), and precipitation (0.001%). Water moves continually through the water cycle of evaporation, transpiration (evapotranspiration), condensation, precipitation, and runoff, usually reaching the sea.

Water plays an important role in the world economy. Approximately 70% of the freshwater used by humans goes to agriculture. Fishing in salt and fresh water bodies is a major source of food for many parts of the world. Much of the long-distance trade of commodities (such as oil, natural gas, and manufactured products) is transported by boats through seas, rivers, lakes, and canals. Large quantities of water, ice, and steam are used for cooling and heating, in industry and homes. Water is an excellent solvent for a wide variety of substances both mineral and organic; as such it is widely used in industrial processes, and in cooking and washing. Water, ice and snow are also central to many sports and other forms of entertainment, such as swimming, pleasure boating, boat racing, surfing, sport fishing, diving, ice skating and skiing. [93]

1.1. Types of natural waters pollution

Although water has the simple formula H_2O, it is a complex chemical solution. "Pure" water essentially is nonexistent in the natural environment. Natural water, whether in the atmosphere, on the ground surface, or under the ground, always contains dissolved minerals and gases as a result of its interaction with the atmosphere, minerals in rocks, organic matter, and living organisms.

Rainwater, seawater and river water (Figure 1.1) and groundwaters (Figure 1.2) generally have very different chemical compositions and differ widely in their concentrations of total dissolved solids (TDS). Average TDS values are: 7mg l^{-1} for rainwater, 118mg l^{-1} for river water and 34 400 mg l^{-1} for seawater. TDS values for groundwater vary too much for an average to be meaningful. TDS is a good indicator of water quality, and standards that have been set for drinking water and for water used in other ways include maximum values for TDS.

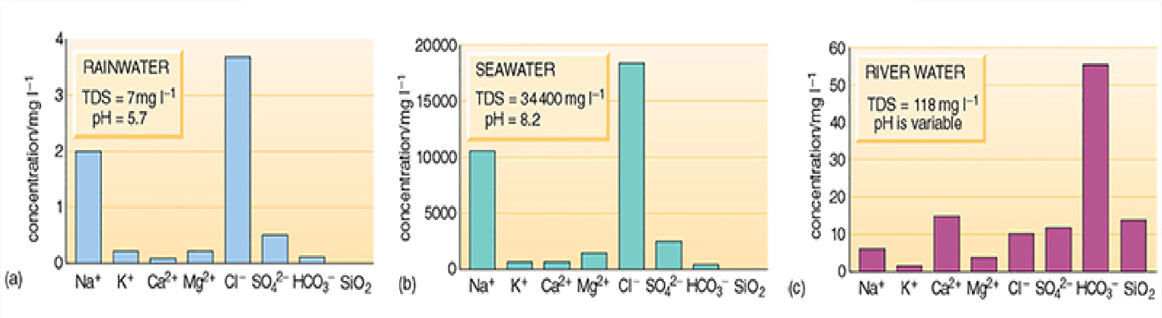


Fig 1.1 The average chemical compositions of (a) rainwater, (b) seawater and (c) river water. Only the major dissolved constituents are shown, and dissolved gases are not included. Different scales are used for each histogram. River water may vary considerably from the composition shown. [58]

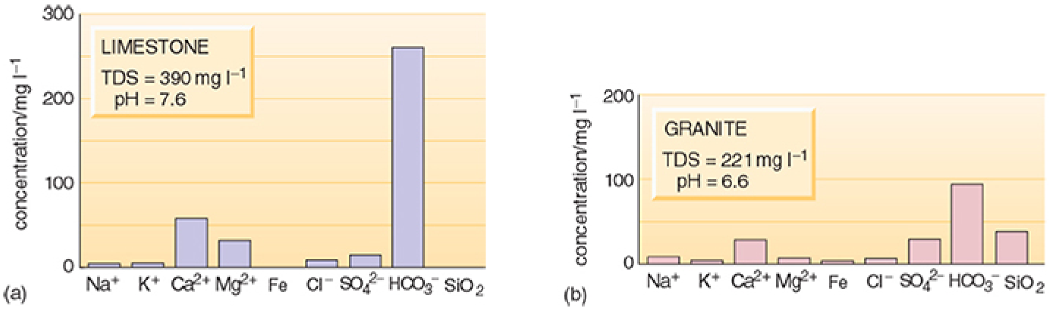


Fig 1.2 The chemical compositions of groundwaters from (a) limestone and (b) granite. (Fe includes both the Fe^{2+} and Fe^{3+} ions.) [58]

Rainwater and seawater (Figure 1.1 a and b) have similar relative proportions of dissolved solids, although rainwater is much more dilute. Most of the dissolved salts in rainwater come from sea spray dispersed into the atmosphere. A major difference in composition is the greater relative proportions of dissolved gases in rainwater, particularly carbon dioxide. Natural rainwater is slightly acidic as a result of this reaction, with an average pH of 5.7, whereas the average pH of seawater is 8.2. Rainwater may be even more acidic in areas where the highly soluble acidic gases sulphur dioxide and nitrogen dioxide (both produced by fossil fuel power generation, transportation and industrial processes) are present in the atmosphere. The pH of most natural waters lies between 5.5 and 8.5. [58]

On the basis of minerals content, water is classified in several ways.

Marotta and Sica classification (1933) represents the first ranking, which takes into consideration temperature, fixed residue and chemical composition, according to a scheme that includes classes and subclasses. They gave the name to each mineral water considering, firstly, the prevalent anion and secondly, the cation; they classified waters as salty-sulfate waters, bicarbonate-sulfate waters, salt-bromine-iodine waters, etc.

Natural waters are widely exploited for various purposes that results in the change of their initial composition due to increasing content of existing components or introduction of substances previously not present in water or nature on the whole. This process is called water pollution. it might also take place due to release of a range of substances with waste and waste waters into water bodies. The concentration of these excessive or novel substances often reaches the point where they interfere with further use of the water by humans or with the natural functioning of ecosystems. In addition to the release of substances, water pollution may take the form of energy, released as radioactivity or heat. Due to this complex character of water pollution it is differentiated by nature into:

- mechanical;
- physical;
- chemical;
- biological.

Mechanical pollution is the input of various mechanical impurities (sand, sludge, silt, etc.) into the water, as well as solid waste (garbage), timber rafting residues, which can significantly worsen the organoleptic characteristics of waters.

Physical pollution deals with various forms of energy released into the waters, leading to changes of its physical parameters. As such, the most important types of physical pollution are thermal and radioactive.

The content of radioactive substances in water, even at very low concentrations, causes radioactive contamination of natural sources, among which the most harmful are long-lived radioactive elements with an increased ability to move in water and to be accumulated by living organisms in their bodies (strontium-90, uranium, radium-226, cesium, etc.).

Radioactive elements enter surface water bodies with discharged radioactive waste, when waste is buried at the bottom, etc. Radioactive elements also enter waters as a result of their fallout to the Earth's surface in the form of radioactive products and waste, and then seep into the interior of the Earth along with atmospheric waters reaching underground waters, as well as on the interaction of groundwater with radioactive rocks.

Thermal pollution is associated with an increase in water temperature as a result of their mixing with more heated surface or waste waters, which leads to a change in the gas and chemical composition of water due to changing solution conditions. This type of pollution leads to the multiplication of anaerobic bacteria, the growth of aquatic organisms and the release of poisonous gases – hydrogen sulfide, methane. The other serious consequence is the eutrophication process, which is also known as water bloom or algal bloom. It occurs due to combination of increased temperature of water and its pollution with nitrous and phosphorous nutrients and represents the accelerated development of microflora and microfauna. According to the existing sanitary standards, the temperature of the reservoir should not increase by more than 3°C in summer and 5°C in winter. [88]

Chemical pollution is the most common pollution of the hydrosphere, formed by chemicals of various nature, including *organic* (phenols, naphthenic acids, pesticides, etc.) and *inorganic* (salts, acids, alkalis). These pollutants can be toxic (arsenic and heavy metals, etc.) or non-toxic. However, many of them are persistent and can gradually concentrate in living organisms producing distant pernicious effects. The list of organic pollutants is constantly expanding, making this group far more dangerous for water bodies stability as environmental component natural resource and habitat.

Biological pollution is expressed in the appearance in the water of pathogenic bacteria, viruses (up to 700 species), protozoa, fungi, etc. This type of pollution is temporary.

1.2. Organic pollution of water

Organic pollutants are substances that negatively affect the environment and are literally any chemical compounds that contain carbon-hydrogen bonds. The latter include oil, various hydrocarbons, phenol, alcohols, acids, aldehydes and ketones, ethers, nitrogen. They may have plant or animal origin or be produced in the process of industrial organic synthesis or processing of fossil fuels.

Organic pollution enters the water in a natural way (products of organisms living activity as well as their bodies) and as a result of human activity (waste burial and discharge, spills, leakages, surface runoff). A common natural organic pollutant is humic compounds. Their presence is determined by their characteristic brown tint. [60]

Anthropogenic organic water pollution occurs due to the work of various types of industry. Household and industrial waste enters rivers along with organic matter, which stops the flow of oxygen into the water.

Wastewater plays an important role in the pollution of the natural waters. They are full of industrial waste and organic matter that degrade water bodies' quality. Storm waters from industrial and urban areas also carry a lot of organic chemicals, in particular, fuels and lubricants, detergents and other chemicals. Agricultural facilities also contribute wastewaters and surface runoff rich in organic matter, including a wide range of highly persistent and hazardous substances used for manipulation with yields and stimulation of growth. Organic matter makes up 58% of the domestic wastewater content.

Organic matter is a wonderful breeding ground for pathogenic bacteria that cause infectious diseases. The deterioration of human health leads to a decrease in labor efficiency, which will seriously affect the country's economy. The quality of water resources will not improve unless measures are taken to remove organic pollution. Otherwise, organic pollution of the environment will become a more acute and urgent problem for the inhabitants of the world. [60]

The quality of natural water is affected by organic pollution more adversely as compared with inorganic substances, as their variety is considerable lower.

Organic water pollutants include:

- Detergents are surfactant or a mixture of surfactants with cleansing properties in dilute solutions. They are usually made of alkylbenzene sulfonates, a family of compounds that are similar to soap and contain aromatic core;
- Disinfection by-products (DBPs), result from water disinfection process when organic and inorganic matter in water react with chemical treatment agents, producing such products as chloroform and aromatic chlorinated substances;
- Food processing waste, which can include oxygen-demanding substances, fats and grease, as well as products of organic matter decomposition;
- Pesticides, a huge range of organohalides and other chemical compounds, which persist in the environment and cause a range of negative effects – attributed to the group of persistent organic pollutants (POPs);
- Petroleum hydrocarbons, including fuels (gasoline, diesel fuel, jet fuels, and fuel oil) and lubricants (motor oil), and fuel combustion byproducts, from storm water runoff
- Volatile organic compounds (VOCs), such as industrial solvents.
- Chlorinated solvents, which are dense non-aqueous phase liquids, may fall to the bottom of reservoirs, since they don't mix well with water and are denser.

- Polychlorinated biphenyls (PCBs) are complex aromatic substances, which are mostly produced as byproducts of industrial processes and are xenobiotic. They are also included into the group of Persistent, bioaccumulative and toxic substances (PBTs).

- Hormones and other Endocrine disruptors (EDCs) – various chemical compounds found in personal hygiene and cosmetic products;

- Pharmaceutical drugs and their metabolites, this can include antidepressant drugs or hormonal medicines such as contraceptive pills – attributed to the group of Environmental persistent pharmaceutical pollutant (EPPPs). These molecules can be small and difficult for treatment plants to remove without expensive upgrades. [92]

Persistent organic pollutants (POPs) are a class of highly hazardous chemical pollutants that pose a serious global threat to human health and the environment. POPs include some pesticides, some industrial chemicals and some unintentionally generated by-products that are formed during certain combustion and chemical processes. Examples of POPs are DDT (dichloro-diphenyl-trichloroethane), PCBs and dioxins.

They have the following four specific properties:

1) Persistence: POPs are chemical pollutants that are not physically, chemically and biologically degradable. Therefore, once a POP is in the environment, it remains there for a long time.

2) Ability to accumulate in biological objects: POPs are chemicals that are readily soluble in fats (lipophilic). They accumulate in the tissues of living organisms in concentrations that significantly exceed those in the environment.

3) Ability to travel long distances: POPs can travel long distances in the environment and can cause harm in locations remote from the original source of POPs entering the environment. POPs are mainly carried by air currents, but they can also be carried by water masses or migratory animal species.

4) Potential for harmful effects: POPs are chemicals that have a negative impact on human health and / or ecosystems.

POPs are widely present in the environment in all regions of the world. Every person contains POPs in their bodies, which are mainly accumulated in adipose tissues. Most fish, birds, mammals and other wildlife are also contaminated with POPs.

Being in the environment, POPs contaminate the food we consume on a daily basis, especially fish, meat, butter and cheese. When people eat food contaminated with POPs, these chemicals accumulate in their fatty tissues. A mother's body transfers POPs to a newborn. In humans and other mammals, POPs penetrate the fetus and affect it while it is still in the womb. Since breast milk also contains POPs, newborns continue to be exposed to POPs during feeding. In non-mammalian species, POPs are passed from mother to offspring through eggs.

Even in small concentrations, which are ubiquitous in common food, POPs can harm humans and other living organisms. There are medical evidences about the links between the following human diseases and disorders due to exposure to some POPs:

- Cancers and tumors, including soft tissue sarcoma, non-Hodgkin's lymphoma, breast cancer, pancreatic cancer, and leukemia;
- Neurological disorders including attention deficit, behavior problems such as aggression and crime, learning disabilities and impaired memory;
- Immunity suppression;
- Reproductive system disorders, including changes in semen, miscarriages, premature birth, low birth weight, change in the sex ratio of newborns, short lactation period in nursing mothers and menstrual irregularities;
- Other diseases, including an increase in the incidence of diabetes, endometriosis, hepatitis and cirrhosis.

In general, chemicals that are considered POPs fall into one of three categories. Some POPs were or continue to be produced deliberately for pesticide use, including insecticides, herbicides or fungicides. Several POPs have been or are still being produced for use as industrial chemicals. In addition, some POPs are produced unintentionally, as unwanted by-products in some chemical industrial processes, or are unintentionally generated during combustion processes, including combustion in the presence of chlorine or other halogens (eg bromine, fluorine). [27] Many of them are included into the Declaration of non-use of Persistent Organic Pollutants, which is amended with new substances from time to time.

One of the main fractions of organic pollutants in the aquatic environment is formed by toxic aromatic hydrocarbons - unsaturated cyclic compounds of the benzene series and their derivatives, polycyclic aromatic hydrocarbons. PAHs are compounds which has two or more fused aromatic rings. They are poorly soluble in water, but are highly lipophilic. These compounds have low vapor pressure. They are adsorbed on particles in the soil, air, water, and sediment. PAHs can undergo photodegradation when exposed to ultraviolet light from solar radiation. These compounds are not emitted into the environment as single compounds, but often come as mixtures, the composition of which depends on the release from different point sources. In the environment, they coexist with chlorinated hydrocarbons, amines, and metals. In the atmosphere, PAHs can react with pollutants such as chlorine, ozone, nitrogen oxides, and sulfur dioxide, yielding diones, chlorinated PAHs, nitro- and dinitro-PAHs, and sulfonic acids, respectively. These compounds are also subjected to microbial degradation in soil and sediments [43,94].

Polycyclic aromatic hydrocarbons (PAHs) are extremely stable in any environment and difficult to degrade. Benzene and its homologues have a faster toxic effect on the body than PAHs. The latter act more slowly, but for a longer time, being chronic toxicants. [22] While toluene, xylene, benzene, naphthalene, etc., being volatile are easily destroyed and removed from water and soil, but have enough time to cause negative health effects.

1.3. Sources of organic pollution with aromatic substances

Benzene is a colorless liquid with a characteristic odor. Benzene enters surface water from enterprises and production facilities of the main organic synthesis, petrochemical, chemical and pharmaceutical industries, in the production of plastics, explosives, ion-exchange resins, varnishes and paints, artificial leather, as well as with wastewater from furniture factories. In the wastewater of coke-chemical plants, benzene is contained in concentrations of 100-160 mg / dm3, in wastewater from caprolactam production - 100 mg / dm3, isopropylbenzene production - up to 20,000 mg / dm3. The source of water pollution can be a transport fleet (used in motor fuel to increase the octane number). Benzene is also used as a surfactant.

Benzene quickly evaporates from reservoirs into the atmosphere (half-evaporation period is 37.3 minutes at 20 ° C). The threshold for sensing the smell of benzene in water is 0.5 mg / dm3 at 20 ° C. At 2.9 mg / dm3 odor with an intensity of 1 point, at 7.5 mg / dm3 - 2 points; fish meat acquires an unpleasant odor at 10 mg / dm3. At 5 mg / dm3, the smell disappears in a day, at 10 mg / dm3, the intensity of the smell per day decreases to 1 point, at 25 mg / dm3 the smell decreases to 1 point after two days.

Smack at 1.2 mg / dm3 - 1 point, at 2.5 mg / dm3 - 2 points. The presence of benzene in water (5 mg / dm3) does not change the processes of biological oxygen consumption, since under the influence of biochemical processes in water benzene is weakly oxidized; in concentrations of 5-25 mg / dm3 benzene does not delay the mineralization of organic substances, does not affect the processes of bacterial self-purification of water bodies.

At a concentration of 1000 mg / dm3 benzene inhibits the self-purification of diluted wastewater, at a concentration of 100 mg / dm3 it inhibits the process of wastewater treatment in aeration tanks, 885 mg / dm3 strongly delays the fermentation of sediment in digesters.

With repeated exposure to low concentrations of benzene, changes are observed in the blood and hematopoietic organs, damage to the central nervous system and the peripheral nervous system, and the gastrointestinal tract. Benzene is classified as a highly suspected carcinogen. The main metabolite of benzene is phenol. Benzene has a toxic effect on aquatic organisms.

Phenols are benzene derivatives with one or more hydroxyl groups. They are usually divided into two groups - vapor-volatile phenols (phenol, cresols, xylenols, guaiacol, thymol) and non-volatile phenols (resorcinol, pyrocatechol, hydroquinone, pyrogallol and other polyatomic phenols).

Phenols in natural conditions are formed in the metabolic processes of aquatic organisms, during the biochemical decomposition and transformation of organic substances, flowing both in the water column and in bottom sediments.

Phenols are one of the most common pollutants entering surface waters with effluents from oil refining, oil shale processing, wood-chemical, coke-chemical, aniline-paint industries, etc. In the waste waters of these enterprises, the content of phenols can exceed 10-20 g / dm3 with very diverse combinations.

In surface waters, phenols can be in a dissolved state in the form of phenolates, phenolate ions, and free phenols. Phenols in waters can enter into condensation and polymerization reactions, forming complex humus-like and other fairly stable compounds. Under the conditions of natural water bodies, the processes of phenol adsorption by bottom sediments and suspensions play an insignificant role.

In unpolluted or slightly polluted river waters, the content of phenols usually does not exceed 20 μg / dm3.

The excess of the natural background can serve as an indication of the pollution of water bodies. In natural waters polluted with phenols, their content can reach tens and even hundreds of micrograms per liter. Phenols are unstable compounds and undergo biochemical and chemical oxidation.

Simple phenols are mainly subject to biochemical oxidation. At a concentration of more than 1 mg / l, the destruction of phenols proceeds rather quickly, the loss of phenols is 50-75% in three days, at a concentration of several tens of micrograms per liter, this process slows down, and the decrease during the same time is 10-15%. Phenol itself is destroyed the fastest, cresols are slower, and xylenols are even slower. Polyhydric phenols are degraded mainly by chemical oxidation.

The concentration of phenols in surface waters is subject to seasonal changes. In the summer, the content of phenols decreases (as the temperature rises, the rate of decomposition increases).

Descent into reservoirs and watercourses of phenolic waters sharply worsens their general sanitary condition, influencing living organisms not only by their toxicity, but also by a significant change in the regime of biogenic elements and dissolved gases (oxygen, carbon dioxide).

As a result of chlorination of water containing phenols, stable chlorophenol compounds are formed, the slightest traces of which (0.1 μg / dm 3) give the water a characteristic taste.

In toxicological and organoleptic terms, phenols are unequal. Vapor-volatile phenols are more toxic and have a more intense odor when chlorinated.

2 standards have been established for the amount of volatile phenols: 0.001 mg / dm3 - maximum permissible concentration for water of reservoirs for domestic and drinking water use, provided that chlorine is used for disinfecting drinking water or when determining the conditions for discharging wastewater that is disinfected with chlorine and in fishery water bodies; 0.1 mg / dm3 is the maximum permissible concentration for the rest of the water bodies. [91]

PAHs can enter the environment both as a result of natural processes and as a result of human activity. As a rule, the composition and structure of PAHs of natural and anthropogenic origin differ significantly, which makes it possible to identify the main sources of PAH input into ecosystems.

Natural sources of PAHs include forest fires, volcanic eruptions, hydrocarbon flows within oil and gas regions, transformation of biomolecules in sedimentary rocks, and biogenic synthesis of PAHs.

Most of the PAHs found in the environment arise from three principal sources: petrolytic, pyrogenic, and diagenic. Pyrogenic PAHs are formed from unfinished, high-temperature burning of organic matter. High-temperature synthesis takes place in volcanoes, geothermal springs, and degassing of the bowels. The consequence of these processes is the formation and release into the environment of pyrogenic PAHs, similar to compounds of technogenic origin: unsubstituted structures and alkyl derivatives, for example, benzpyrene, fluoranthene, naphthalenes, phenanthrenes, pyrenes, benzperylene.

PAHs of petrogenic origin (coal and oil) can enter the environment when emanating from productive horizons PAHs [56,12]. These PAHs have preponderantly alkylated structures. In crude oil, PAHs, mainly consisting of two and three benzene rings, contain from 0.2 to 7%, and according to some data they can reach more than 30%. In most cases, hydrocarbons from benzene to phenanthrene make up about 90% of the aromatics of petroleum. Hydrocarbons of coal and petroleum, as a rule, contain more alkylated homologues than unsubstituted PAHs, with the number of alkyl radicals from 2 to 5.

Diagenic PAHs are derived from biogenic material due to anaerobic processes. They are present in older sediments and early industrial activity [30]. Attempts to identify the onset of PAHs (petrogenic or pyrogenic) in field studies are prevented by the distribution of these compounds regardless of source, in the environment; therefore, the PAH signatures from one source can be obscured by PAHs from another source [90].

Polyarenes released into the environment as a result of human activity are formed mainly during the operation of industrial enterprises, internal combustion engines, thermal power plants and boiler houses operation. A wide range of PAHs, including phenanthrene, benzopyrene, etc., were found in the emissions of coke-chemical, metallurgical, oil and shale refineries, aluminum and other enterprises. Emergency oil spills and emissions from water transport can also be sources of PAHs. PAHs of anthropogenic origin are mainly represented by pyrogenic compounds formed as a result of combustion of organic raw materials.

The main source of PAHs entering the environment in cities is emissions from mobile and stationary sources. In the atmosphere, polyarenes can be stored in the gas phase, or be sorbed on solid particles. Lighter PAHs containing less than 4 rings in the structure are found mainly in the gas phase in atmospheric air and decompose during the day as a result of oxidation and photooxidation reactions. Larger polyarene molecules (4 or more rings) in the atmosphere are sorbed by dust and soot particles, then they are deposited on the underlying surface or water area and washed out by atmospheric precipitation. Chrysene occupies an intermediate position, which in the atmosphere is evenly distributed between the solid and gas phases. In the cold season, compounds containing from 2 to 4 rings are also subjected to adsorption on aerosols. Such compounds are more resistant to degradation and can be transported over considerable distances. In general, the half-life of PAHs in the environment ranges from 5 to 10 years.

The main processes of the transfer of polyarenes from the atmosphere to the surface of land and water areas are dry deposition, washout by precipitation, and deposition from the gas phase. The first two processes are of prime importance. The residence time of PAHs in the atmosphere depends on the size of the particles on which they are sorbed and the meteorological conditions. Submicron particles can be in the atmosphere for weeks, and when they enter water bodies, such particles remain in suspension for a long time. When emitted from vehicles, almost all compounds entering the atmosphere are deposited within 50 meters from the road and washed away from the territory into water bodies, where they accumulate in bottom sediments.

Levels of PAH in the geosphere and hydrosphere are affected by both dry and wet sediment as well as sediment of contaminated refuse. However, PAH levels in the biosphere are impacted by contact with the polluted air and biomagnifications through the food chain [23]. Partitioning between air and water, sediment and water, and biota and water are key factors for the environmental persistence of PAHs. The closeness of PAHs for organic materials in sediments and soil and lipids in biota are high enough to cause accumulation in the above-mentioned matrices with long-lasting consequences for environmental health.

The concentrations of PAHs in bodies of water from different geographical regions are presented in Figure 1.3.

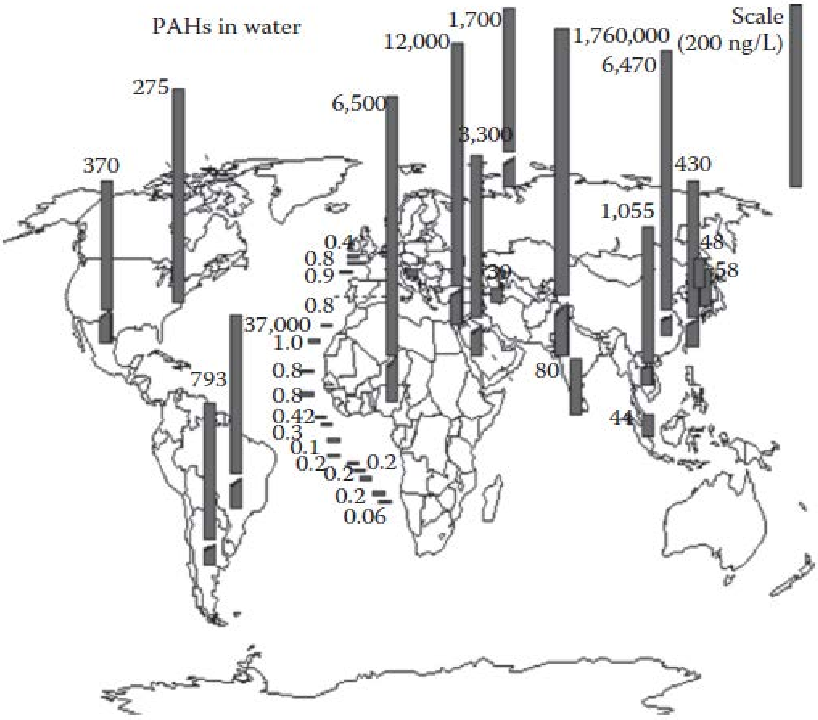


Fig. 1.3. Spatial variations in water PAH concentrations (ng/l) measured in different parts of the world

The relational contributions of various combustion sources to the environmental PAHs on a global basis and for several countries are shown Figure 1.4. On a global scale, biomass burning (both wildfires and biofuel combustion) contributed to 73.7% of the total global PAH emissions. No less important are consumer products, domestic coal combustion, and traffic oil combustion, which together contributed to 15.4% of global emissions. Amid the other sources, major industrial activities contributed less than 10% to the total global PAH emissions.

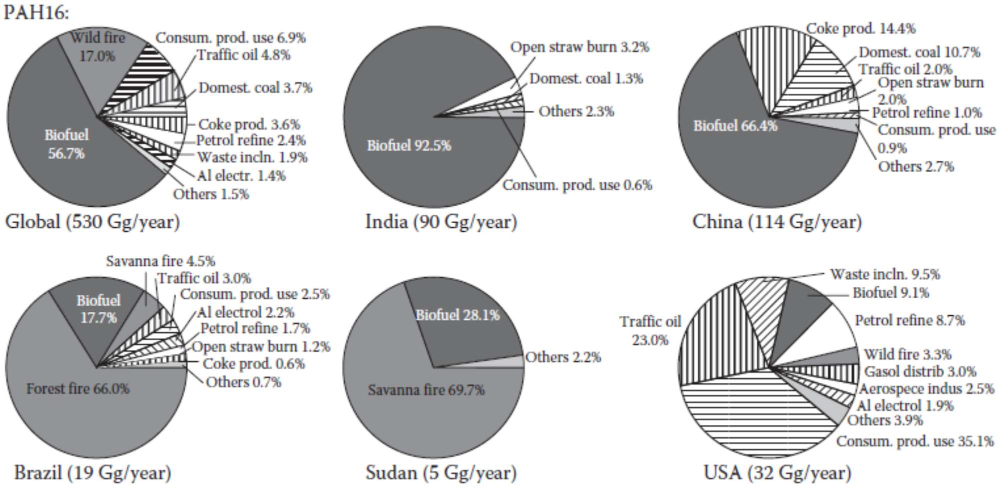


Fig. 1.4. Relative contributions of various sources to PAH16 (priority pollutants)

In an aqueous medium, PAHs, due to their hydrophobicity, tend to sorption on the surface of particles, especially organic matter. [73] Thus, PAHs in water occur in particulate, dissolved, and suspension phases. Atmospheric deposition (dry and wet) and land runoff are major sources of PAH pollution in the aquatic environment. Wastewater and refinery stream discharge PAHs into urban bodies of water while refuse burning, and wet and dry depositions contribute to PAH pollution in rural bodies of water. A coal ash spill from a coal-fired electric power plant in Harriman, Tennessee, released 9.4 million cubic yards of coal ash into the surrounding environment in 2008, a large amount of which was let into the Emory River [82]. Environmental disasters similar to this contribute to a significant loading of three to four ring PAHs that constitute a larger percent of coal ash [4] into the aquatic environment, affecting the quality of water. The emission rates for PAHs discharging into coastal waters could reach up to 100 Mton/year [82].

The toxic and carcinogenic characteristics of PAHs conditioned their inclusion into environmental monitoring programs of several countries. As a result, the PAH pollution from point sources (sewage and industrial effluents, oil shipping and refinery operations) has been successfully cut, whereas PAH pollution from non-point sources (surface runoffs and atmospheric deposition) is hard to abate and still constitutes major inputs into the environment.

Phenols are another dangerous group of organic pollutants with low MPCs. Special attention is paid to the study of the photocatalytic decomposition of these substances. Chlorophenols are well-known environmental pollutants due to their high toxicity. Infection with chlorinated compounds is currently one of the most serious environmental problems. They constitute the most important group of toxic non-biodegradable compounds [31]. Chlorophenols are used as herbicides and fungicides and are exceeded in wastewater from the paper industry. For example, 2-chlorophenol is used in pesticides, herbicides and wood preservatives [42]. In particular, 2-chlorophenol is listed as a major pollutant by the US EPA [89].

Most phenols are toxic substances, some of them are classified as hazardous waste, and some of them are carcinogens [41]. Direct or indirect exposure to certain phenolic compounds, namely bisphenol, β - estradiol, ethinyl estradiol, alkylphenols, diethylstilbestrol, estrone, resorcinol, etc., which can affect the biological functions of living organisms regulated by the endocrine system [39]. It is understood that these compounds lead to an increase in the incidence of cancer, reproductive disorders and developmental abnormalities, which has attracted the attention of scientists in the United States, Europe and Asia [62,70].

1.4. Effects of aromatic substances of biota and human health

1.4.1. Effects of simple aromatic substances on living organisms

Phenols are one of the most common pollutants that enter surface waters with industrial effluents. The discharge of phenolic waters into water bodies and watercourses sharply worsens their general sanitary condition, influencing living organisms not only by their toxicity, but also by a significant change in the regime of biogenic elements and dissolved gases (oxygen, carbon dioxide).

The number of known phenolic compounds is very large. To date, several thousands of them are known, and their number is growing every year. Phenolic compounds are usually divided into two groups:

- vapor-volatile phenols (phenol, cresols, xylenols, guaiacol, thymol);
- non-volatile phenols (resorcinol, pyrocatechol, hydroquinone, pyrogallol and other polyatomic phenols).

Volatiles are more toxic and have a strong odor.

Usually, phenols in natural conditions are formed in the metabolic processes of aquatic organisms, during the biochemical decay and transformation of organic substances, flowing both in the water column and in bottom sediments. Phenolic compounds of living plant tissues can be considered potentially toxic substances that can inhibit the growth of pathogenic fungi or reduce the rate of reproduction of viruses.

Phenols are weak acids (the pKa of phenol itself is 9.98). The high reactivity of phenols in oxidation reactions finds technical application when phenolic compounds are used as inhibitors of the autooxidation of oils and fats and is of great importance in the biosynthesis of natural phenolic compounds. The most important property of phenols in terms of isolation and identification is the ability to form salts with metals.

With a few exceptions, all phenolic compounds are solid and vary in color from light yellow to red, brown, or purple.

Phenols are one of the most common pollutants entering surface waters with effluents from oil refineries, oil shale processing, timber-chemical, coke-chemical, aniline-paint industries, as a result of timber rafting, as well as with effluents from the hydrolysis industry (processing of non-food plant raw materials from the pulp and paper industry and partly from the textile industry).

In industrial wastewater, the content of phenols can exceed 5-10 g / l with very diverse combinations, while the maximum permissible concentration of phenols in drinking water and water of fishery reservoirs is 1 μg / l.

The concentration of phenol in the effluents of coke-chemical plants is especially high - up to 20 g / l, and a modern coke-chemical plant discharges up to 4-10 tons of phenol into water bodies per day.

The excess of the natural background for phenol can serve as an indication of the pollution of water bodies. In natural waters polluted with phenols, their content can reach tens and even hundreds of micrograms per 1 liter.

The water of the reservoir acquires a color, a specific smell, becomes covered with a fluorescent film that interferes with the natural course of biological processes in the reservoir.

At a concentration of 75 mg / l, phenol inhibits the biological treatment process in a reservoir, at a concentration of 0.01-0.1 mg / l, an unpleasant taste appears in fish meat; the unpleasant taste and smell of water disappear only when phenol is diluted to a concentration of 0.11 mg / l.

In surface waters, phenols can be in a dissolved state in the form of phenolates, phenolate ions, and free phenols.

Phenols in waters can enter into condensation and polymerization reactions, forming complex humus-like and other fairly stable compounds. Under the conditions of natural water bodies, the processes of phenol adsorption by bottom sediments and suspensions play an insignificant role.

The discharge of phenolic waters into water bodies and watercourses sharply worsens their general sanitary condition, influencing living organisms not only by their toxicity, but also by a significant change in the regime of biogenic elements and dissolved gases (oxygen, carbon dioxide).

As a result of chlorination of water containing phenols, stable chlorophenol compounds are formed, the slightest traces of which (0.1 μg / dm3) give the water a characteristic taste and smell.

In toxicological and organoleptic terms, phenols are unequal. Vapor-volatile phenols are more toxic and have a more intense odor when chlorinated. The most pungent odors are produced by simple phenol and cresols.

Phenol and phenolic compounds are widely used in various industries. If in an enterprise work with large quantities of pure phenol compounds and outside specially designated premises, then they can cause allergies, asthma, eczema. The disease does not manifest itself immediately, but after weeks and months of daily contact with pure compounds in unadapted conditions.

The presence of phenols in the atmospheric air, according to the research of specialists, also leads to diseases of the circulatory system.

Nitrophenolic compounds are very toxic - nitrocene (a product of coal-tar phenols), dinitrophenol, etc.

These compounds are used as insecticides, fungicides and herbicides. Influencing the oxidative processes in the tissues, they cause the dissociation of oxidative forcing, which, in turn, enhances the processes of cellular oxidation, increases the tissue oxygen demand and disrupts heat production and thermoregulation.

In water bodies, the maximum permissible concentration for phenol is 0.001 mg / l. [67]

Phenol poisoning is an acute or chronic intoxication provoked by the inhalation of vapors of a substance, its fine dust formed during condensation of vapors, as well as the ingress of a toxicant on the skin. Symptoms depend on the type of compound. The most common signs are coughing, dizziness, burns in the respiratory tract, and seizures. Pathology is diagnosed based on the history and clinical picture. Toxic-chemical research is not informative. Treatment includes skin treatment with 40% ethanol, sodium thiosulfate, alkaline inhalation. For oral lesions, gastric lavage with a suspension of activated carbon is indicated.

Phenol poisoning occurs during industrial accidents. Intoxication is difficult due to a high dose of a toxic substance. The poison is delivered by transdermal and inhalation. Lethal disorders develop if 25-50% of the surface of the human body comes into contact with the toxicant. The most dangerous are monoatomic compounds (carbolic acid). Polyatomic substances (pyragallol) are less toxic.

Other reasons:

- Drinking contaminated water. Phenol enters water bodies when the rules for waste processing by industrial organizations are violated. There are known cases of the discharge of toxic substances into drinking reservoirs. People using such water may experience symptoms of intoxication, usually chronic. Acute lesions are rare.

- Ingestion of food. Vegetables grown in fields contaminated with chemicals have the ability to accumulate harmful components. When eating dishes made using these products, the xenobiotic enters the body, causing signs of mild or moderate intoxication.

- Fires. Phenol poisoning occurs by inhalation of smoke generated during the combustion of chipboards, plastics. It is combined with the defeat of other gaseous products: carbon monoxide and carbon dioxide, hydrocyanic acid, sulfur dioxide, ammonia, phosgene. The signs of suffocation and hypoxia of the hemic type come to the fore.

- Use in medicine. Phenols (carbolic acid) have been used until recently as an antiseptic skin treatment. When the drug is applied to a large area or when high concentrations are used, poisoning developed. Today, QC is not used for application to the patient's body due to its potential toxicity.

- Cosmetological procedures. Symptoms of exotoxicosis are observed in women who have undergone the peeling procedure using carbolic acid or its derivatives. Chemical exotoxicosis occurs when processing a large surface, as well as due to a violation by a cosmetologist of the permissible dosages of the drug.

The effect of phenols on the body is multifaceted, depending on the route of entry of the poison, the time of exposure and the frequency of contact with the toxic substance. With regular inhalation of vapors, pathological plethora of internal organs, their inflammatory infiltration, occurs. Areas of hemorrhage are formed around the vessels. First of all, the lungs are affected, then the liver and kidneys. Revealed proteinuria, metabolic acidosis. The heart and spleen are less affected than other structures.

Acute inhalation phenol poisoning is characterized by the formation of edema and hyperemia of the upper respiratory tract. A mechanical obstruction is determined, which is accompanied by signs of respiratory failure of varying degrees. Severe cases end in toxic pulmonary edema. The initial excitement of the respiratory center is noted, followed by its oppression. The neurotropic effect of xenobiotics is manifested by convulsions, impaired coordination.

When carbolic acid comes into contact with the skin, symptoms of a chemical burn are revealed. Their severity depends not only on the concentration of the solution, but also on the time of its exposure. Even 2-3% of the composition is capable of provoking gangrene if it has not been removed within 2-3 hours. 70-80% of the product burns fabrics almost instantly. When liquid forms of poison or its crystals enter the stomach, ulceration is formed, and an inflammatory process develops. Bleeding is possible. The picture resembles that of poisoning with cauterizing liquids.

The division of phenol poisoning can be carried out according to the type of poisonous component (monoatomic, polyatomic, chlorinated), for reasons that caused phenol poisoning (industrial, alimentary, iatrogenic), along the routes of poison intake (inhalation, oral, transdermal). Classification by severity is considered significant. There are the following levels of chemical damage:

- Light poisoning. Mainly local signs of intoxication. Victims complain of irritation of the eyes and respiratory tract. The general condition is not disturbed. Minor systemic phenomena may be noted: headache, weakness, a subjective feeling of lack of air, which is not confirmed by the data of an objective examination.
- Poisoning of moderate severity. General and local symptoms of the lesion are determined. There are moderate changes in consciousness without loss of consciousness. The state of health is significantly impaired, however, until the development of complications, there is no threat to life. Hospitalization is required in the general department of a toxicological hospital.
- Severe poisoning. There are immediate vital risks caused by significant changes in the functioning of internal systems, metabolic acidosis, neurotropic effects of a toxicant. With inhalation lesions, loss of consciousness occurs, with oral lesions, there are signs of a burn of the esophagus and stomach of II-III degree. With transdermal lesions, similar injuries form on the skin.

Oral poisoning provokes symptoms such as intense burning in the mouth and throat immediately after ingestion of poison, abdominalgia, muscle weakness, cyanosis of the skin. When taking concentrated solutions, dark smudges on the lips and chin are detected. Later, diarrhea, vomiting with an admixture of blood, psychomotor agitation, clonic muscle contraction develops. In severe lesions, depression of the central nervous system, coma, a critical decrease in blood pressure, centralization of blood circulation, and other symptoms of exotoxic shock are found.

Inhalation trauma is characterized by the clinic of mechanical asphyxia. The patient is pale, frightened, covered with clammy cold sweat, restless. Increased physical activity is noted. On examination - generalized cyanosis, the inclusion of auxiliary muscles in the breathing process, fluttering of the wings of the nose. The visible mucous membranes of the mouth and throat are edematous, hyperemic. Common symptoms are a sharp headache, dizziness, lack of coordination, a feeling of suffocation. In severe cases, there is a coma, reflex respiratory arrest, convulsions.

Percutaneous phenol poisoning leads to chemical burns. At the site of contact, the skin becomes wrinkled, pale, and peels off after a few days. The victim complains of a burning sensation, tingling sensation, numbness of the damaged area. When a large zone is damaged, general phenomena are found: hemolysis of erythrocytes, an increase in hematocrit, a violation of the function of excretion systems. A short-term increase in body temperature, hyperkinesis, changes in the heart, respiratory system develop.

Chronic intoxication is manifested by nausea in the morning, sweating, decreased muscle tone. There are complaints of mental instability, irritability, insomnia. Some patients have itching, salivation. 95% of victims note the appearance of a dry cough, especially pronounced during the working day. Perhaps the development of anemia, concentric narrowing of the field of vision to red, pain in the epigastric region. 40% of people have a feeling of palpitations, shortness of breath. [66]

Benzene is one of the most important chemical products, widely used in many industries, and is one of the most common environmental pollutants [64]. Benzene is recognized as a category 1 human carcinogen by the International Agency for Research on Cancer [57].

The danger of benzene, as well as aromatic hydrocarbons in general, for the organism during prolonged exposure is determined by the polytropic nature of the damaging action and the ability to form aggressive metabolites in the process of biotransformation [59].

Bioactivation of benzene can lead to the formation of electrophilic metabolites such as phenol, hydroquinone, and catechol. The resulting electrophilic metabolites can form adducts with hemoglobin, serum albumin, and bone marrow proteins, disrupting their structure [81]. Potential mechanisms of benzene toxicity have been investigated along the following lines:

- metabolism of benzene in the liver and transport to the bone marrow for secondary metabolism [74, 80];
- oxidative stress caused by reactive oxygen species formed during the metabolism of aromatic compounds [83, 100];
- chromosomal changes, including translocations, deletions and aneuploidies [98];
- damage to tubulin proteins, histones, topoisomerase II and others [77];
- dysfunction of the immune system [61, 97].

Benzene, as an active mutagen, causes chromosomal abnormalities similar to those observed in the therapy of associated myelodysplasia and acute myeloid leukemia [65]. One of the possible mechanisms underlying pathologies caused by benzene is the induction of genetic changes leading to chromosomal aberrations, translocations, aneuploidy and deletion of the long arm [79], changes in cell differentiation and immune surveillance. Various chromosomal effects occur after exposure to alkylating agents and topoisomerase II inhibitors (ongoing balanced translocations or inversions) used in chemotherapy. The effect of benzene or its metabolites is associated with the deletion of the long arm of chromosomes 5 and 7 [99] and translocations involving the region of the twenty-first chromosome [78]. It has been reliably established that exposure to benzene leads to the development of leukemia through several different mechanisms.

The external environmental exposure to benzene increases the content of proteins in plasma [95]. It was also shown that under the influence of benzene, a decrease in the expression of proteins occurs, which indicates a decrease in immune reactivity and a violation of lipid metabolism [101]

As a result of the effect of low doses of benzene on fibroblasts, cell lines of pneumocytes and hepatocytes, one of the stress proteins located in the endoplasmic reticulum is expressed. At the same time, no significant changes in the expression of other stress proteins were observed [17]. Based on this, it is assumed that the presence of benzene leads to incorrect folding of proteins in the endoplasmic reticulum, thereby adversely affecting their secretion.

Benzene metabolites form adducts with hemoglobin and albumin, attaching to the side chain of cysteine. The dependence of the concentration of such adducts on the benzene content in the environment was shown [72]. Modified proteins are effective biomarkers of oxidative stress, since they are key molecules in various structural and functional aspects of the body's activity, and their functions depend on structure and conformation. Changes in the structure of the polypeptide chain under conditions of oxidative stress can lead to dysfunction of proteins and a slowdown in their degradation (and, consequently, their accumulation), as well as to large-scale functional consequences, subsequent cellular dysfunction, tissue damage and pathology. For this reason, oxidative stress caused by benzene metabolites is considered as the main factor in benzene-induced pathology [8], although the metabolism of benzene itself is not sufficient to fully describe the toxicity of this compound.

Benzene metabolites, such as catechol, hydroquinone, 1,2,4-trihydroxybenzene, parabenzoquinone, when exposed to mononuclear cells in human peripheral blood in vitro, can stimulate the production of chemokines, proinflammatory cytokines eotaxin [28]. Later studies showed that exposure to benzene significantly affects the expression of at least twenty genes involved in the regulation of apoptosis, immune response, defense response, stress response, inflammatory response, and chromatin assembly [54].

Benzene metabolites play a large role in DNA damage. However, DNA is not the only target. Certain metabolites can affect proteins involved in maintaining DNA integrity and genomic stability. This has been demonstrated most clearly for the inhibition of topoisomerase II, leading to double-stranded DNA breaks. Inhibition of enzymes involved in DNA replication, such as topoisomerases, by benzene metabolites is one of the possible mechanisms by which benzene can induce chromosomal abnormalities. It has been shown that in the presence of human myeloperoxidase and hydrogen peroxide, hydroquinone is activated and acts as a potent inhibitor of topoisomerase II [36]. Topoisomerase II is a nuclear ATP-dependent enzyme that plays an important role in a number of processes related to the maintenance of DNA functions. The available data show that numerous mechanisms are involved in the development of benzene-induced leukemia, and inhibition of topoisomerase II may represent an important stage in the development of some types of leukemia [32].

Other mechanisms that potentially contribute to carcinogenicity are overexpression of transcription factors, activation of oncogenes and cell signaling [5]

1.4.2. Effects of polyaromatic substances on living organisms

Among the substances-ecotoxicants, polyaromatic compounds occupy one of the first places in terms of damage to the environment. Utilization of these substances is, at best, reduced to "burial" in specially designated places.

Benzopyrene (BP) is used as a PAH indicator as it is almost always found where other PAHs are present. But the relative share of BP content in the level of environmental pollution is small. For example, in the exhaust gases of cars, the average relative concentration of BP in relation to the sum of all PAHs is 2.8%.

The toxicity of PAHs is highly structure dependent, so highly carcinogenic PAHs can be small or large. Seven PAHs have been classified as probable human carcinogens: benzanthracene, benzopyrene, benzofluoranthene, benzofluoranthene, krisen, dibenzanthracene, and indenopyrene. [69]

Several of the PAH compounds have been reported to cause cancer and toxicity in a plenty of animal species including humans. Most of the literature on effects of PAHs on human health are mainly focused on their potential to cause cancers of the skin, lung, breast, scrotum, bladder, and colon, etc. [52, 55]. Excess incidences of these cancers have been associated with a wide spectrum of occupational settings like aluminum production, coke production, coal gasification, steel and iron foundries, tar distillation, shale oil extraction, roofing, road paving, carbon electrode production, chimney sweeping, calcium carbide production, diesel engine repair, and firefighting [53].

In addition to cancer, the ability of PAHs to cause developmental, reproductive, and neurotoxicities has been paid considerable attention in recent years, thanks to the efforts of several research groups working with animal models and humans (reviewed in Hood et al. [33-35] and Ramesh and Archibong [71]). The potential targets of PAH action that may result in toxicity or cancer in humans is schematically illustrated in Figure 1.5.

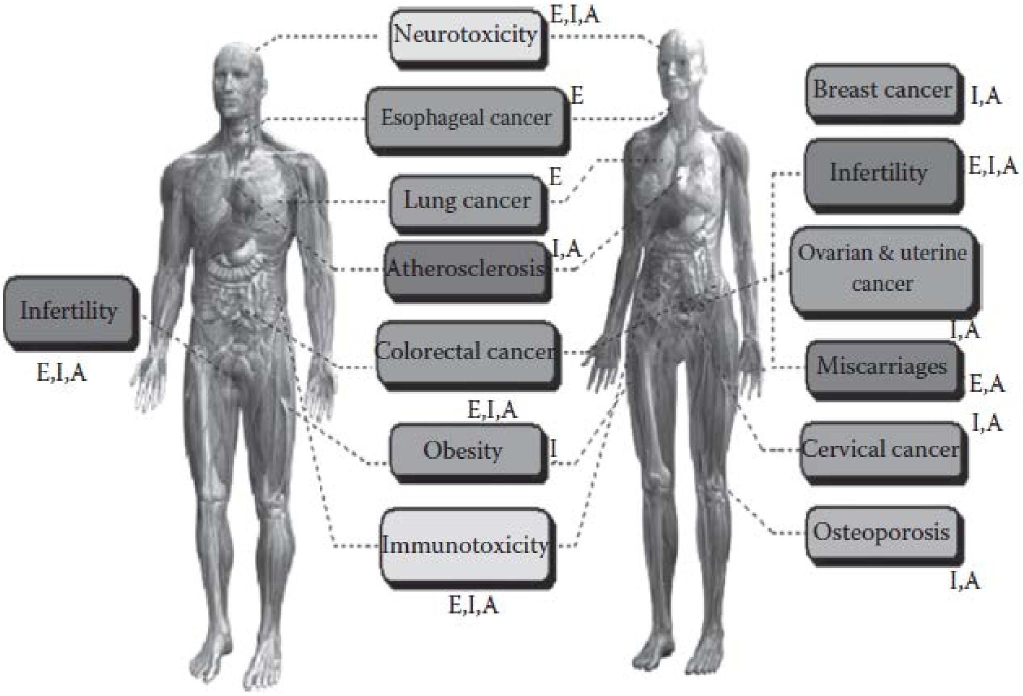


Fig. 1.5. Schematic representation of various systems targeted by PAHs and the resulting toxic effects. "A" represents that the denoted "health effect" was supported by in vivo (animal model) studies; "E" represents that the denoted "health effect" was supported by epidemiology studies; "I" represents that the denoted "health effect" was supported by in vitro studies.

1.5. Conclusions to Chapter

After analyzing the above information, we can say that both simple and complex organic compounds pose a great danger to the environment and human health. Therefore, in the further course of our work, we consider methods for determining organic substances in water, as well as methods for purifying water from toxic organic components.

CHAPTER 2

METHODOLOGY

2.1. Methods of analysis of phenols in the environment

*Photometric technique***.** The principle of this method is the interaction of phenols distilled off in the presence of potassium hexacyanoferrate (III) with 4-aminoantipyrine. During this reaction, colored compounds are formed, which are then extracted. Then their optical density is measured on a spectrophotometer at a wavelength of $\lambda = 470$ nm, or on a photometer with a light filter in the 460-490 nm range.

This technique requires the preparation of a large number of auxiliary solutions, a certain level of competence of the laboratory assistant, and may also be insufficiently accurate, since volatile phenols do not fully react with 4-aminoantipyrone, and, accordingly, can be determined photometrically.

However, it is this method that has found wide application in industrial wastewater control. Its accuracy is quite sufficient for monitoring the quality of waste and other types of water, and modern technologies allow the use of sensors with automatic sampling, carrying out any intermediate operations, if required, and introducing the necessary reagents into these samples. An example of such automated systems is the BlueScan or ISA multivariable sensors.

Chemiluminescent method. The method of water analysis is not very accurate and difficult to use. Its principle is to measure the intensity of chemiluminescence caused by the passage of Fenton reactions in the test sample in comparison with a standard aqueous solution of phenol. In the aqueous phase, this technique makes it possible to determine the concentration of phenol up to 1 µg / dm3, which is not always sufficient to obtain comprehensive information on phenolic contamination.

In general, this method requires the use of phosphors and a standard phenol solution, which further reduces its accuracy, since a standard phenol solution cannot contain all the possible phenols found in wastewater. This leads to a decrease in the overall accuracy of the method. It is also worth mentioning that the purity of the phosphor compounds used plays an important role in chemiluminescent methods of analysis.

The voltammetric method for the determination of phenols is associated with the use of electrochemical processes in order to obtain information on the content of phenols in water. In the process of voltammetric analysis, a preliminary deposition of the test substance on a highly selective electrode occurs, after which the precipitate is dissolved using electrochemical processes. Due to the dissolution of the substance deposited on the electrode, a change in the potential of the indicator electrode manifests itself, which is recorded and interpreted in the form of a volt-ampere curve. According to this curve, the researcher can judge the concentration of phenols in the sample under study. This method is quite fast and accurate. It does not require preliminary concentration of samples, therefore it is often used for in-line quality control of wastewater.

Chromatographic analysis methods are widely used in chemical laboratories. The class of these physicochemical methods includes a wide range of different techniques, such as gas, high-performance liquid, gel-permeation, thin-layer, gas-liquid and other types of chromatography. As part of the analysis of various waters for phenol content, various approaches to chromatography are used. For example, to analyze the content of phenols, a sample is introduced into a chromatographic column filled with a sorbent suitable for a specific analyte. A combination of eluents is selected that will ensure high selectivity of the chromatography process, which leads to the sorption of phenols onto the sorbent. Further, the chromatographic column is washed, the analytes are subjected to desorption and analysis by other physicochemical methods. Also, gas chromatography, high-performance liquid and gas-liquid chromatography is used to a limited extent, but all these methods require different options for preliminary sample preparation, or any other additional preparatory steps, in addition to the preparation of the chromatographic equipment itself.

The method is quite accurate, but the chromatography equipment is expensive and requires highly skilled operator. Therefore, chromatographic methods are used in laboratories and not in the field. [21]

Chromatography is a method of separation and determination of substances based on the distribution of components between two phases - mobile and stationary. The stationary phase is a porous solid (often called a sorbent) or a liquid film applied to a solid. A mobile phase is a liquid or gas flowing through a stationary phase, sometimes under pressure.

The components of the analyzed mixture (sorbates), together with the mobile phase, move along the stationary phase. It is usually placed in a glass or metal tube called a column. Depending on the strength of interaction with the sorbent surface (due to adsorption or by some other mechanism), the components will move along the column at different speeds. Some components will remain in the upper layer of the sorbent, others, to a lesser extent interacting with the sorbent, will end up in the lower part of the column, and some will completely leave the column together with the mobile phase (such components are called unretained, and their retention time determines the “dead time” of the column).

In this way, complex mixtures of components are quickly separated. The following advantages of chromatographic methods should be emphasized:

1) Separation has a dynamic character, and the acts of sorption-desorption of the separated components are repeated many times. This is due to the significantly higher efficiency of chromatographic separation in comparison with static methods of sorption and extraction.
2) When separating, various types of interaction between sorbates and the stationary phase are used: from purely physical to chemisorption. This makes it possible to selectively separate a wide range of substances.
3) Chromatography is a hybrid method that combines the simultaneous separation and determination of several components.
4) Chromatography allows you to solve both analytical problems (separation, identification, determination) and preparative (purification, isolation, concentration). The solution of these tasks can be combined by performing them in the “on-line” mode.

Numerous methods are classified according to the state of aggregation of the phases, the mechanism of separation, and the separation technique.

For our research, the method of high-performance liquid chromatography was chosen.

Liquid chromatography (LC) is a method for the separation and analysis of complex mixtures of substances in which the mobile phase is a liquid. The mobile phase in liquid chromatography performs a double function:

1) it provides the transfer of desorbed molecules along the column (similar to the mobile phase in gas chromatography);

2) regulates the equilibrium constants, and, consequently, retention as a result of interaction with the stationary phase (adsorbed on the surface) and with the molecules of the substances being separated.

In LC, the nature of the mobile phase is significantly more important. As a result of the combination of a limited number of sorbents and an unlimited number, different in composition, mobile phases, it is possible to solve an extremely large number of problems encountered in practice. The LC method is applicable for the separation of a much wider range of substances than gas chromatography, since most of the substances are not volatile, and many substances are unstable at high temperatures. LC separation usually occurs at room temperature.

LC is subdivided into variants in accordance with the nature of the main manifested intermolecular interactions:

- in sieve chromatography, the separation of components is carried out due to the difference in the solubility of molecules during their passage (filtration) through the sorbent layer;
- in adsorption chromatography - due to the difference in the adsorption of molecules passing through a layer of sorbent particles covered with a stationary phase in the form of a thin layer or surface-grafted radical groups;
- in ion exchange and ion chromatography - due to the difference in the ability to exchange ions with ion exchangers.

For the analysis of environmental objects, the most widely use HPLC in adsorption and ion-exchange options [75].

2.2. Methods of organic pollution neutralization

Table 2.1.

Methods of organic pollution neutralization

Method	**Description**	**Advantages and disadvantages**
1	2	3
Biodegradation	For this technique the various microorganisms, such as *Pseudomonas, Mycobacterium, Alcaligenes, Bacillus, Acinetobacter, Arthrobacter, Rhodococcus, Flavobacterium, Caulobacter* can be used. During the implementation of this method, the benzene ring in aromatic compounds decomposes by the interaction with the microorganisms and simpler substances are formed that participate in the next biological processes of microorganisms.	Cleaning both soil and water from pollutions Bioremediation of polluted areas Possibility of water cleaning in the large scale Long time of method application

continuation of table 2.1.

1	2	3
Photo-Fenton oxidation	To date, the application of the photo-Fenton oxidation process for PAHs treatment were from contaminated soil (review paper), landfill leachate, municipal solid waste leachate, sanitary landfill leachate, aniline wastewater, ammunition wastewater, saline aqueous solutions and potable water. For the implementation of this technique polluted aqueous solution with a specific pH, ferrous sulfate and hydrogen peroxide with a specific concentration, specific wavelength of UV light (365 nm), stirrer speed (300 rpm) and room temperature are required. During the process, the photocatalytic decomposition of PAHs occurs using the Fenton reaction.	Possibility of cleaning of various kinds of water (from industrial to potable) Difficult conditions for method usage
Degradation using potassium zinc hexacyanoferrate nanocubes	This method allows decompose the most of toxic PAHs to simpler hydrocarbons. For the implementation potassium ferrocyanide, zinc nitrate, acetonitrile are required. The method is realizing in the UV chamber. During the process, aromatic hydrocarbons are decomposing by the influence of UV irradiation. Nanoparticles of potassium zinc hexacyanoferrate are used as a catalyst.	High-yield of the technique Possibility of decomposition of PAHs with high concentration Long time of method application (from several hours to several days)

end of table 2.1

1	2	3
Photochemical degradation	Photochemical degradation is a major process for PAHs decomposition. The main component of the method is the various types of solar radiation (UV-A, UV-B and PAR). By the influence of light aromatic hydrocarbons are decomposing into the simpler substances (alkanes, etc.).	Possibility of decomposition of high concentration substances Short application time (2-10 h) Difficult conditions of the method
Electrochemical degradation	In the technique, PAHs are neutralized by passing electricity through aqueous phase in various electrolytic solutions. Substances are oxidizing in these conditions. The method mainly uses sodium chloride as an electrolyte.	Short application time (0,5-2 h) Possibility of decomposition of various types of aromatic hydrocarbons Laboratory scale High temperature of application (> 200 °C)

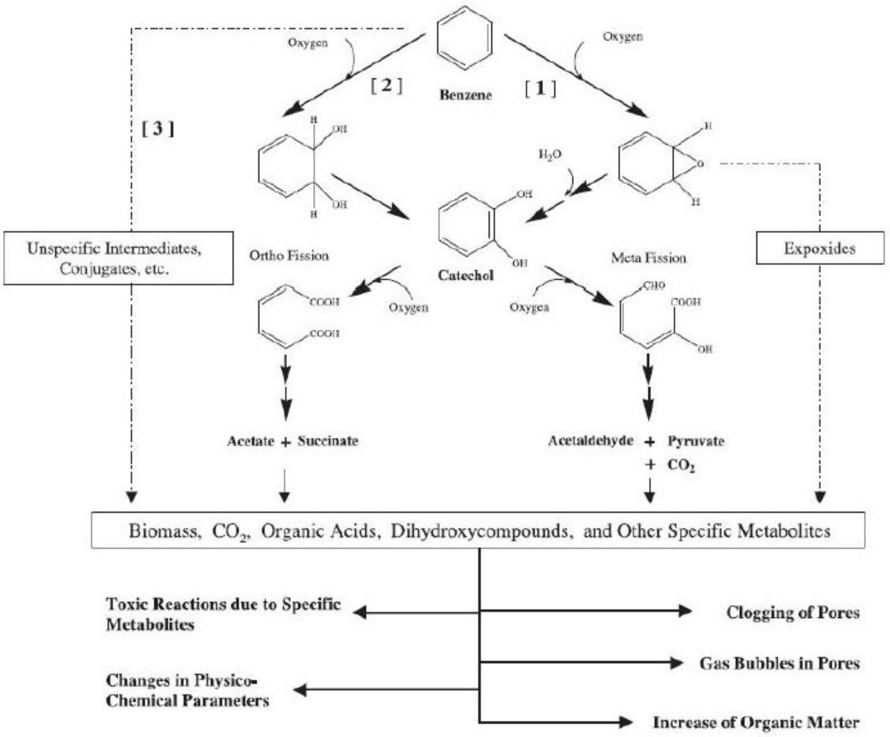


Fig. 2.1. Scheme of the microbiological decomposition and biodegradation

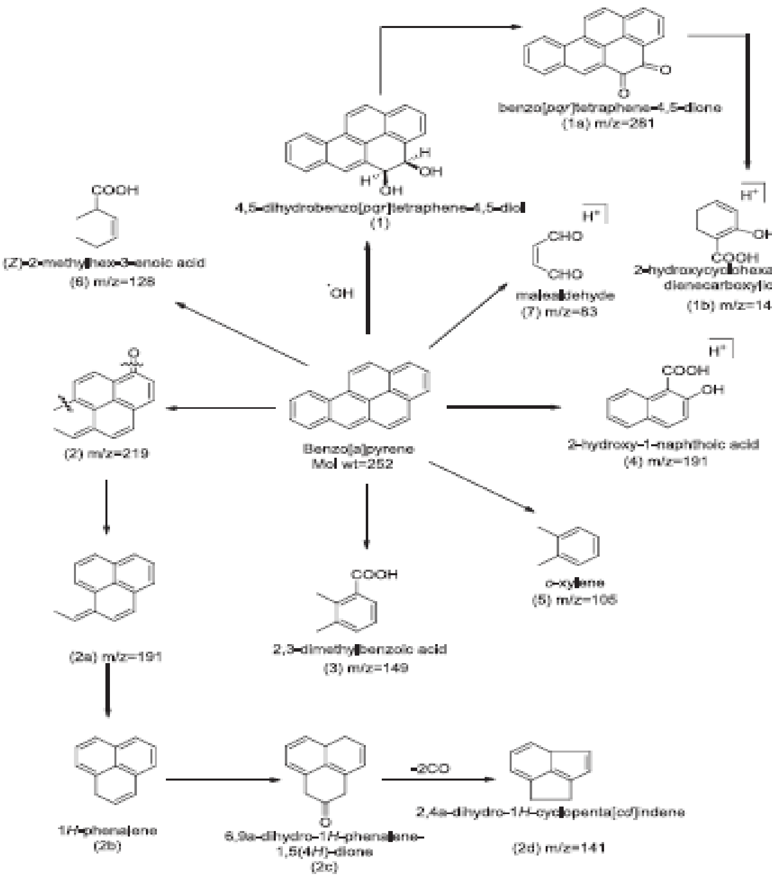


Fig. 2.2 Example of the degradation using potassium zinc hexacyanoferrate nanoparticles

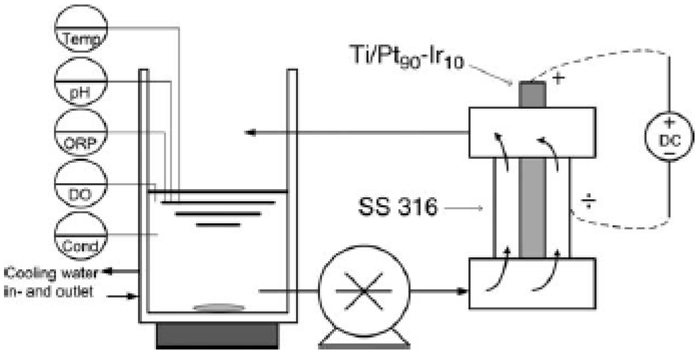


Fig. 2.3. Unit for the electrochemical decomposition of PAHs

2.3. Photocatalysis

Photocatalysis is a change in the rate or excitation of chemical reactions under the action of the light in the presence of substances (photocatalysts) that dominate the quanta of the light and participate in the chemical transformations of the reaction participants, repeatedly yielding to them in the mixed interactions and regenerating their chemical system after each cycle of such complementary ones.

There are two different approaches to photocatalysis:

1) from chemistry to catalysis to photocatalysis (i.e. equation 2.1 → 2.2 → 2.4)

2) from chemistry to photochemistry to photocatalysis (i.e. equation 2.1 → 2.3 → 2.4).

Thus, we can define photocatalysis based on these approaches. In a broad sense, the term photocatalysis describes a photochemical process in which a photocatalyst accelerates the process, as any catalyst must be in accordance with the definition of catalysis.

$$A \rightarrow B \qquad (2.1)$$

$$A + \text{Catalyst} \rightarrow B + \text{Catalyst} \qquad (2.2)$$

$$A + h\upsilon \rightarrow B \qquad (2.3)$$

$$A + h\upsilon\ \text{Catalyst} \rightarrow B + \text{Catalyst} \qquad (2.4)$$

The catalyst can accelerate the photoreaction by interacting with substrate (s) either in the ground state, or in its excited state, or with the primary product (catalyst), depending on the photoreaction mechanism. Thus, photocatalysis is a catalytic process that occurs on the surface of semiconductor materials when exposed to light. Photocatalysis includes three processes: excitation, bulk diffusion, and surface transfer of photoinduced charge carriers. These processes are influenced by the bulk structure, surface structure, and electronic structure of semiconductor photocatalysts [28].

Most photocatalytic reactions are redox reactions. The key step in the photocatalytic reaction is the transfer of electron (s) between the substrate and the excited state of the photocatalyst. A schematic diagram of the photocatalytic reaction is shown in Fig. 2.4.

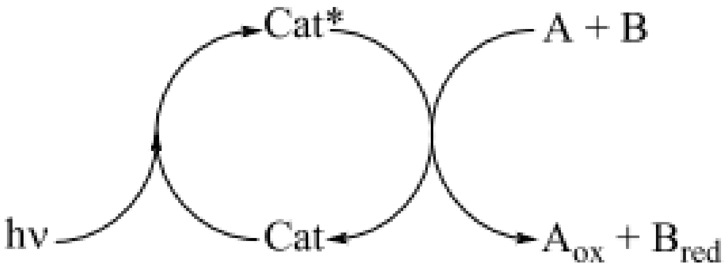


Fig 2.4. *Schematic diagram of the photocatalytic reaction*

There are 2 photocatalysis systems: homogeneous photocatalysis and heterogeneous.

2.3.1. Homogeneous photocatalysis

Homogeneous photocatalysis for hydrogen production is usually carried out in an aqueous or non-aqueous (liquid) phase. The process includes at least one catalyst dissolved in a liquid phase. Homogeneous photocatalysis is based on the interaction of complex molecular structures and water in solution. Several molecular complexes are involved in the process, performing different functions such as photosensitization, charge separation, charge transfer, acceptance electron or donation and catalyzing.

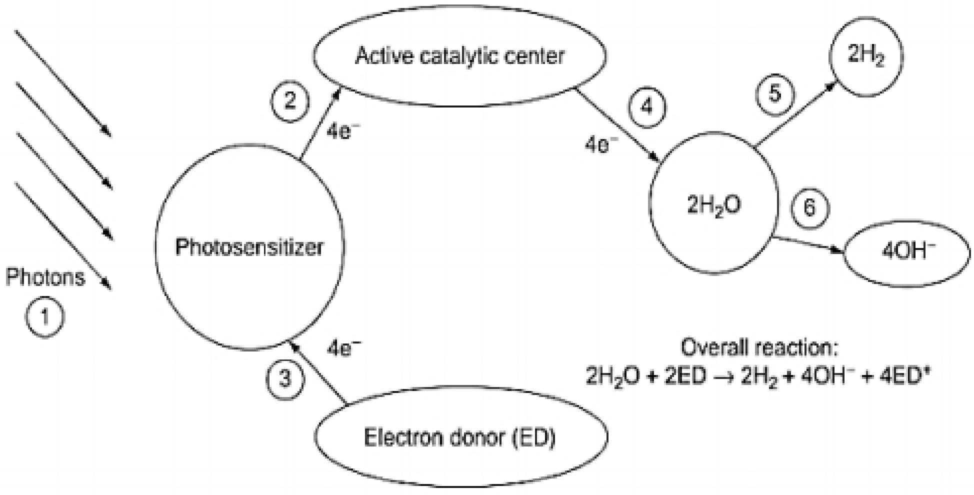


Fig 2.5. *Conceptual description of homogeneous systems, evolving hydrogen from water separation.*

Let us consider the mechanism of the process of hydrogen formation in homogeneous photocatalysis (Fig 2.5.):

Events are triggered by process 1, which is the absorption of photons in the photosensitizer (PS), so PS enters an excited state:

$$PS + h\nu \rightarrow PS^* \qquad (2.5)$$

For reactions that promote hydrogen development, PS interacts with the catalyst and then transfers an electron according to process 2:

$$PS^* + ACC \rightarrow PS^+ + ACC^-, \qquad (2.6)$$

where ACC stands for "active catalytic center"

PS becomes reactive and recovers an electron from an electron donor dissolved in solution according to process 3, namely

$$PS^{+} + ED \rightarrow PS + ED^{+}, \qquad (2.7)$$

this time PS is reactivated and the electron donor remains stable in solution. The active site catalyzes the decomposition of water by facilitating electron transfer for the complete reaction, since catalytic cycles are necessary, so PS must absorb photons four times.

The catalytic process 4 develops in accordance with

$$4H_2O + 4ACC^{-} \rightarrow 2H_2 + 4OH^{-} + 4ACC \qquad (2.8)$$

Multicomponent systems for homogeneous photocatalysis present an inherent disadvantage in that the molecular components that perform various functions such as photosensitization, charge separation, electron transfer and catalysis are not related. Thus, the quantum efficiency of the process decreases as many processes compete with each other.

A recent approach to improve the efficiency of water dissociation is the development of supramolecular systems that serve multiple functions. In such systems, the PS is connected to an active site with bridging ligands and charge transfer pathways.

Thus, when a photosensitizer excited by light releases an electron that moves along a developed path, it reaches a higher probability in the active center [90].

2.3.2. Heterogeneous photocatalysis

Heterogeneous photocatalysis is a discipline that includes a wide variety of reactions: moderate or complete oxidation, dehydrogenation, hydrogen transfer, metal precipitation, water detoxification, gaseous pollutant removal, etc. According to the last two points, this can be considered as one of the new "advanced oxidation technologies”, (AOT) for air and water purification [63].

Heterogeneous photocatalysis has been demonstrated as an inexpensive and sustainable technology for treating a variety of pollutants in air and water, including organic and heavy metals, etc., with Japan, USA, India and China as the main users of this technology [49].

Heterogeneous photocatalysis can be carried out in various media: gas phase, pure organic liquid phases, or aqueous solutions. With regard to classical heterogeneous catalysis, the overall process can be decomposed into five independent steps:

1) Transfer of reagents in the liquid phase to the surface
2) Adsorption of at least one of the reagents
3) Reaction in the adsorbed phase
4) Desorption of product (s)
5) Removing products from the interface area

In heterogeneous catalysis, the photocatalyst is usually found in solid phase, and the dissociation of water occurs in the liquid phase. Other substances that can form hydrogen can be used instead of water, but the heterogeneous photocatalyst will be in a different phase than the reaction mixture [20].

The most common heterogeneous photocatalysts are transition metal oxides and semiconductors, which have unique characteristics. Unlike metals, which have a continuum of electronic states, semiconductors have a region of void energy, where there are no energy levels available to facilitate the recombination of an electron and a hole, produced by photoactivation in a solid. The region of voids that extends from the top of the filled valence band to the bottom of the free conduction band is called the forbidden band [6]. When a photon with energy equal to or greater than the material's band gap is absorbed by the semiconductor, an electron from the valence band is excited from the conduction band, creating a positive hole in the valence band. Such a photogenerated electron-hole pair is called an exciton.

An excited electron and a hole can recombine and release the energy obtained when the electron is excited in the form of heat. Exciton recombination is undesirable, and higher levels result in an ineffective photocatalyst. For this reason, efforts to create functional photocatalysts often emphasize the extension of the exciton lifetime by improving electron-hole separation using a variety of approaches that often rely on structural features such as phase heterojunctions (e.g., anatase-rutile interfaces), noble metal nanoparticles, silicon nanowires and cationic substitution. The ultimate goal of photocatalyst design is to facilitate the reaction between excited electrons with oxidants to produce reduced products and / or the reaction between generated holes with reducing agents to produce oxidized products. Redox reactions occur on the surface of semiconductors due to the generation of positive holes and electrons. In an oxidative reaction, positive holes react with moisture present on the surface and form a hydroxyl radical.

Here MO stands for metal oxide:

$$\text{UV} + \text{MO} \rightarrow \text{MO (h + e-)} \quad (2.9)$$

Oxidative reactions due to photocatalytic effect:

$$h^+ + H_2O \rightarrow H^+ + OH \quad (2.10)$$

$$2\ h^+ + 2H_2O \rightarrow 2\ H^+ + H_2O_2 \quad (2.11)$$

$$H_2O_2 \rightarrow 2 \bullet OH \quad (2.12)$$

Reductive reactions due to the photocatalytic effect:

$$e^- + O_2 \rightarrow \bullet O_2^- \quad (2.13)$$

$$O_2^- + HO \bullet 2 + H^+ \rightarrow H_2O_2 + O_2 \quad (2.14)$$

$$HOOH \rightarrow HO \bullet + \bullet OH \quad (2.15)$$

Ultimately, hydroxyl radicals are generated in both reactions. These hydroxyl radicals are highly oxidative in nature and non-selective with a redox potential (E0 = +3.06 V) [48].

2.4. Existing photocatalytic water purification technology

The search for an effective and economical method for the purification of wastewater containing chlorophenols is currently an urgent task. Photocatalysis has become one of the most promising technologies for the decomposition of organic contaminants to non-toxic compounds over the past decade.

Traditional wastewater treatment methods to remove environmental pollutants include adsorption with activated carbon, chemical oxidation, and biological digestion. There are limitations and disadvantages to each of these methods. For example, adsorption with activated carbon involves phase transfer of pollutants, but does not include decomposition, which can cause further contamination [50]. Chemical oxidation cannot completely mineralize all organic matter and is only used to remove pollutants that are present in high concentrations [19]. Biological treatment is characterized by a slow reaction rate and has drawbacks due to the requirements for the utilization of activated sludge and control of the pH of the medium and temperature [51].

Photocatalysis is a modern oxidation process and is considered the most attractive process due to its increased oxidative capacity, low cost, and chemical stability [96], Some of the benefits of photocatalytic processes include:

1. fast photodegradation of pollutants;
2. the absence of the formation of high molecular weight compounds, such as polycyclic compounds;
3. simple hardware design for photocatalytic processes;
4. highly efficient oxidation at lower concentrations of pollutants. [40]

A photoreactor is an apparatus designed to carry out photocatalytic reactions, which are accompanied by processes of mass and heat transfer. The design and typical features of photochemical reactors affect their efficiency and operational safety.

For a deeper course of the reaction and an increase in the degree of conversion of a substance, it is necessary that the photons of light taking part in the reaction are actively absorbed by the organic compound in the solution. The selection of the source with the maximum radiation energy is carried out after studying the main absorption bands in the spectra of the starting reagents and the solvent in which the photochemical reaction will take place. A necessary condition for optimizing the photocatalytic reaction is the coincidence of the wavelengths of the absorption bands of the substances and the radiation source. As a result of the absorption of the light flux, a significant release of heat occurs, which can lead to local temperature rise. Consequently, there is a need for efficient stirring of the reaction mixture and removal of excess heat [9].

There are the following types of photoreactors:

1. Photochemical immersion reactors are reactors where the radiation source is immersed in a container with a solution. Such reactors are highly efficient due to the full use of the radiation from the light source. The body of the immersion lamp is in contact with the reaction mixture, therefore, it is necessary to regulate the temperature regime and constantly maintain intensive stirring. The reactor is a hollow cylinder, and the mixing of the entire reaction mass is carried out using a magnetic stirrer and supplying a gas stream in the lower part of the reactor. A diagram of a photoreactor of this type is shown in Figure 2.6.

Emitter 1 is immersed in cylindrical vessels, one of which 2 serves as a cooling jacket, and 3 is a photochemical reactor. The cooling jacket prevents the contact of the heated surface of the emitter with the surface of the photoreactor and maximally cools the nearest layer of the reaction mass. High wattage lamps can be air cooled or water cooled to dissipate heat. Instead of cooling water, a colored solution can be supplied to jacket 2 from the thermostat, which will act as a coolant and a color filter for transmitting light of a certain wavelength range.

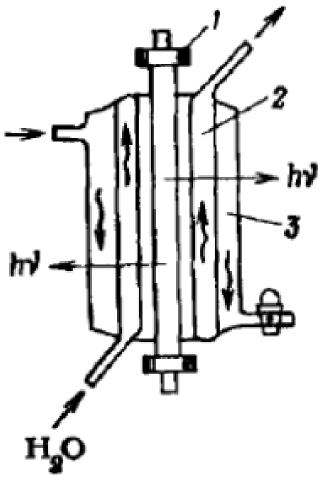


Fig 2.6. *Photoreactor for a mercury lamp: 1 - lamp; 2 - cooling jacket; 3 - photochemical reactor [13]*

2. low-temperature immersion photochemical reactors - used in the case of photochemical reactions that must be carried out at low temperatures. Maintaining and controlling the low temperature is carried out by placing the immersion photoreactor in a vessel with a mixture of ice, water and ethylene glycol or in a Dewar vessel with dry ice. Figure 2.7. shows an industrial low-temperature immersion reactor for irradiation of reagents [23].

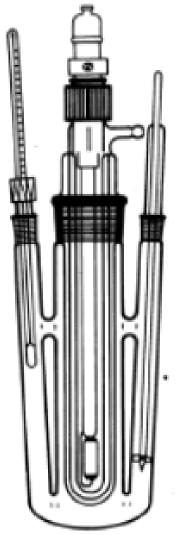


Fig 2.7. *Photoreactor for irradiation of reagents at low temperatures*

3. flow-through reactors - in reactors of this type, effective mixing and constant renewal of the reacting layer are carried out due to the recirculation of the reaction mixture. Recirculation allows for rapid mineralization and results in the formation of a small amount of undecomposed toxic product [2]. Flow-through photoreactors operate most efficiently at low concentrations of dissolved organic matter.

The laboratory setup of a flow-through annular reactor is shown in Figure 2.8. The scheme includes systems for monitoring and recording the decrease in the concentration of toxic substances after UV irradiation 6. The spectrometer records the absorption and fluorescence spectra, which can be used to judge the ongoing processes. There are two excilamps in the reactor: a KrCl * excilamp with a radiation wavelength of 222 nm, a XeCl * excilamp with a wavelength of 308 nm. To collect the CO2 formed as a result of deep oxidation of the substance, there is a glass vessel 7. The power consumption of the photoreactor does not exceed 100 W [30].

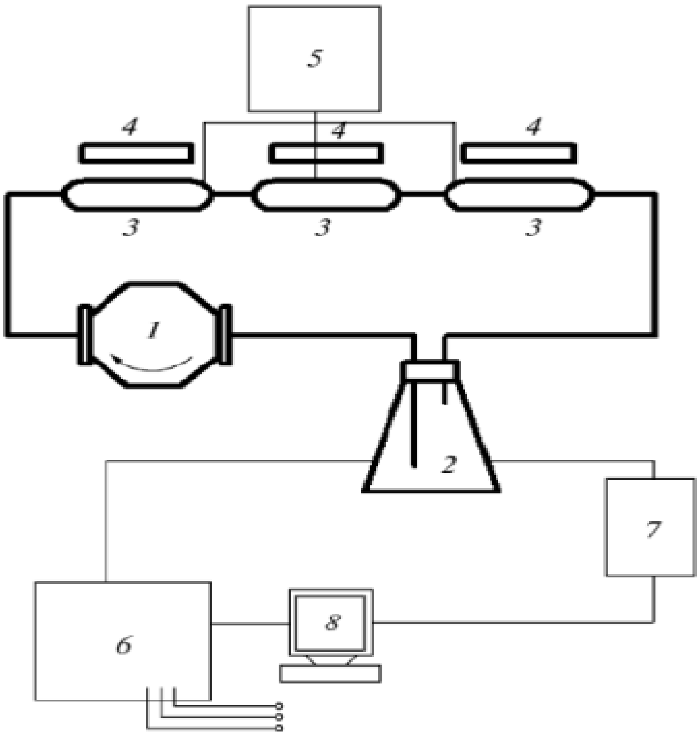


Fig 2.8. *Diagram of a flow reactor:*

1 - peristaltic pump; 2 - glass vessel with the test solution; 3 - excilamps; 4 - fans; 5 - power supply unit for excilamps; 6 - diagnostic system; 7 - vessel for collecting CO2; 8 - computer [9]

Today, photoreactors are being developed that would use the energy of sunlight to disinfect water.

A photoreactor with a parabolic solar collector is shown in Figure 2.9. (A). It consists of several manifolds, a tank and a pump. Each manifold consists of 8 glass tubes in series. At the start of the experiment, chemicals are added to the reservoir and mixed by recirculating water until adsorption equilibrium is reached in the system. Then the covers are removed from the collectors to start the photocatalysis process. Solar photoreactor STEP, shown in Figure 2.9. (B), consists of a rectangular vessel in the form of a ladder with 21 steps. The photocatalyst is attached to a substrate. The photoreactor is covered with a glass sheet to limit the evaporation of water. The covers are removed from the manifolds to start the photocatalysis process.

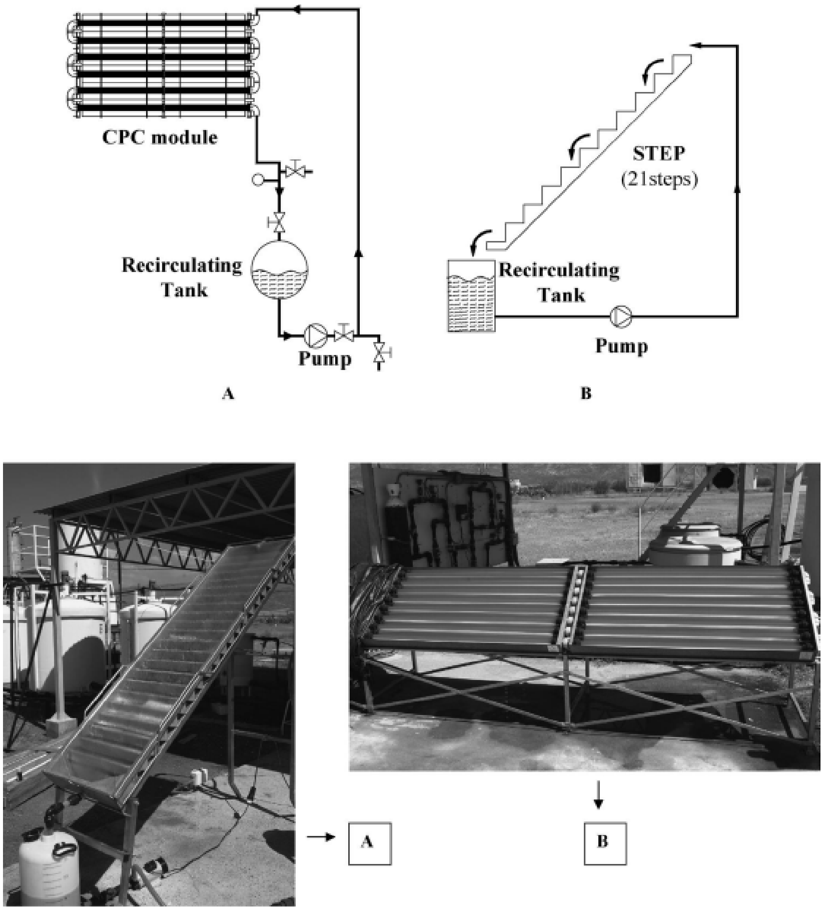


Fig 2.9. *Schemes and photographs of pilot photoreactors: (A) with a parabolic solar collector; (B) photoreactor STEP [68.18]*

Professor D. Ollis carried out a comparative analysis of water purification plants with an insignificant level of pollution for ozonation, UV ozonation, sorption on activated carbon, photocatalysis. The cheapest is water purification based on the principle of photocatalysis and sorption. The unit cost of water purified in the first way is slightly higher than in the second. With an increase in the power of installations, this difference tends to zero [96].

2.5. Conclusions to Chapter

Based on the above, heterogeneous photocatalysis is a promising method that, along with existing purification technologies, can be used to detoxify wastewater from organic pollutants.

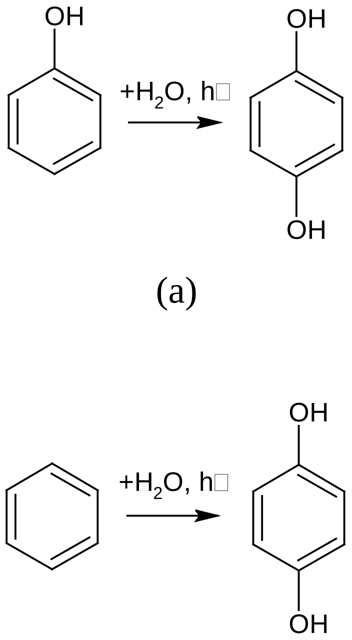
Oxide semiconductor materials are used as photocatalysts. Under the influence of electromagnetic radiation, highly reactive free radicals are generated on their surface, which are involved in the photodegradation of organic pollutants. The implementation of the FC process under the influence of visible light will make the destructive technology cheap and safe.

CHAPTER 3

EXPERIMENT DESIGN FOR PHOTOCATALYTIC WATER PURIFICATION FROM AROMATIC SUBSTANCES

3.1. Phenol and benzene degradation, Reagents and equipment used, Synthesis of substances, CNTs composites, Processing of photocatalysis

Both benzene and phenol degrade in the aqueous phase to form hydroquinone due to water and light influence. The mechanism of the degradation is given in a fig. 3.1.



(a)

(b)

Fig. 3.1. Phenol and benzene degradation reaction:
(a) – phenol; (b) – benzene

As can be seen in the figure, hydrogen is split off from the molecules of both substances and is replaced by a hydroxyl group from a water molecule. The hydrogen from the benzene and phenol molecule combines with the hydrogen from the water molecule. The reaction produces hydroquinone and hydrogen. Subsequently, hydroquinone can be oxidized. The result is benzoquinone and hydrogen. The oxidation reaction of hydroquinone is shown in fig. 3.2.

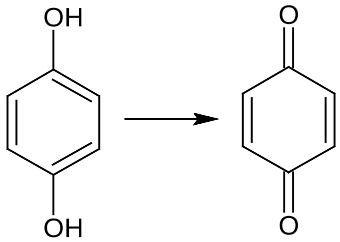


Fig 3.2. Hydroquinone degradation reaction

In our work different equipment was used. Magnetic stirrers, UV- and visible-light lamps, and self-made reactor were used to carry out the reactions, vials for chromatograph, milligram scales, microliter pipettes and deionized water for clarity of results. We also used a centrifuge and filters to remove small particles that could clog the chromatograph column. An aqueous solution of the substance used was added to the reactor, as well as the catalyst. The concentration of substances in water was equal to:

- for phenol: 4 g/l; 1 g/l; 0.5 g/l; 0.25 g/l; 0.16 g/l; 0.8 g/l.
- for benzene: 1.14 g/l.

The amount of catalyst - 100 mg. The reactor was placed on a magnetic stirrer under a lamp for a certain time.

Obtained mixtures were studied by HPLC. For the studying chromatograph “Perkin Elmer HPLC Series 200” was used. Parameters of the research showed below:

- Detector: DAD (detectors A and B)
- Wavelength: 205 nm – detector A, 254 nm – detector B
- Temperature: 10 - 30 °C
- Pressure range: 145-195 MPa
- Chromatograph phases A and D – acetonitrile or methanol, B and C – water
- Flow rate 0.3 – 1
- Injection volume 5 – 20 µl
- Detector time 15 – 40 min
- Injection Source – Autosampler

- Loop size – 200 µl
- Excess volume - 10 µl
- Air cushion – 10 µl
- Sample syringe size - 250 µl
- Needle level – 10%
- Flush volume - 1000 µl
- Flush cycles - 2
- Post-injection cycles – 1
- Detectors bandwidth – 20 nm
- Detectors reference wavelength – 360 nm

Fig 3.3. Equipment for experiments

Fig 3.4. Chromatograph and PC for results analyzing

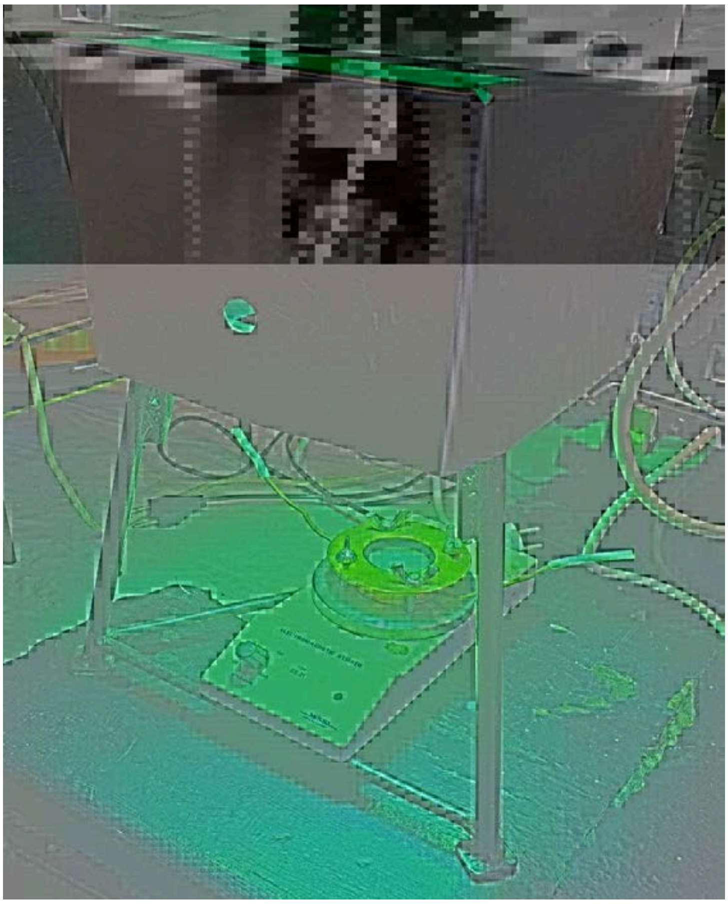


Fig 3.5. Carrying out an experiment

Within the framework of science work different substances were used for the process. Mainly, benzene and phenol were used. Aqueous solutions with the different concentration were used:

- Benzene solutions: 4 g/l; 1 g/l; 0.5 g/l; 0.25 g/l; 0.16 g/l; 0,8 g/l.
- Phenol solutions: 1.14 g/l.

All characteristics of the compounds used are wrote in table 3.1.

Table 3.1

Physicochemical characteristics of the substances used

Systematic name	Benzene
Formula	C_6H_6
Molar mass, g/mol	78.11
Density, g/cm^3	0.879
Water solubility, mg/mL	1-5

Systematic name	Phenol
Formula	C_6H_5OH
Molar mass, g/mol	94.11
Density, g/cm^3	1.07
Water solubility, mg/mL	50-100

Titanium dioxide (IV) and its derivatives as the catalysts were used. A list of all the substances used is given in table 3.2.

Table 3.2

Description of the catalysts used

Catalysts	**Composition**
TiO_2	Annealed titanium dioxide
CNTs (TiO_2-coated)	TiO_2-coated carbon nanotubes obtained in the laboratory
TiO_2 (rutile)	Rutile-structured titanium dioxide
TiO_2 (Ni-coated)	Nickel-coated titanium dioxide
TiO_2 (Pt-coated)	Platinum coated titanium dioxide

end of table 3.2.

TiO_2 / CNTs (commercial)	Titanium dioxide composite with commercial carbon nanotubes
TiO_2 / CNTs (obtained)	Titanium dioxide composite with carbon nanotubes obtained in the laboratory
$BiFe_{0.8}Mn_{0.2}O_3$	Bismuth ferrite obtained in the laboratory

Titanium dioxide was annealed for use in all experiments and synthesis. Annealing was carried out in the furnace at 400°C for 4 hours. Then, the obtained powder was dried at the air.

Different amounts of catalyst were used depending on the substances used, the experimental conditions, etc. Most often, 5 mg, 10 mg, 15 mg, 50 mg, 75 mg, 100 mg of catalyst powder were taken.

Some catalysts used in my work were synthesized in the laboratory. These include carbon nanotubes composites with titanium dioxide, as well as TiO_2 coated with various substances.

Within the photocatalytic degradation of phenol has been used carbon nanotubes composites with titanium dioxide as catalysts for the process. In summary, 2 samples for the photocatalysis were taken. In the first composite used carbon nanotubes were obtained in the laboratory, as well in the second one CNTs were bought in Sigma-Aldrich.

Carbon nanotubes used in this composite were synthesized by CVD method in the laboratory.

For the photocatalytic reaction self-made reactor was used.

30 mL of an aqueous solution of substance used and 5 - 100 mg of the catalyst powder are placed in the reactor. The reaction mixture is magnetically stirred under the UV- or visible light for 0.5, 1, 2, 4 or 8 h. Then, obtained suspension is filtered to obtain a pure solution without dispersion. Afterwards, 5-20 µL of the sample is loaded into a vial and examined by HPLC.

The sample is moved to the detector by the acetonitrile or methanol (A and D), and water flow (B and C). The study is carried out at 10-30 °C and 145-195 MPa for 15 or 40 min.

The obtained peaks of water and phenol or benzene are examined by HPLC software. The main peak characteristics are the peak height and area. Also, clear solution of substance used are studied. Then, the conversion of the reaction is calculated by the formula 3.1:

$$W = \frac{S_a}{S_b} \times 100, \tag{3.1}$$

where S_a – peak area after the reaction; S_b – peak area before the reaction.

The measurement error is ±10%. This is due to the error in the study by HPLC.

3.2. Results of the conducted experiments

Working with phenol, we experimented with the concentration of phenol in solution, as well as with the type and amount of catalyst. We used solutions of phenol with a concentration of 4 g/l; 1 g/l; 0.5 g/l; 0.25 g/l; 0.16 g/l; 0.8 g/l. The catalysts we used were: TiO_2; CNTs; TiO_2 (with rutile structure); TiO_2 (Ni-coated); TiO_2 (Pt-coated); TiO_2/CNTs; $BiFe_{0.8}Mn_{0.2}O_3$.

The first experiment was carried out under the following conditions: lamp with visible light, 50/50 acetonitrile and water phases, 0.8 g/l of phenol in water, and 5 mg of titanium dioxide with a rutile structure, time 5-10-20-30 minutes, as well as a selection of a pure sample was carried out to calculate the conversion.

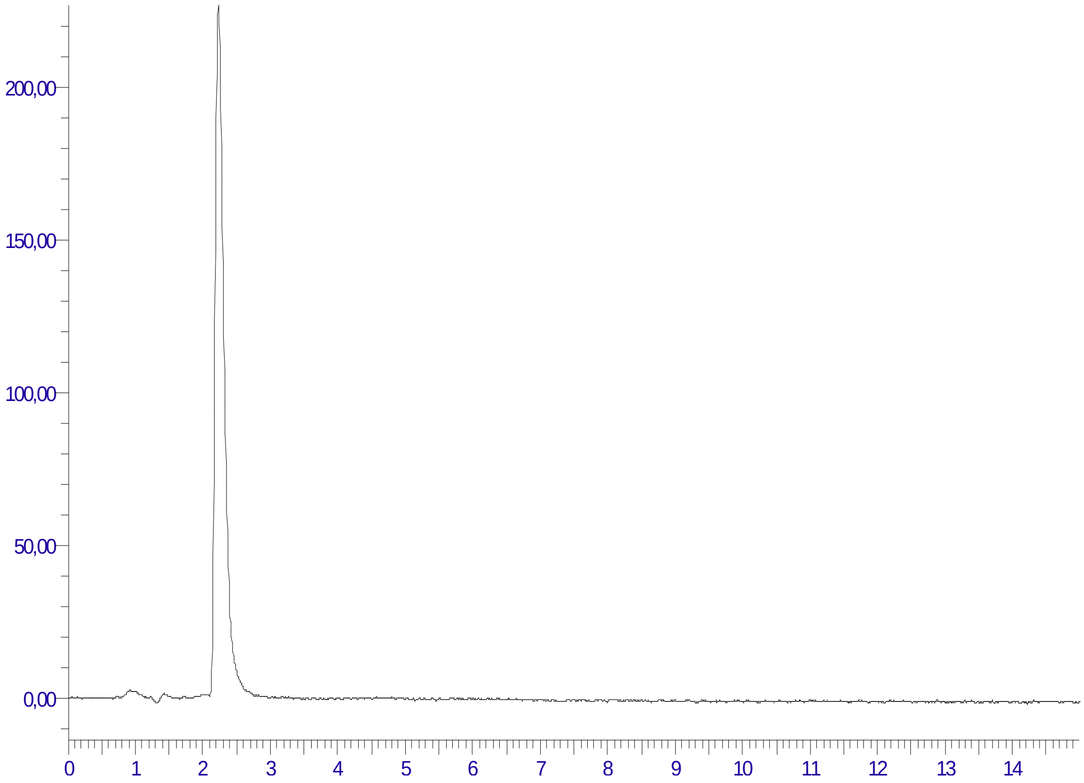


Fig. 3.6. A solution of phenol that has not undergone photocatalysis

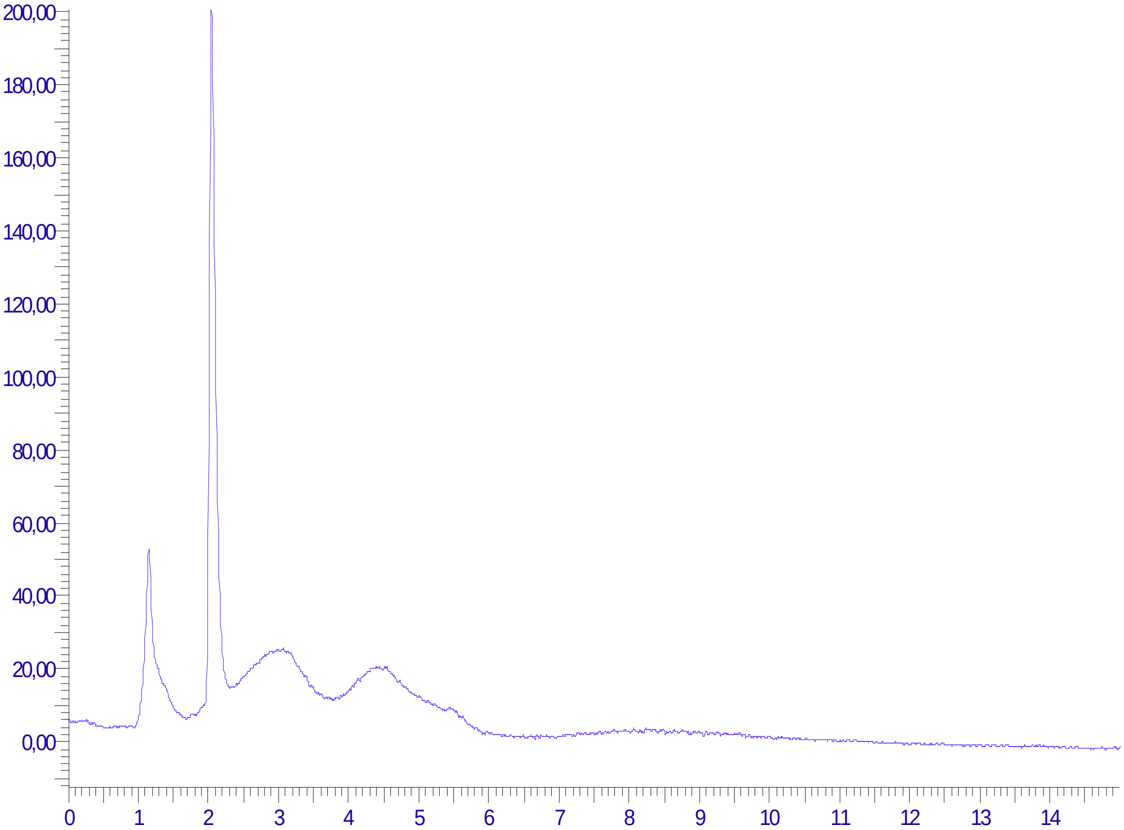


Fig. 3.7. Phenol solution photocatalyzed for 5 minutes with TiO_2 (rutile)

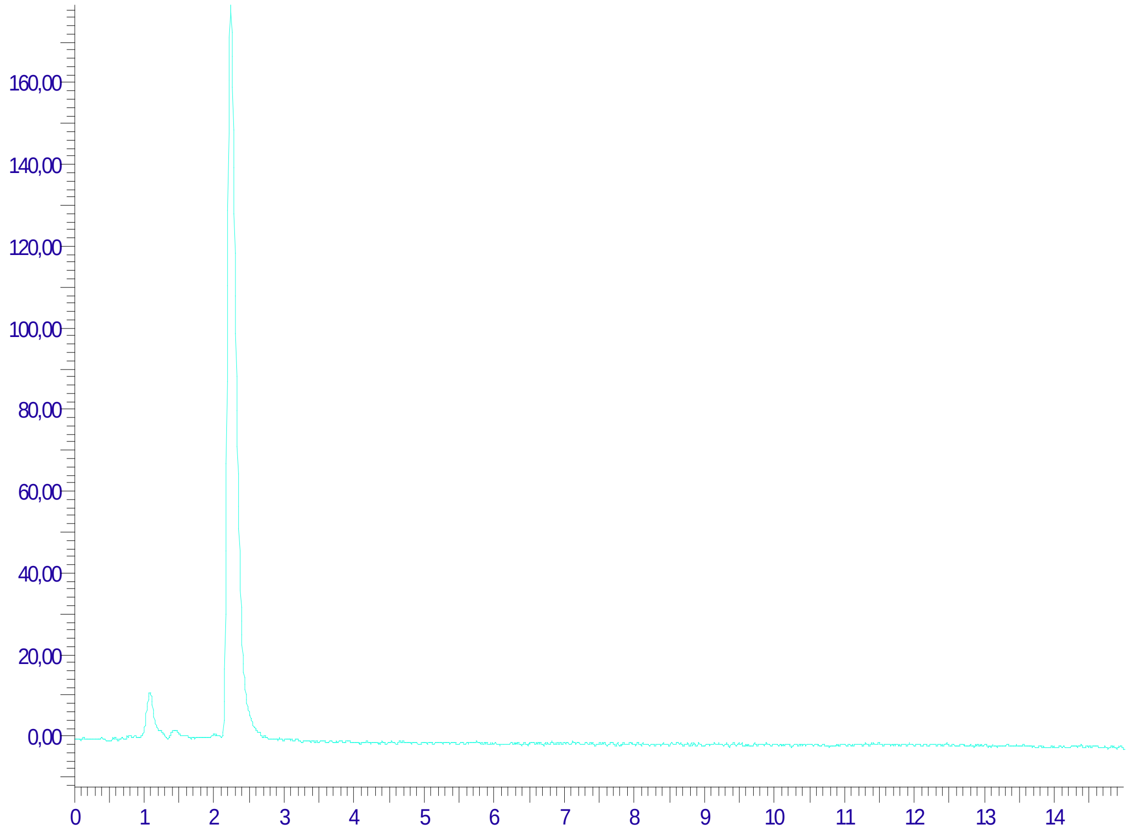


Fig. 3.8. Phenol solution photocatalyzed for 10 minutes with TiO_2 (rutile)

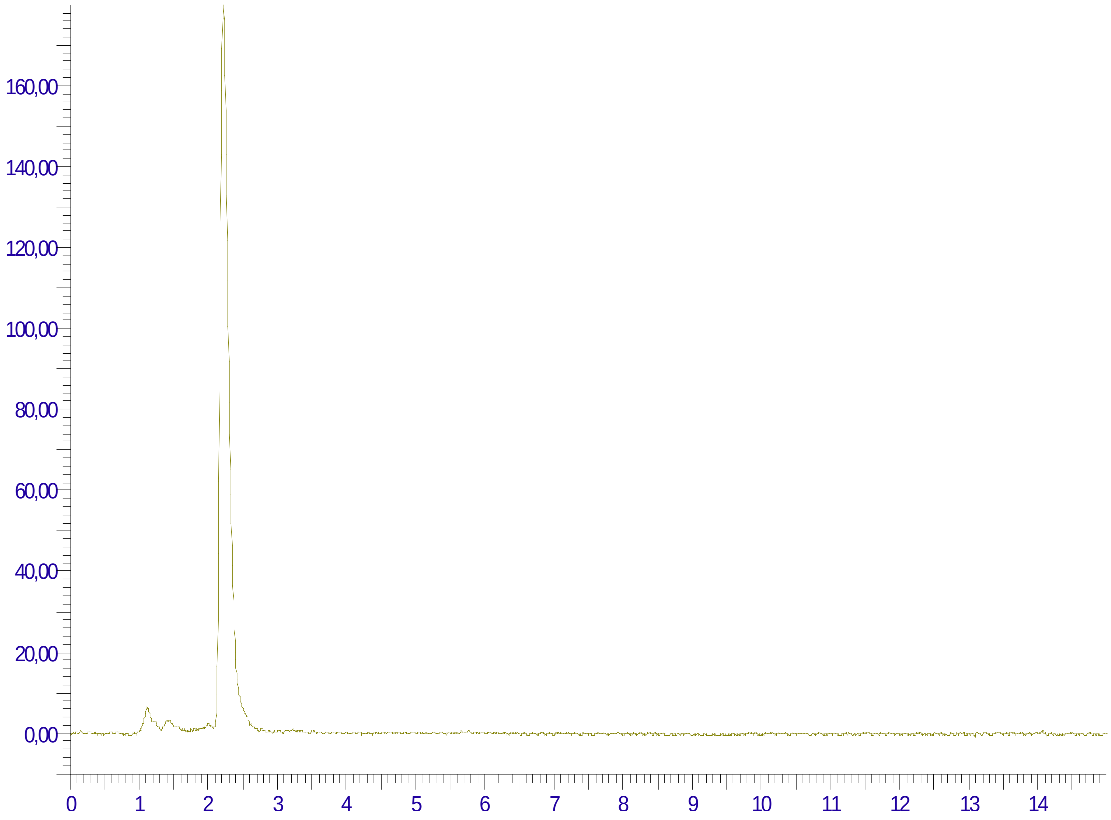


Fig. 3.9. Phenol solution photocatalyzed for 20 minutes with TiO_2 (rutile)

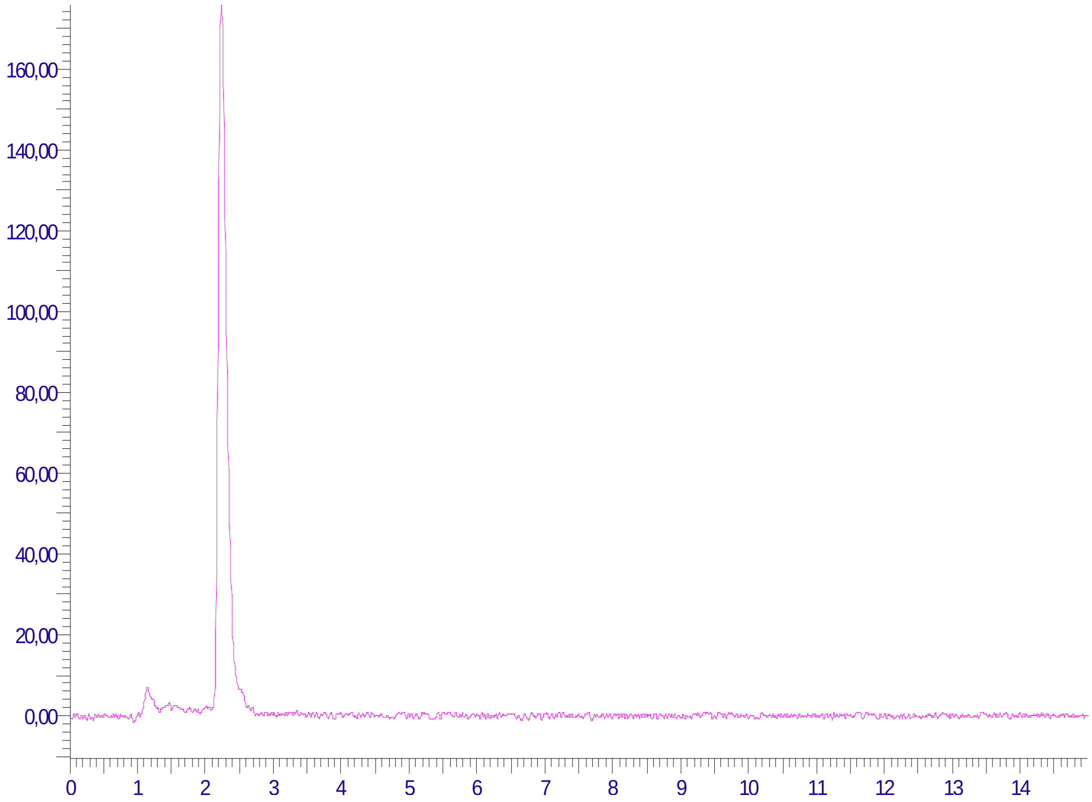


Fig. 3.10. Phenol solution photocatalyzed for 30 minutes with TiO_2 (rutile)

With the help of the TotalChromNavigator program and its GraphicEdit component, we have analyzed the amount of phenol that has undergone photocatalysis. Conversion in 5 minutes – 35.19%; 10 minutes – 25.77%; 20 minutes – 24.32%; 30 minutes – 25.96%. Such a strong difference with the results at the fifth minute is due to the shift in the baseline.

In the next experiment, we used the catalyst platinum coated titanium dioxide, in the amount of 10 mg.

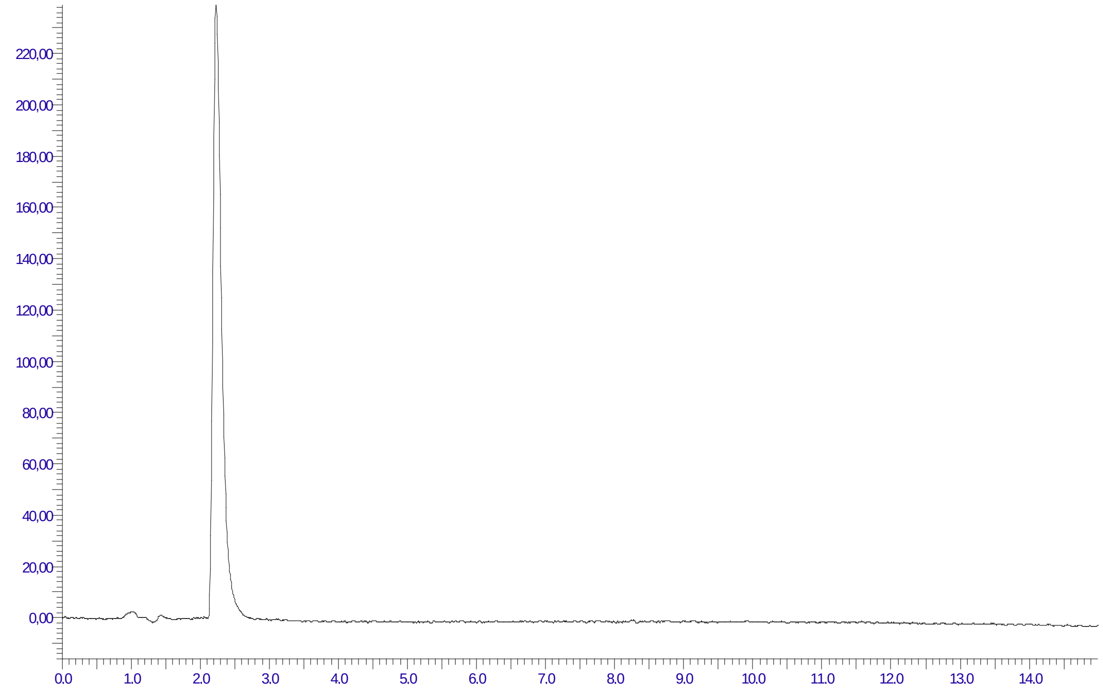


Fig. 3.11. A solution of phenol that has not undergone photocatalysis

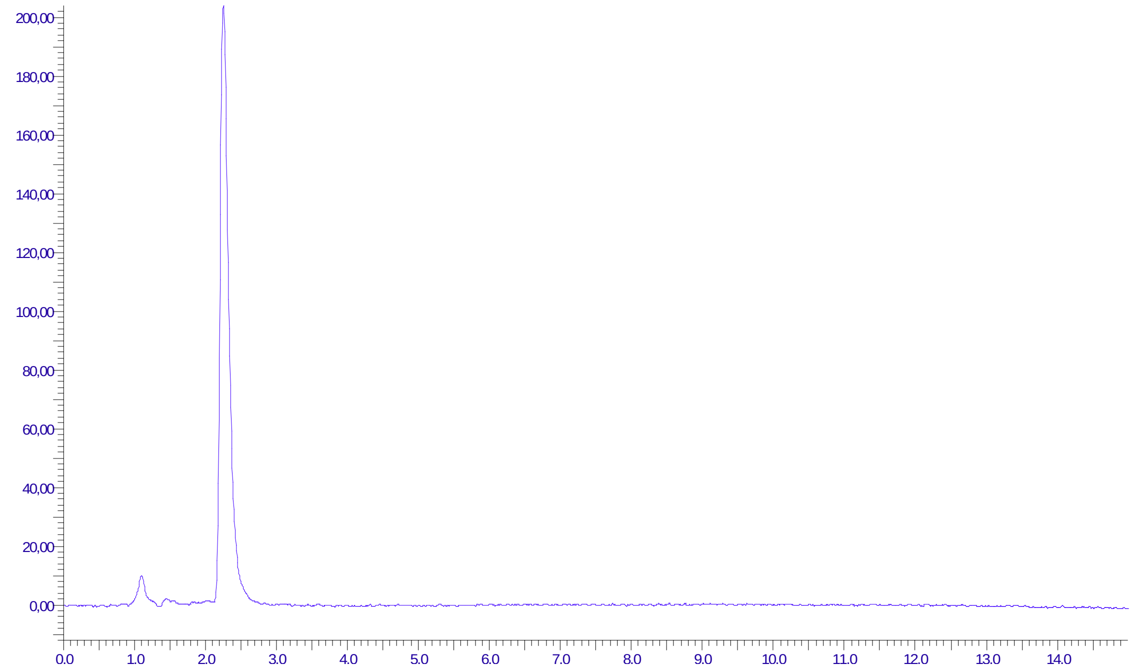


Fig. 3.12. Phenol solution photocatalyzed for 30 minutes with platinum coated TiO_2

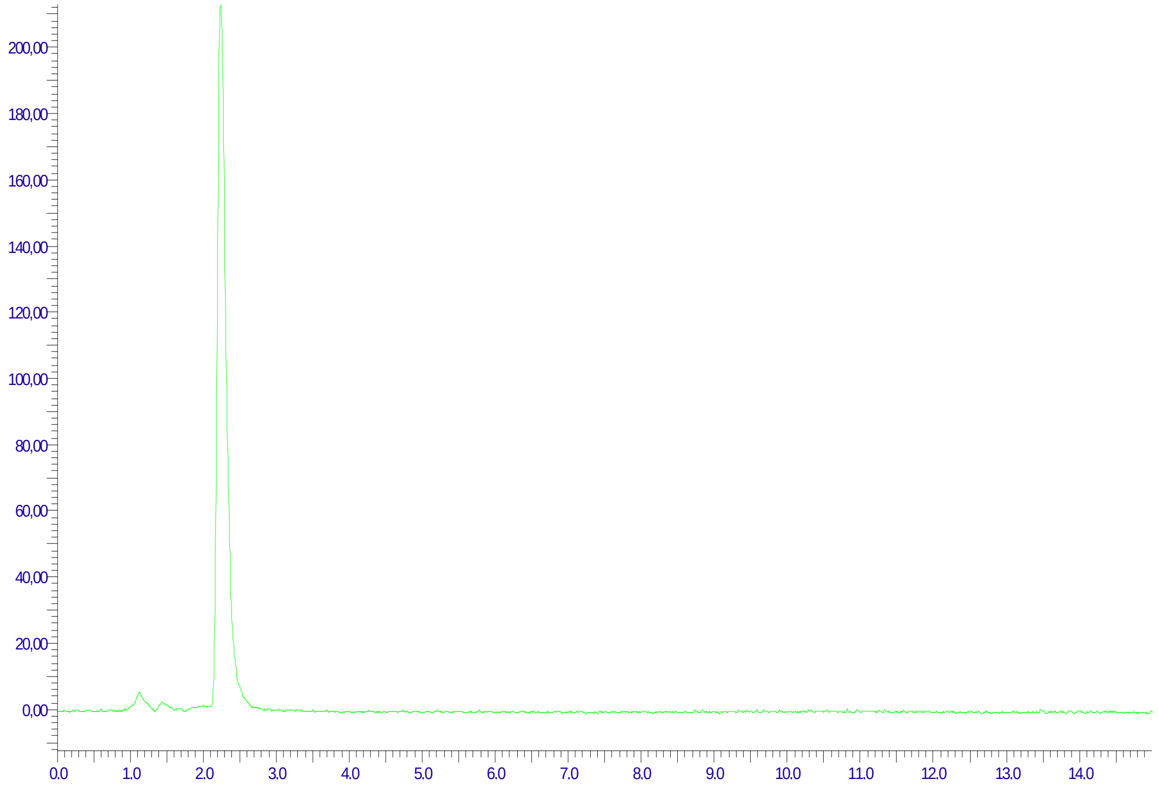


Fig. 3.13. Phenol solution photocatalyzed for 60 minutes with platinum coated TiO_2

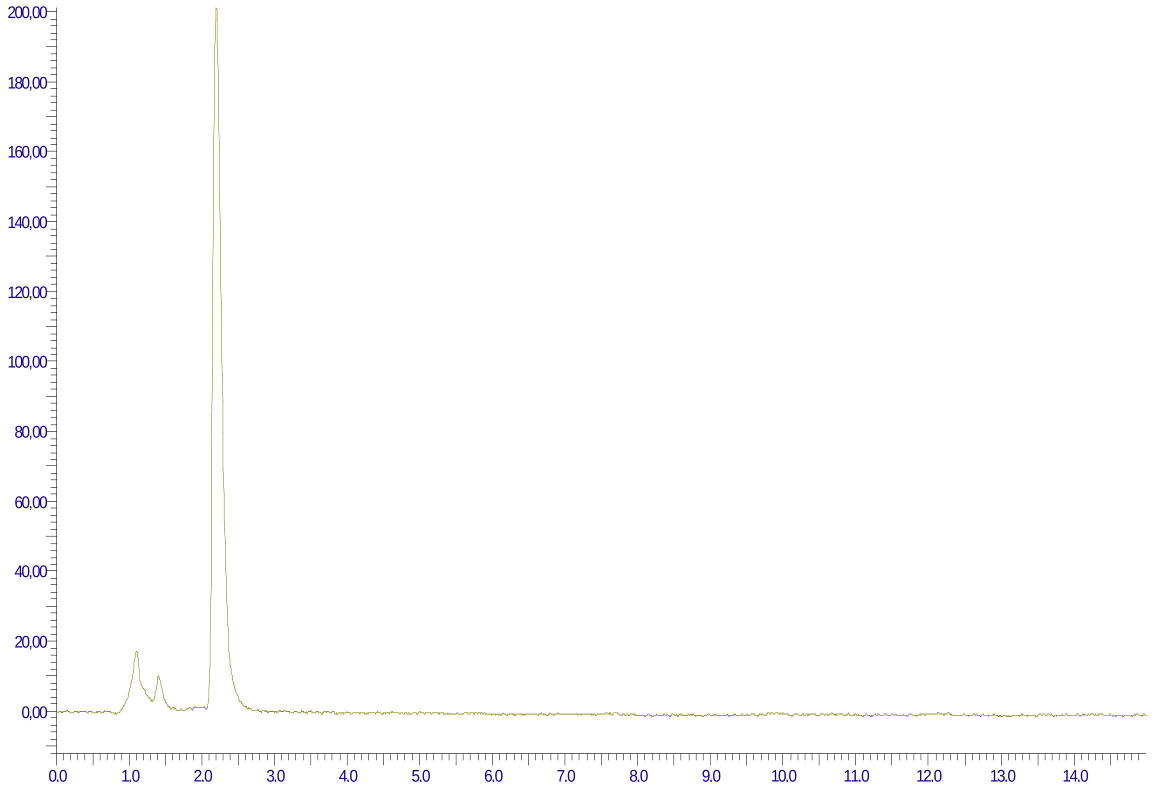


Fig. 3.14. Phenol solution photocatalyzed for 120 minutes with platinum coated TiO_2

Conversion on 30 minutes – 24.56%; 60 minutes – 12.99%; 120 minutes – 19.33%.

Then we selected the optimal amount of titanium dioxide with a rutile structure to increase the efficiency of the experiment. We took 50-75-100 mg of the catalyst and compared their effectiveness when under the lamp for 30 minutes.

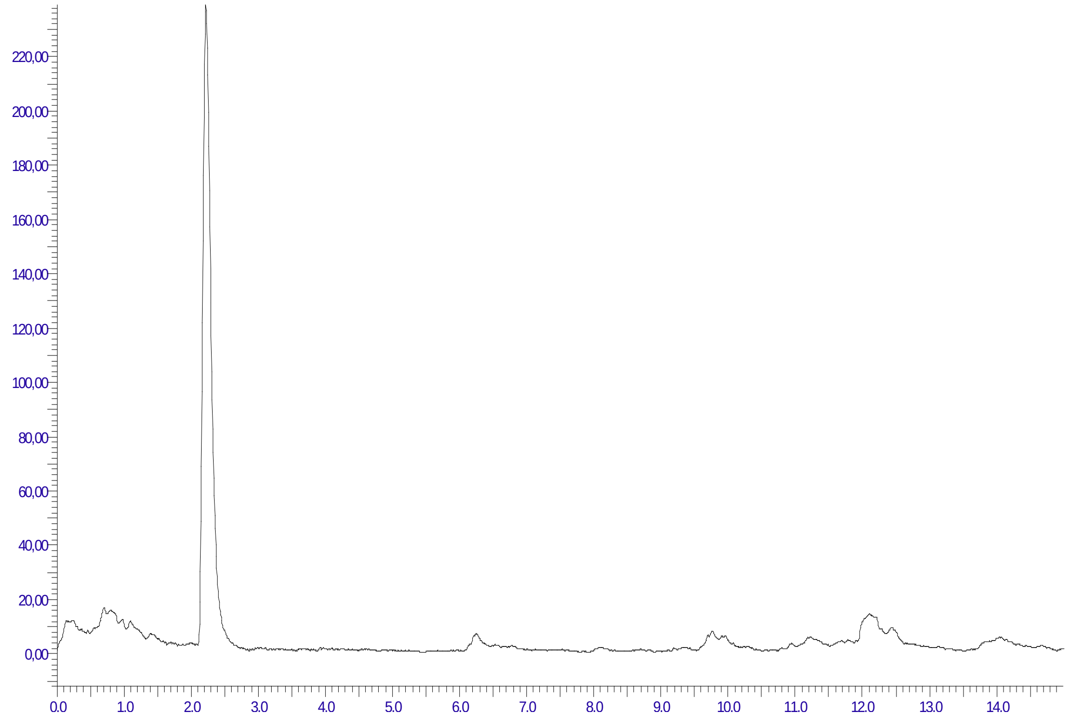


Fig. 3.15. A solution of phenol that has not undergone photocatalysis

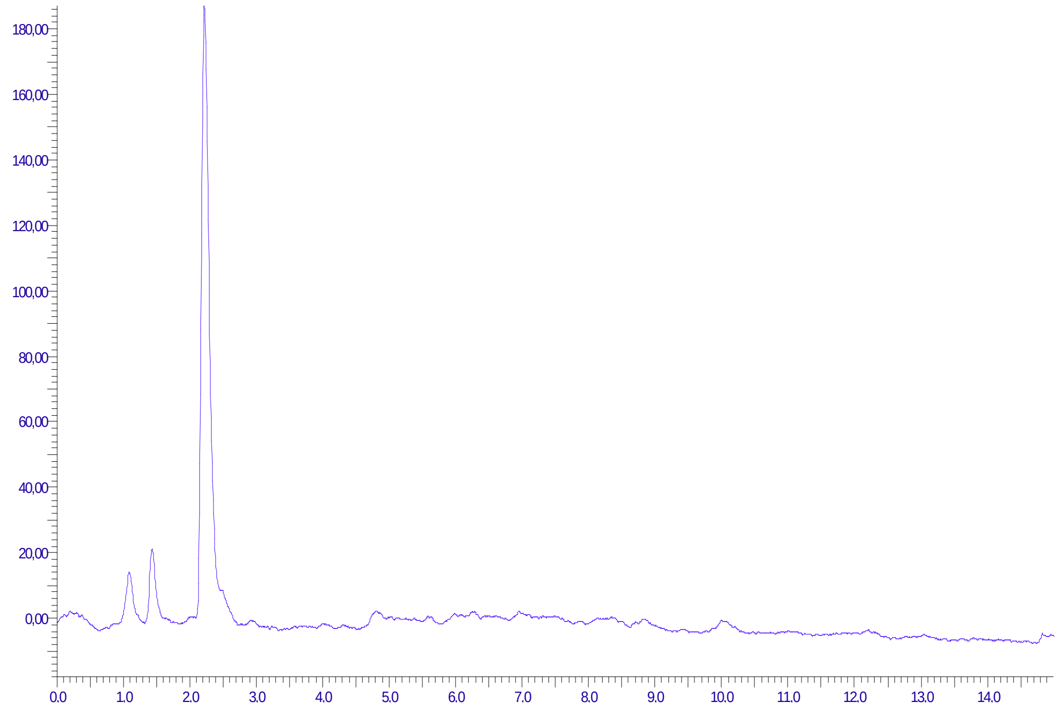


Fig. 3.16. A solution of phenol photocatalyzed for 30 minutes with 50 mg TiO_2 (rutile)

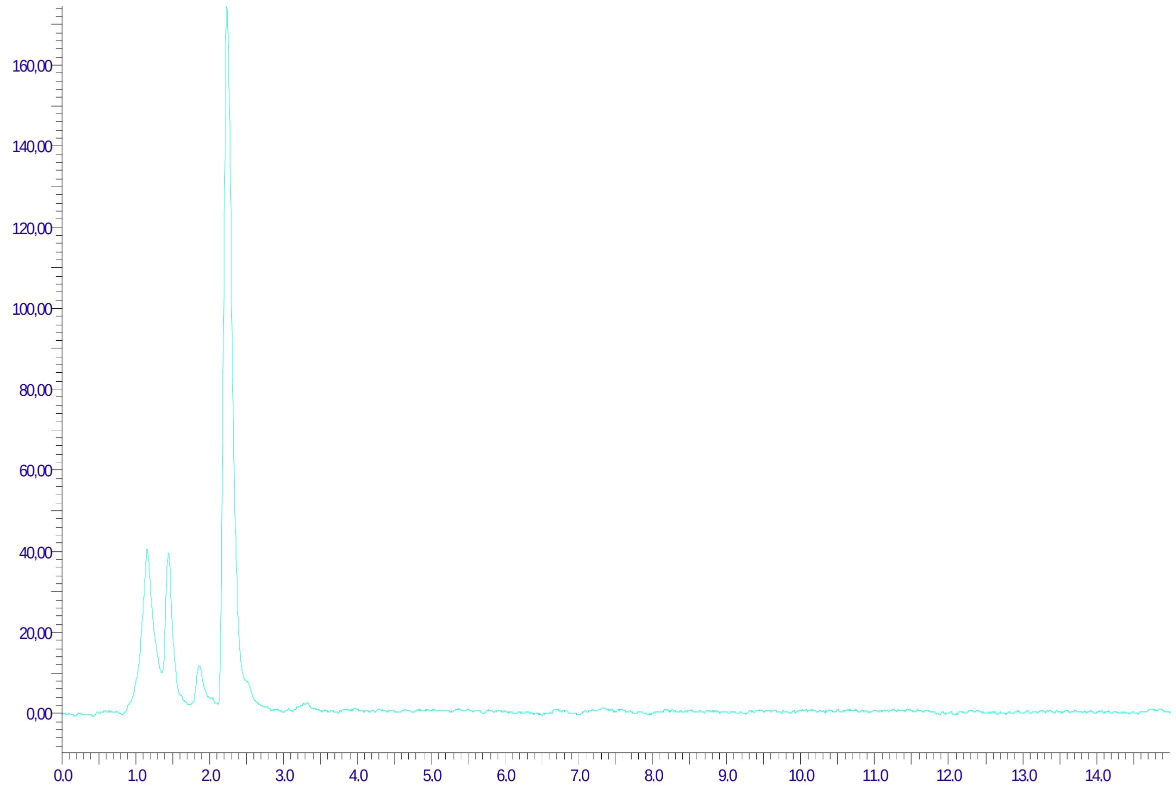


Fig. 3.17. A solution of phenol photocatalyzed for 30 minutes with 75 mg TiO_2 (rutile)

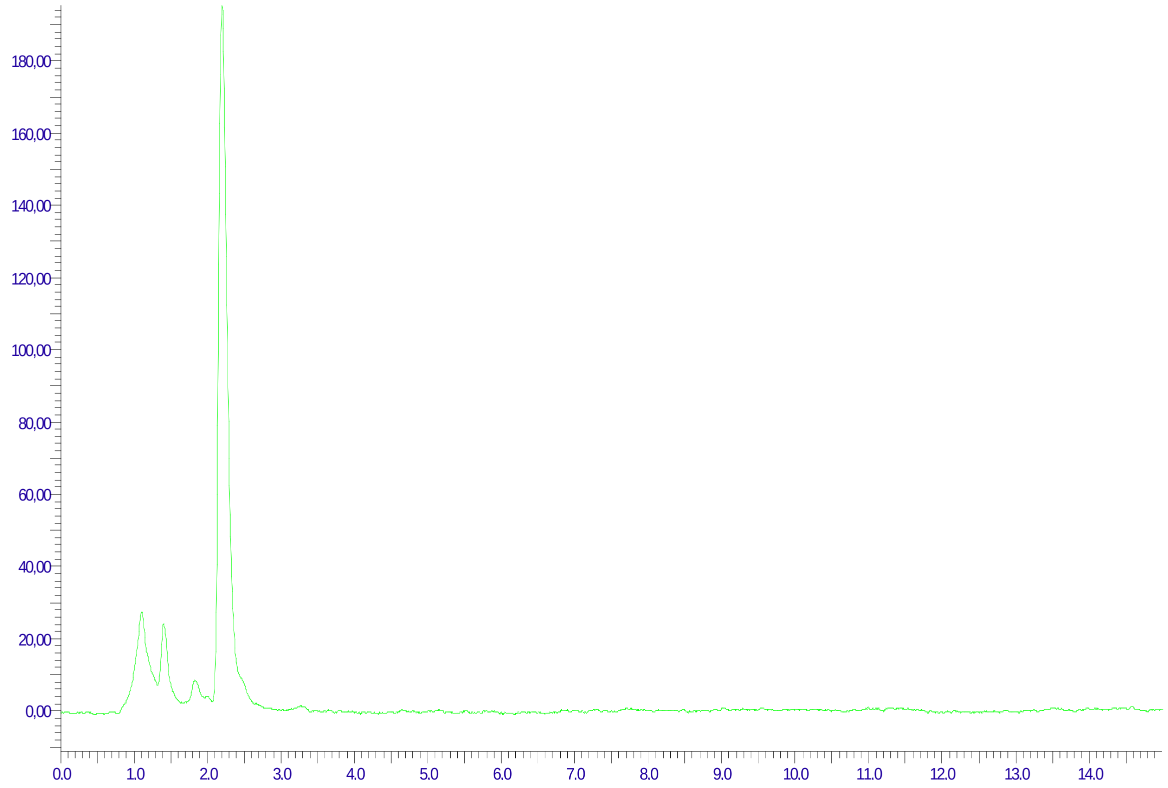


Fig. 3.18. A solution of phenol photocatalyzed for 30 minutes with 100 mg TiO_2 (rutile)

Conversion at 50 mg – 20.57%, 75 mg – 29.42%, 100 mg – 20.74%.

Next, we took a mercury lamp with ultraviolet and visible light and compared the effectiveness of 100 mg of TiO_2 in relation to 100 mg of nickel-covered TiO_2. We also changed the concentration of the solution and diluted it to 0.16 g/l.

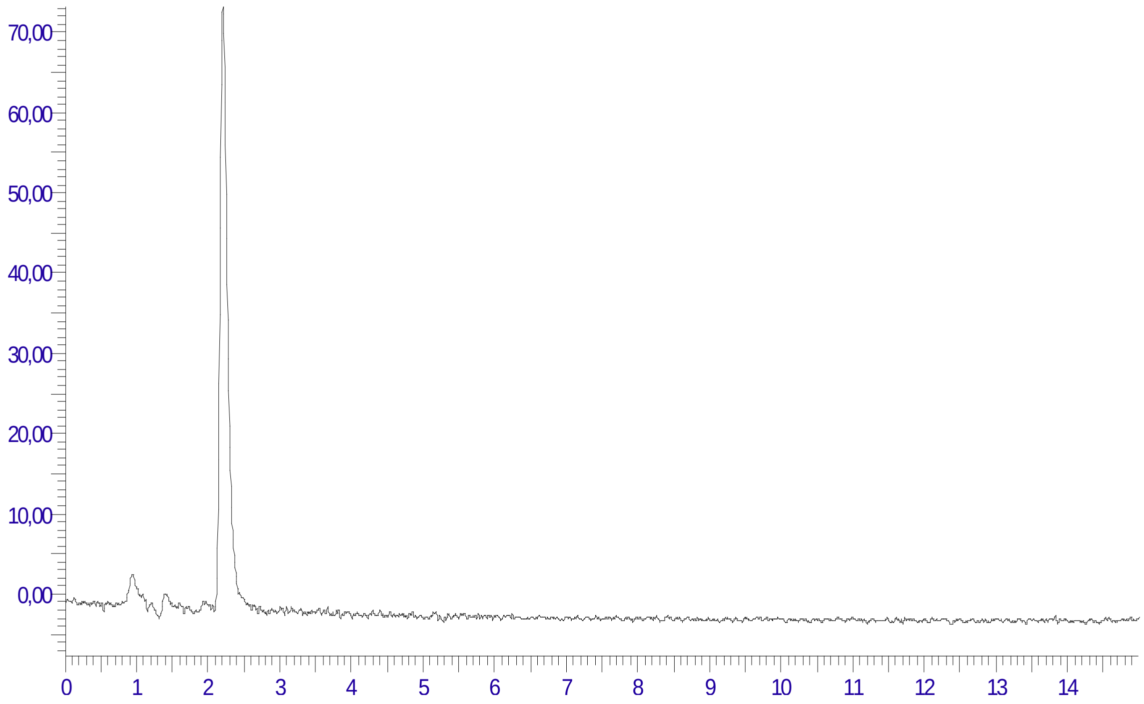


Fig. 3.19. A solution of phenol that has not undergone photocatalysis

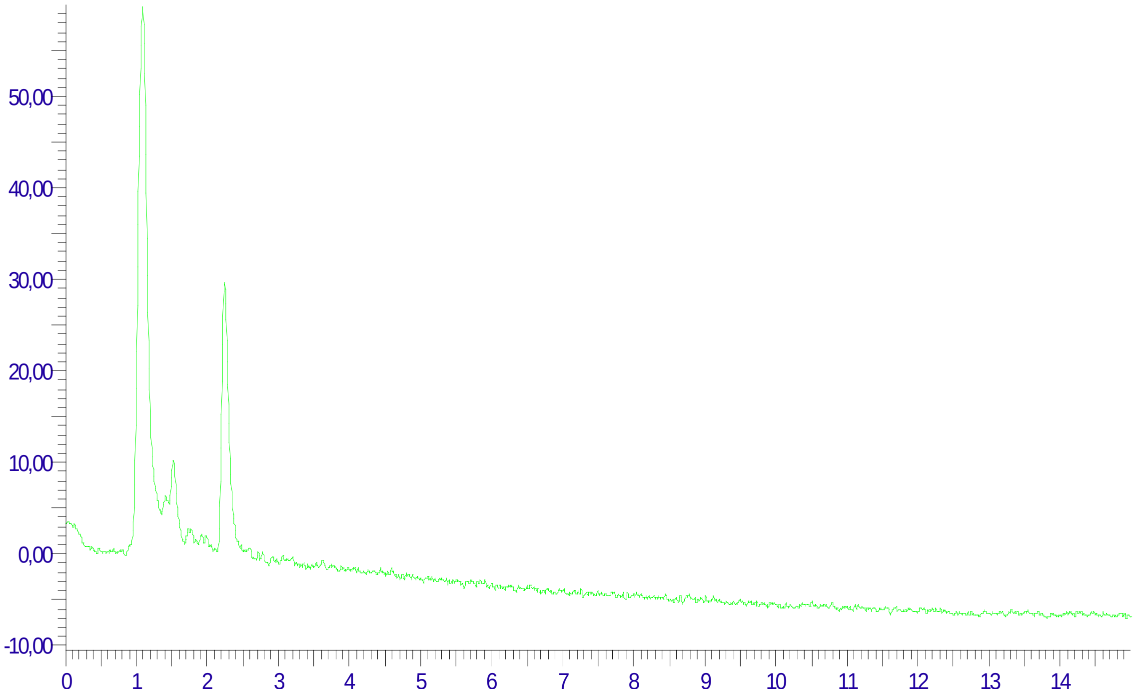


Fig. 3.20. A solution of phenol photocatalyzed for 30 minutes with 100 mg TiO_2 (rutile)

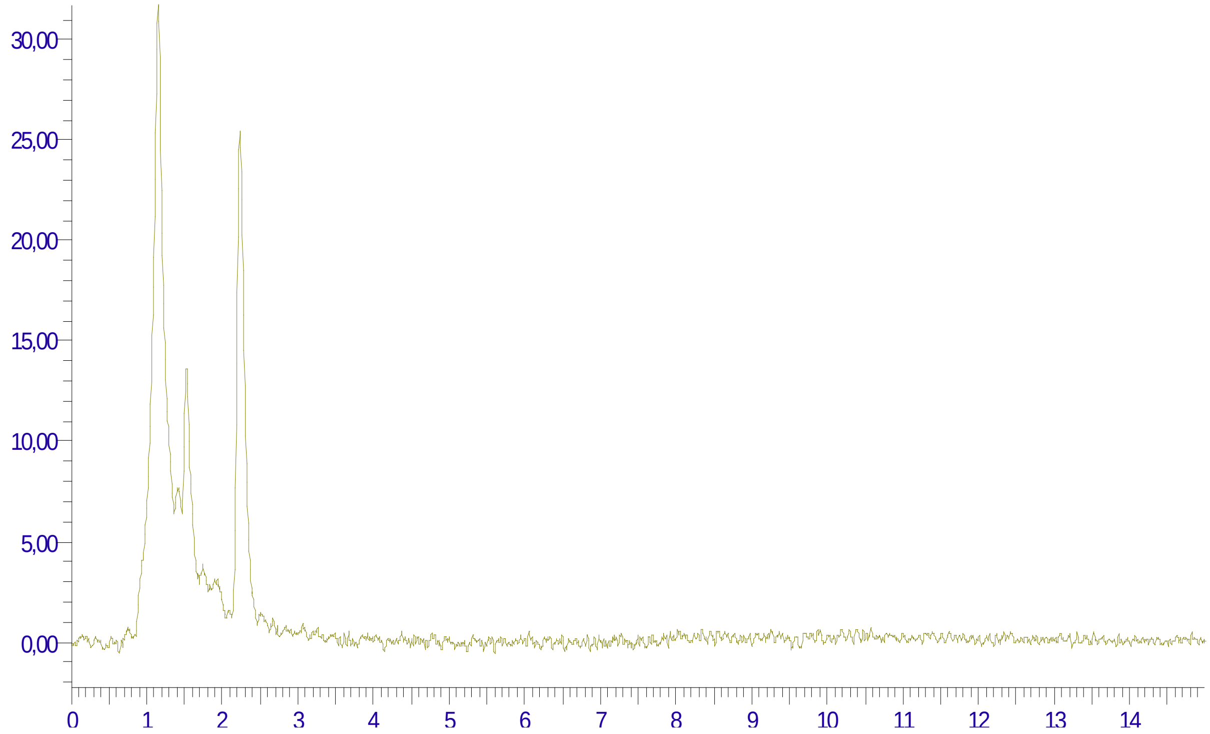


Fig. 3.21.A solution of phenol photocatalyzed for 60 minutes with 100 mg TiO_2 (rutile)

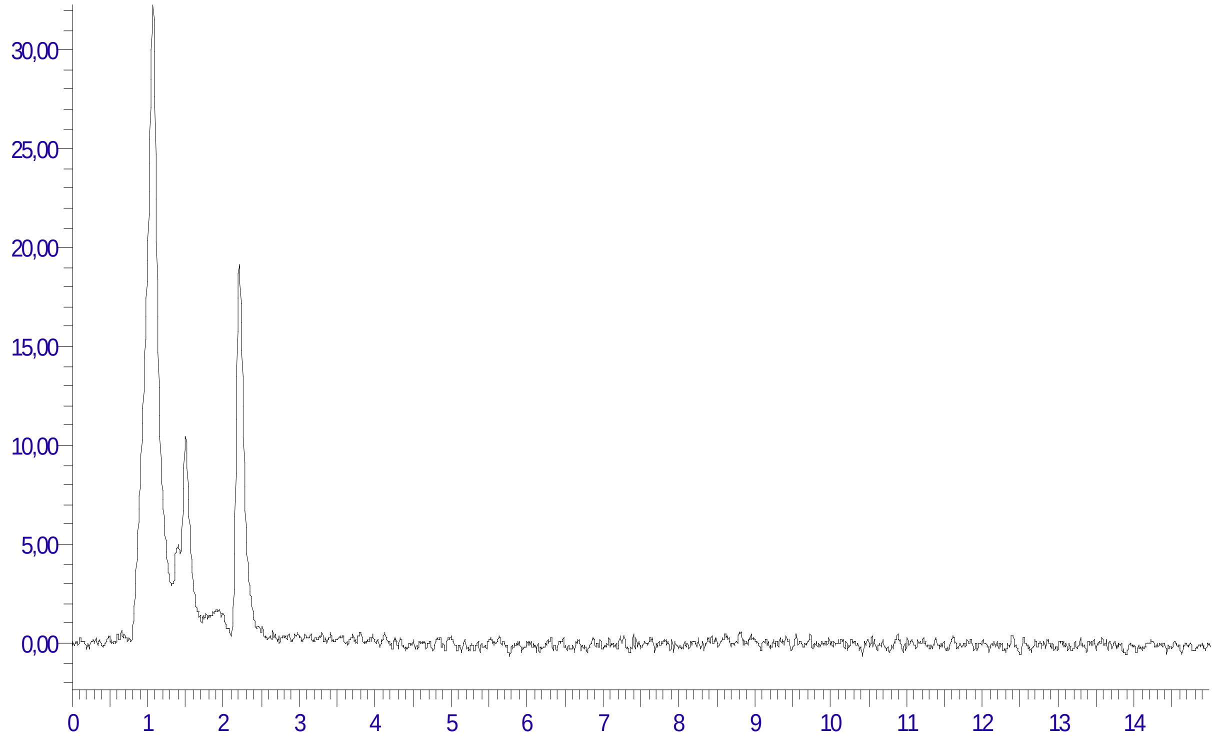


Fig. 3.22. A solution of phenol photocatalyzed for 120 minutes with 100 mg TiO_2 (rutile)

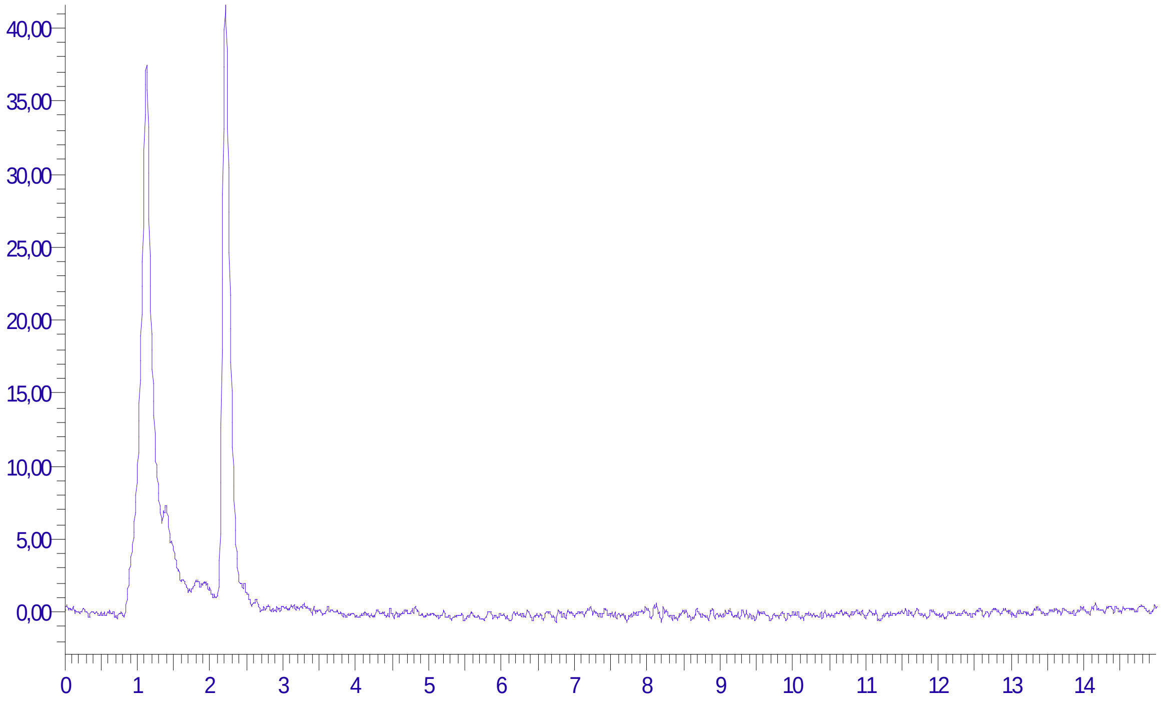


Fig. 3.23. A solution of phenol photocatalyzed for 30 minutes with 100 mg TiO_2 Ni-coated

Conversion at 30 minutes (TiO_2) – 63.33%; 60 (TiO_2) – 70.62%; 120 (TiO_2) – 75.9%; 30 (TiO_2 Ni-coated) – 48.14%. Which in this case confirms the higher efficiency of Ni-coated as a catalyst.

We also considered the possibility of working with a solution with a concentration of 4 g/l and 100 mg of TiO2, but the conversion was: at 30 minutes – 11.37%, at 60 – 11.43%; by 120 – 5.89%, which showed that for these conditions, the concentration of 4 g/l is high and weakly amenable to photocatalysis. Concentrations of 0.5 and 0.25 mg/l were also too strong for these conditions.

Then we chose the main working concentration (0.16 g/l) and tried TiO_2 Pt-coated as a catalyst in the amount of 10 mg, time frame: 15-30-60-120-240 minutes, 3 samples were also taken at each time interval. Further results will be presented as an average.

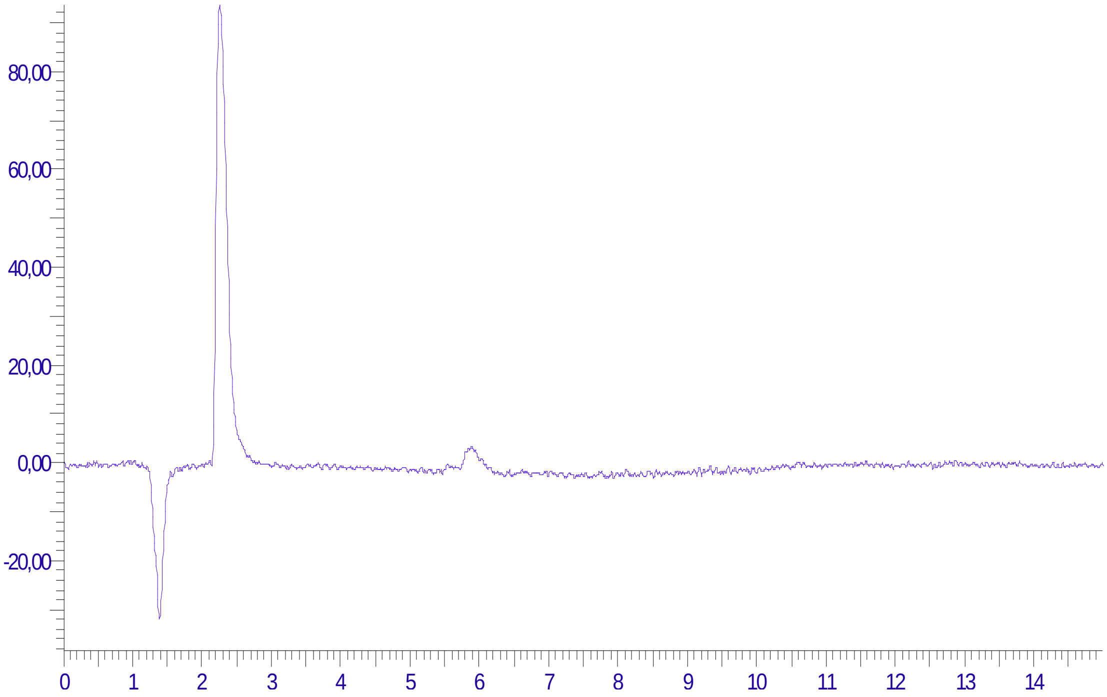


Fig. 3.24. A solution of phenol that has not undergone photocatalysis

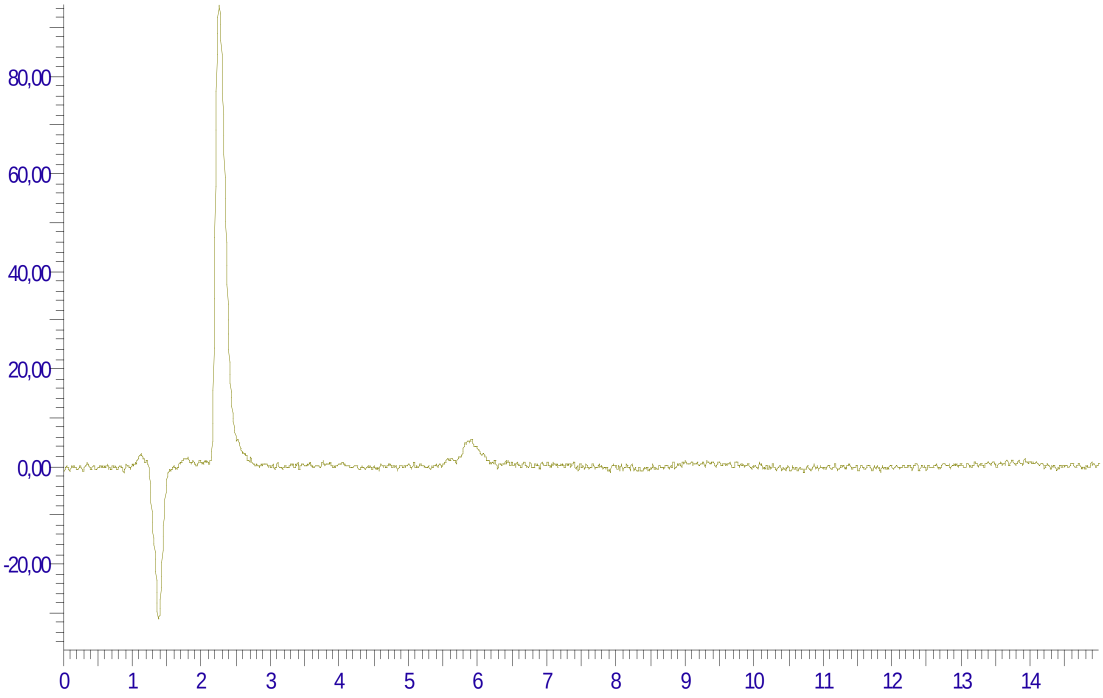


Fig. 3.25. A solution of phenol photocatalyzed for 15 minutes with 10 mg TiO_2 Pt-coated

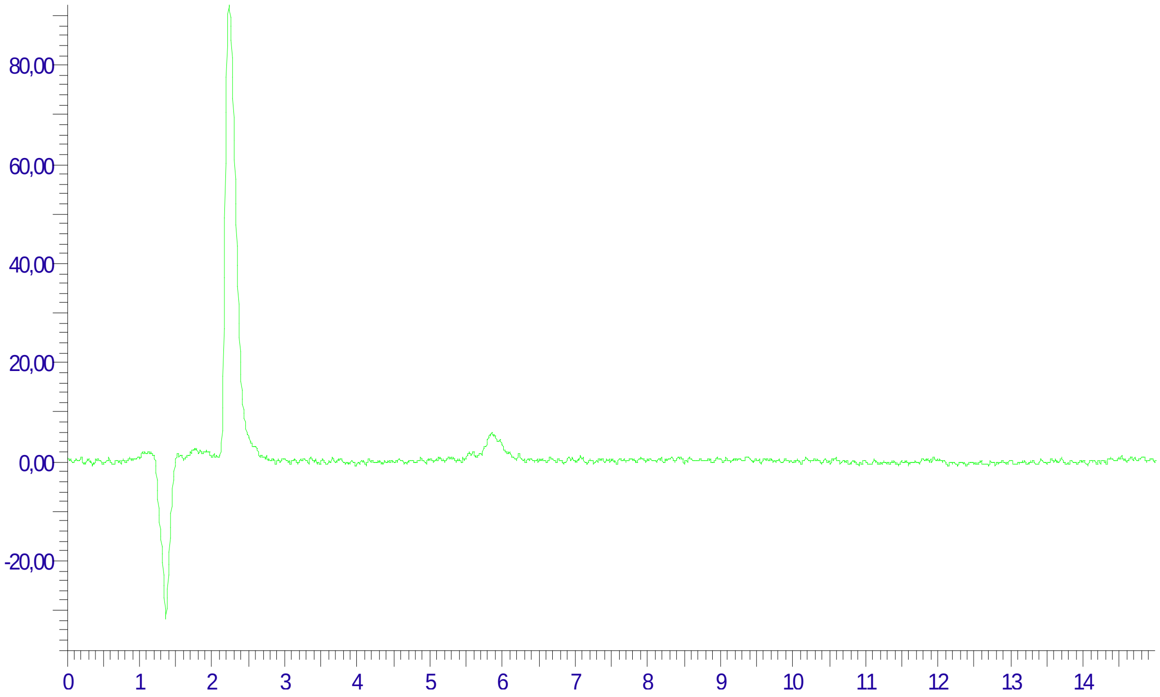


Fig. 3.26. A solution of phenol photocatalyzed for 30 minutes with 10 mg TiO_2 Pt-coated

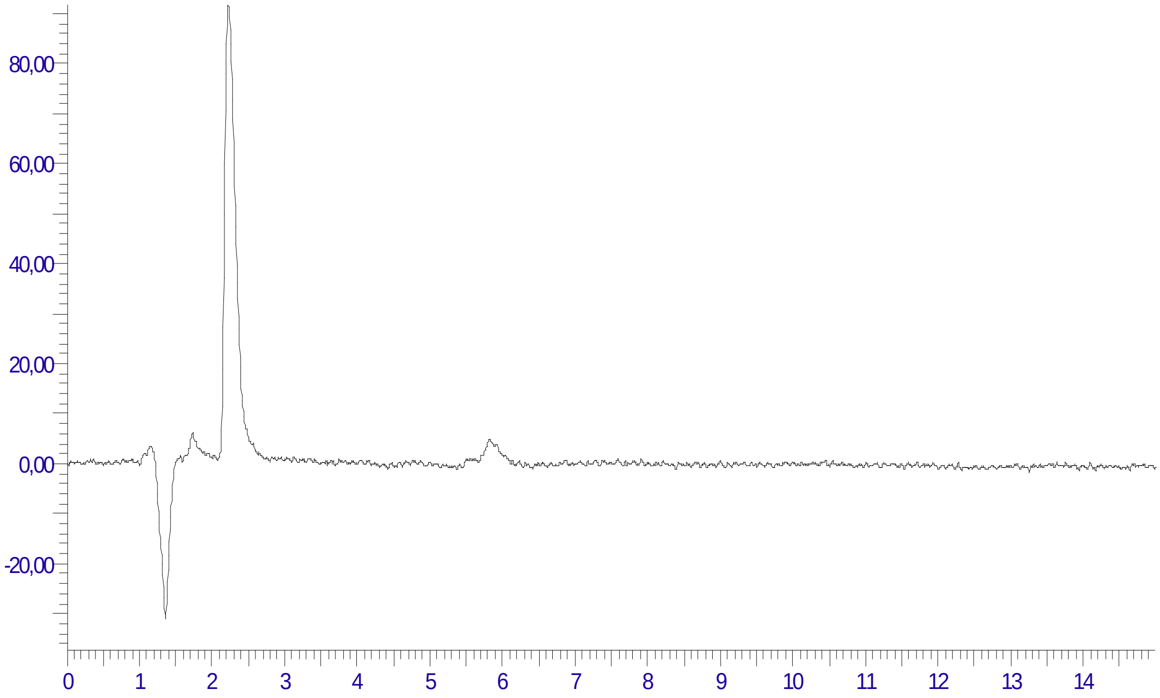


Fig. 3.27. A solution of phenol photocatalyzed for 60 minutes with 10 mg TiO_2 Pt-coated

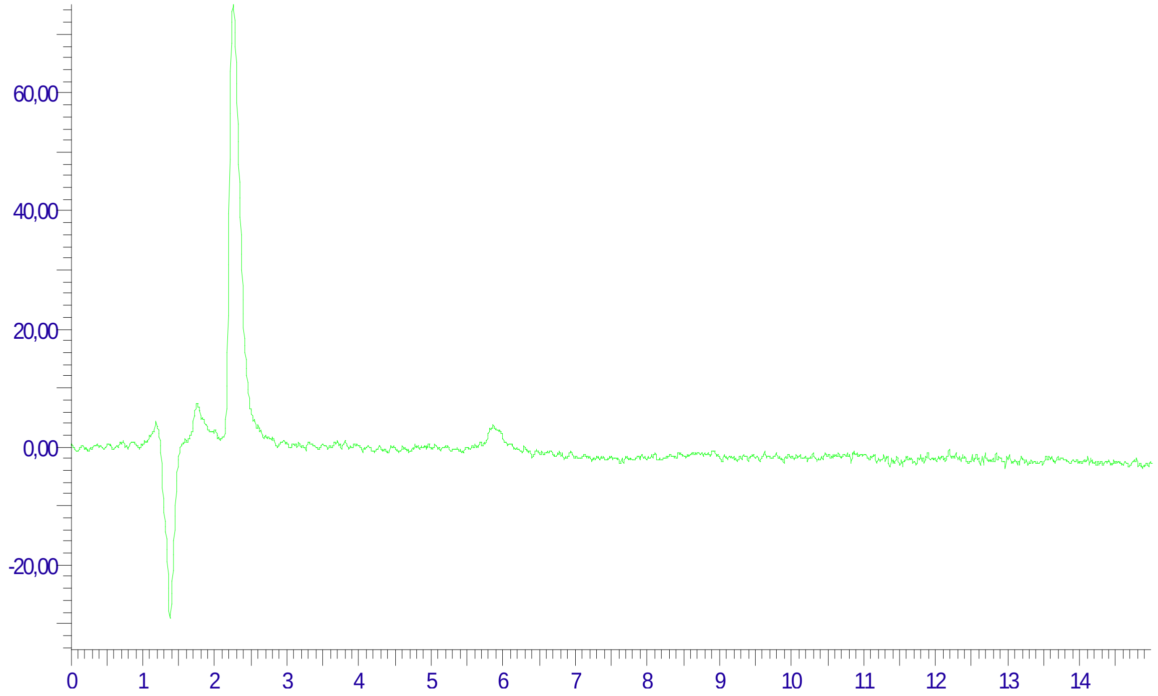


Fig. 3.28. A solution of phenol photocatalyzed for 120 minutes with 10 mg TiO_2 Pt-coated

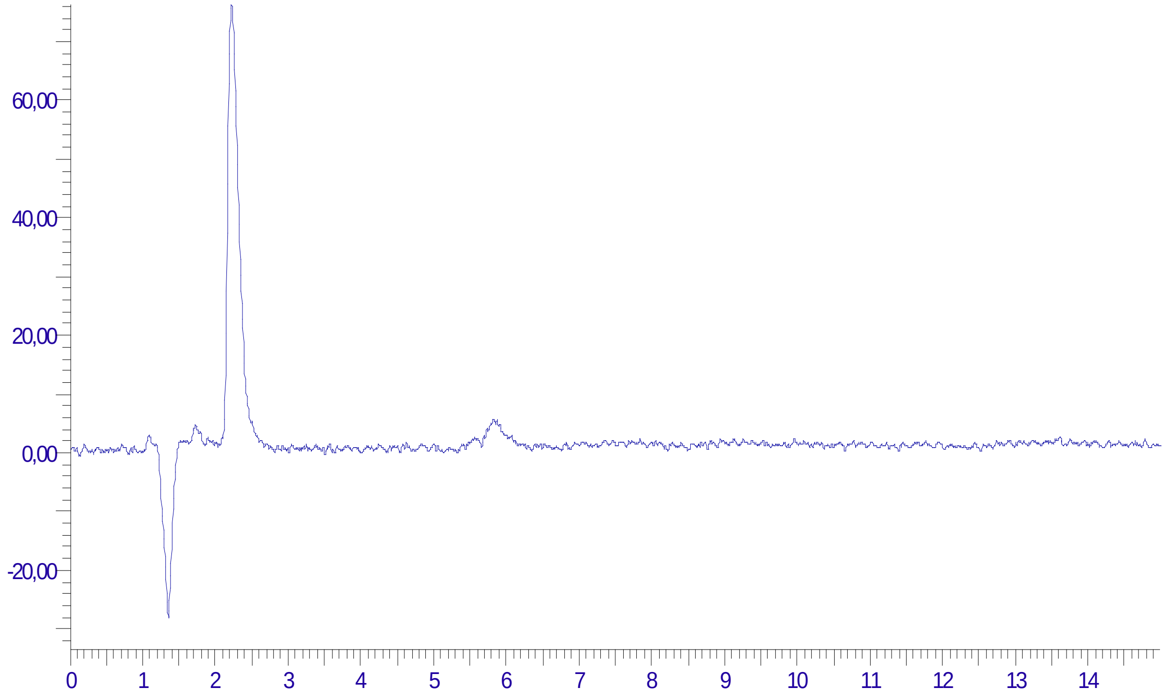


Fig. 3.29. A solution of phenol photocatalyzed for 240 minutes with 10 mg TiO_2 Pt-coated

Conversion in 15 minutes – 5.86%; 30 – 6.03%; 60 – 8.37%; 120 – 29.33%; 240 – 28.35%, which shows the greater effectiveness of TiO_2 Pt-coated over long periods of time.

Next, we used $BiFe_{0.8}Mn_{0.2}O_3$ for the experiment, in an amount of 15 mg. 3 samples were taken from each time interval: 15-30-60-120-240 minutes.

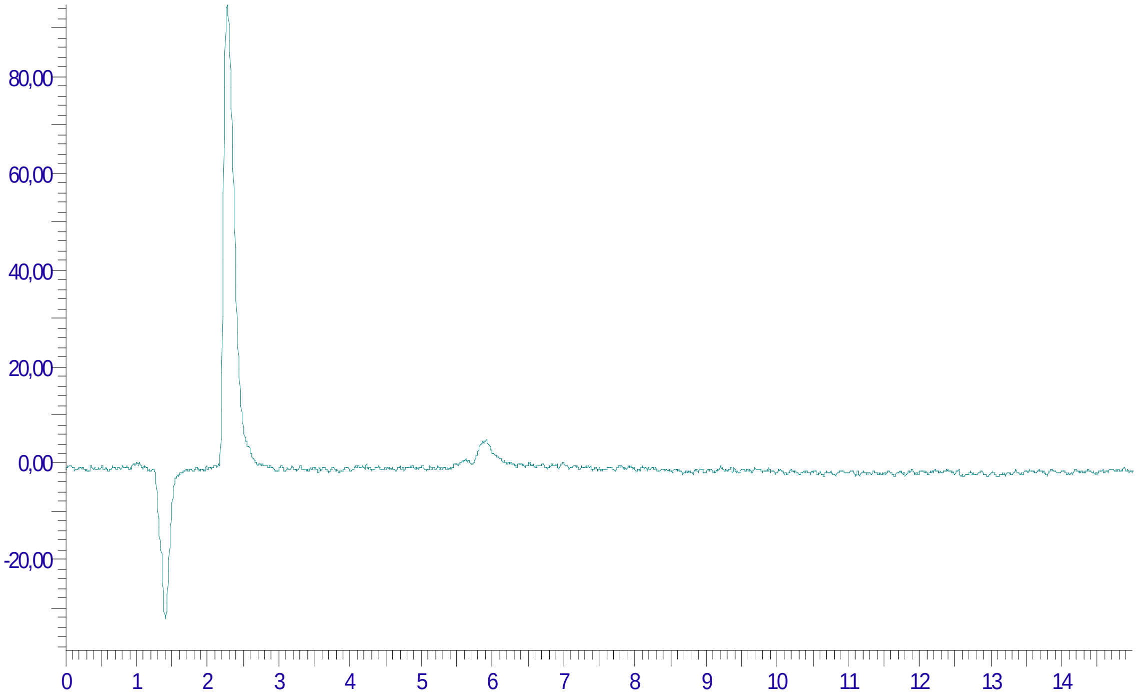


Fig. 3.30. A solution of phenol that has not undergone photocatalysis

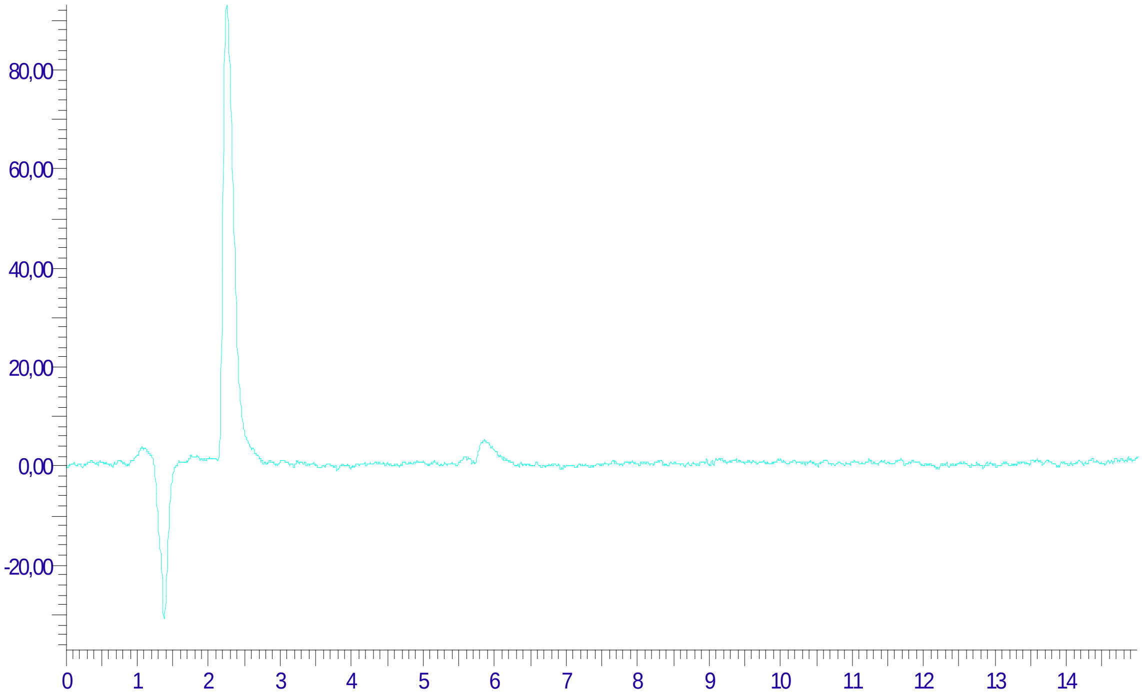


Fig. 3.31. A solution of phenol photocatalyzed for 15 minutes with 15 mg $BiFe_{0.8}Mn_{0.2}O_3$

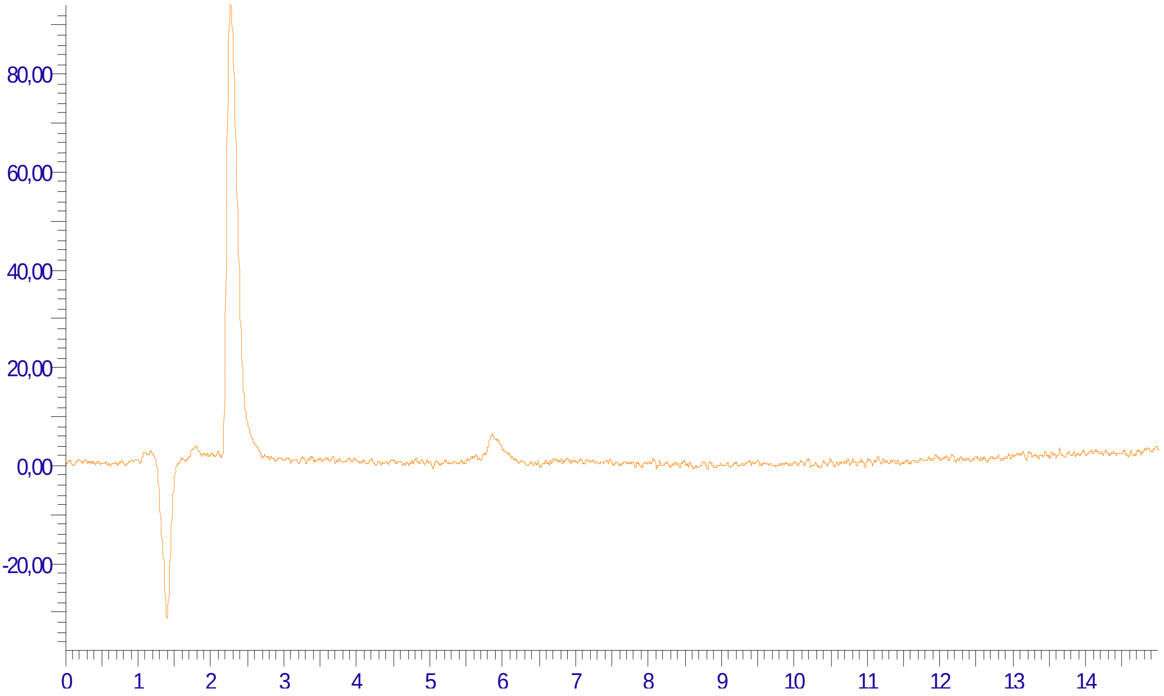


Fig. 3.32. A solution of phenol photocatalyzed for 30 minutes with 15 mg $BiFe_{0.8}Mn_{0.2}O_3$

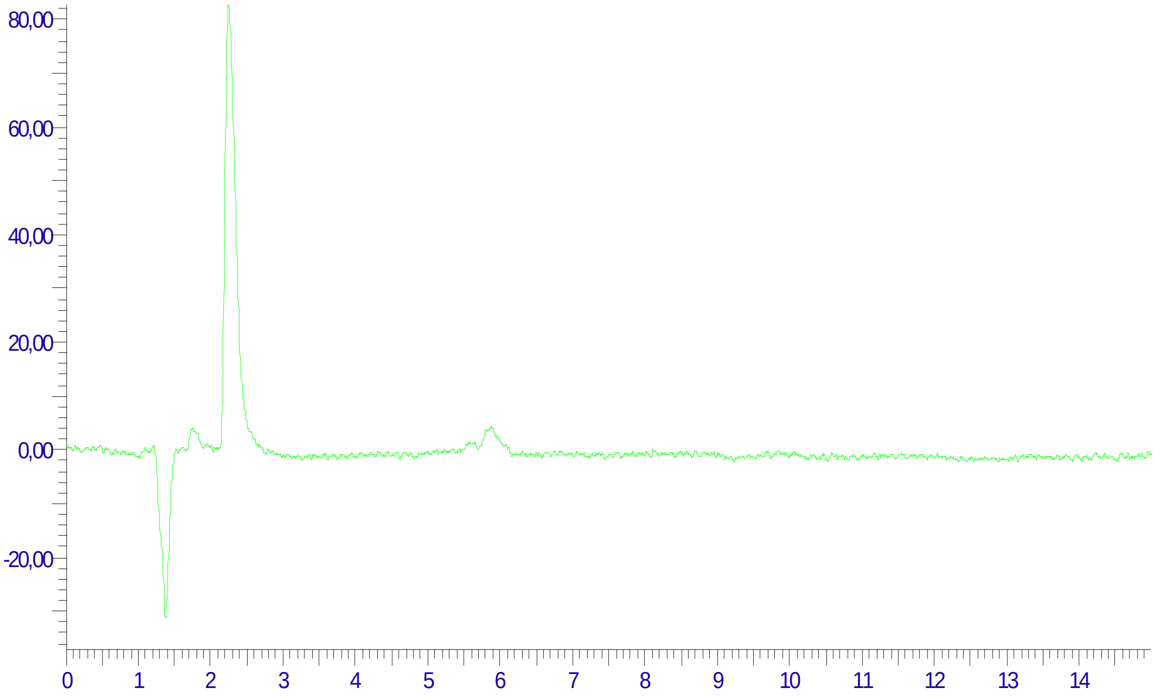


Fig. 3.33. A solution of phenol photocatalyzed for 60 minutes with 15 mg $BiFe_{0.8}Mn_{0.2}O_3$

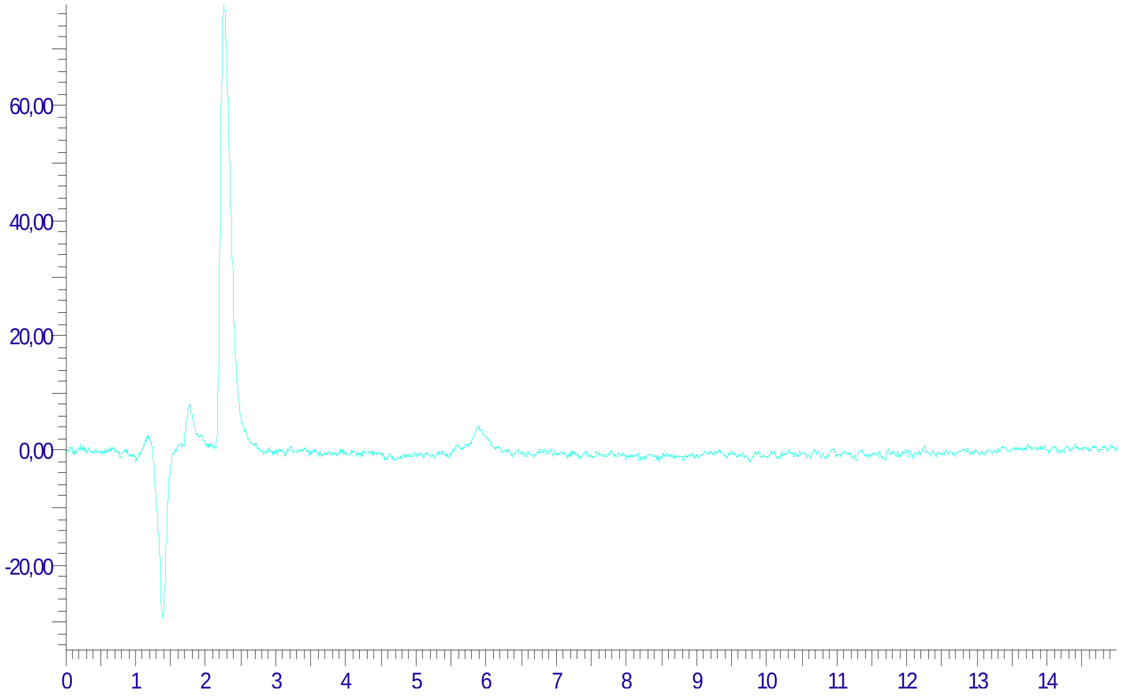


Fig. 3.34. A solution of phenol photocatalyzed for 120 minutes with 15 mg $BiFe_{0.8}Mn_{0.2}O_3$

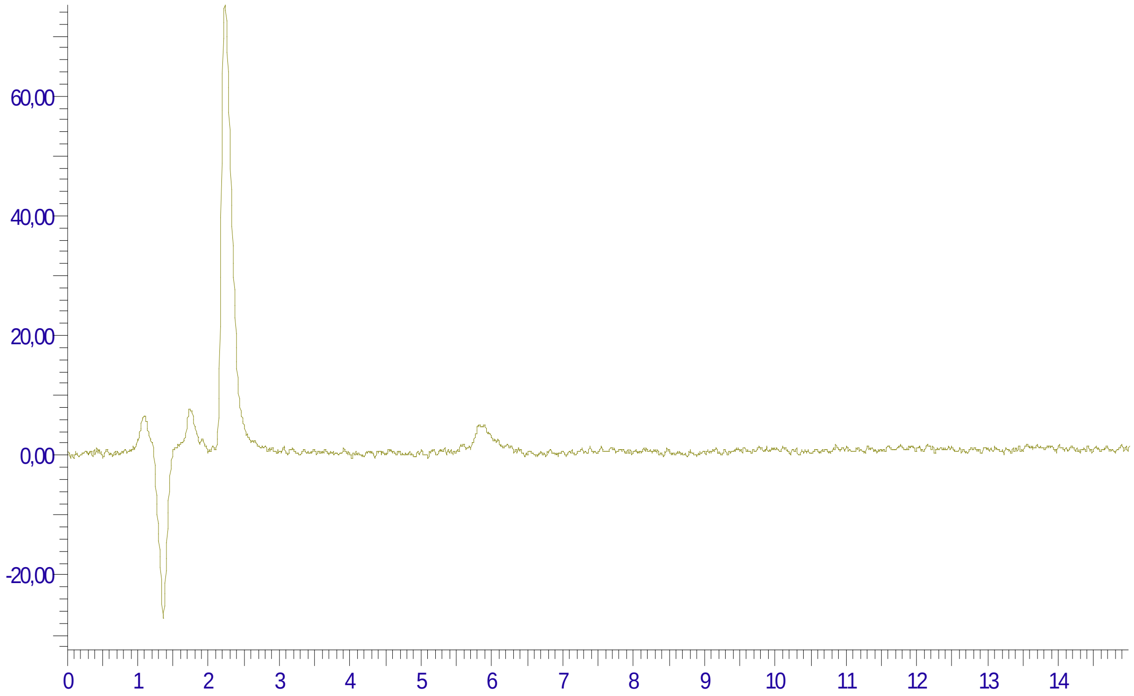


Fig. 3.35. A solution of phenol photocatalyzed for 240 minutes with 15 mg $BiFe_{0.8}Mn_{0.2}O_3$

Conversion in 15 minutes – 5.94%; 30 – 8.87%; 60 – 17.45%; 120 – 26.46%; 240 – 28.08%, which, in comparison with platinum, shows a slightly higher efficiency at shorter time intervals, and at large it works no worse.

The last experiment we conducted was an experiment with 10 mg TiO_2/CNTs, 3 samples from each time interval: 15-30-60-120-240 minutes.

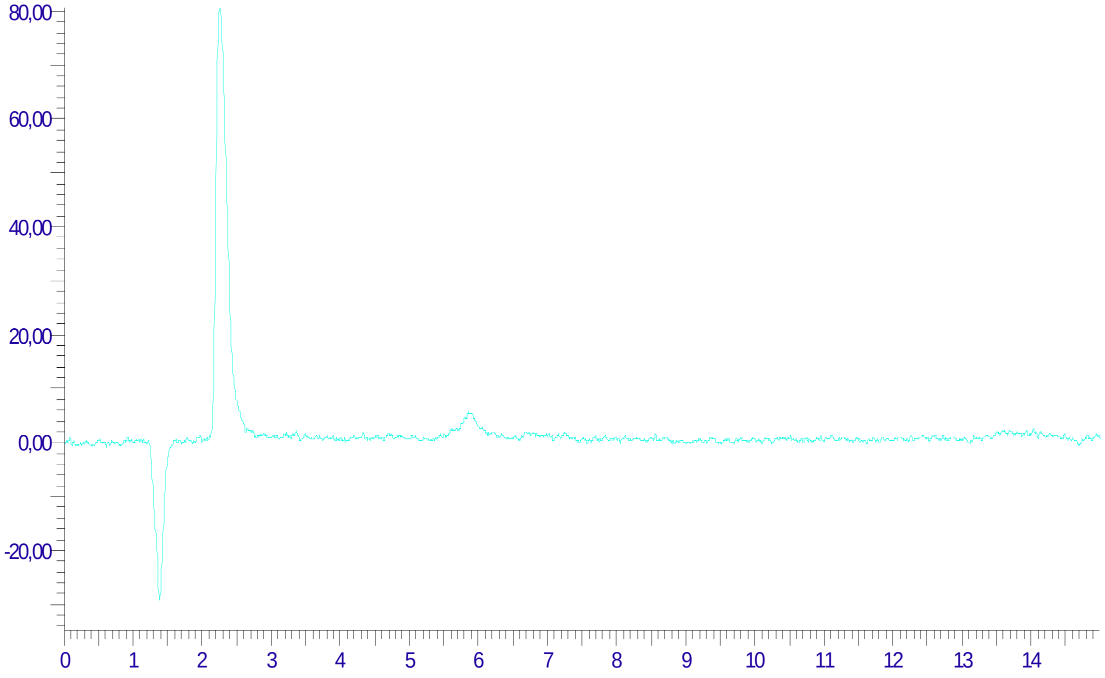


Fig. 3.36. A solution of phenol that has not undergone photocatalysis

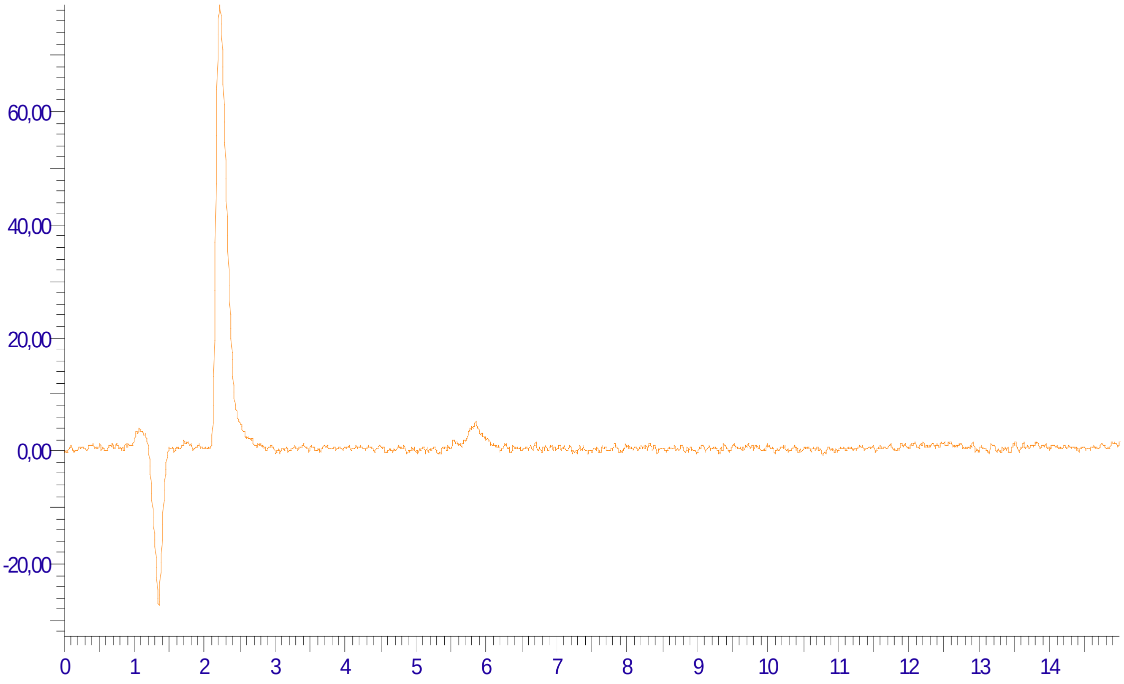


Fig. 3.37. A solution of phenol photocatalyzed for 15 minutes with 10 mg TiO_2/CNTs

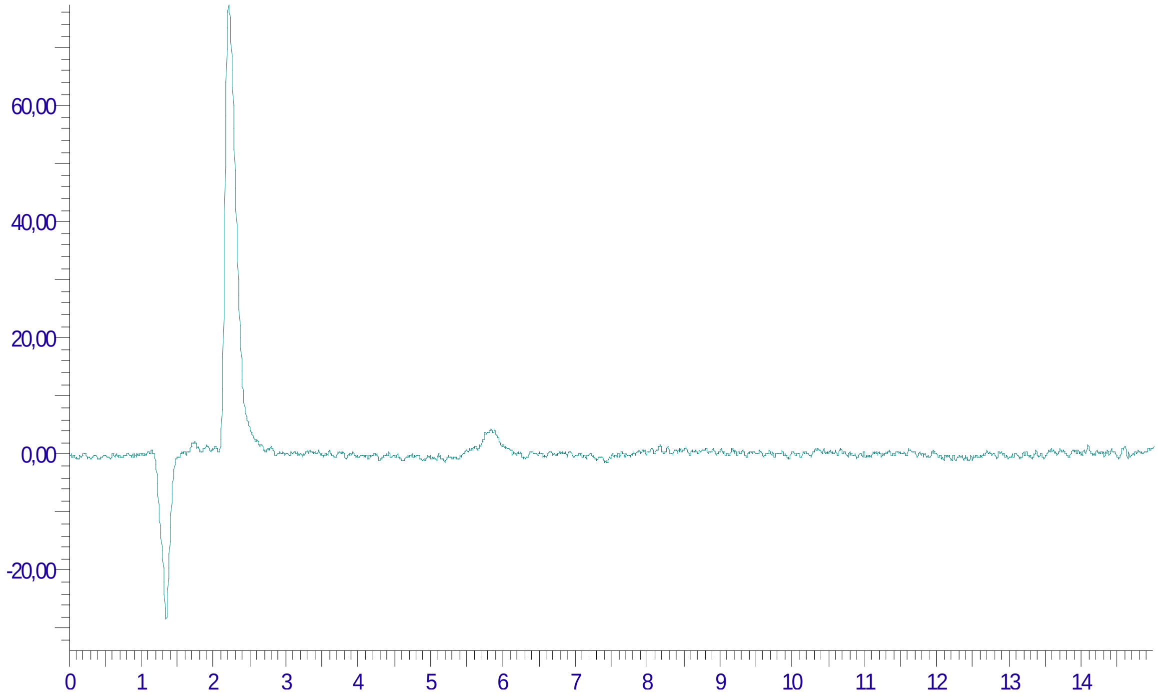


Fig. 3.38. A solution of phenol photocatalyzed for 30 minutes with 10 mg TiO_2/CNTs

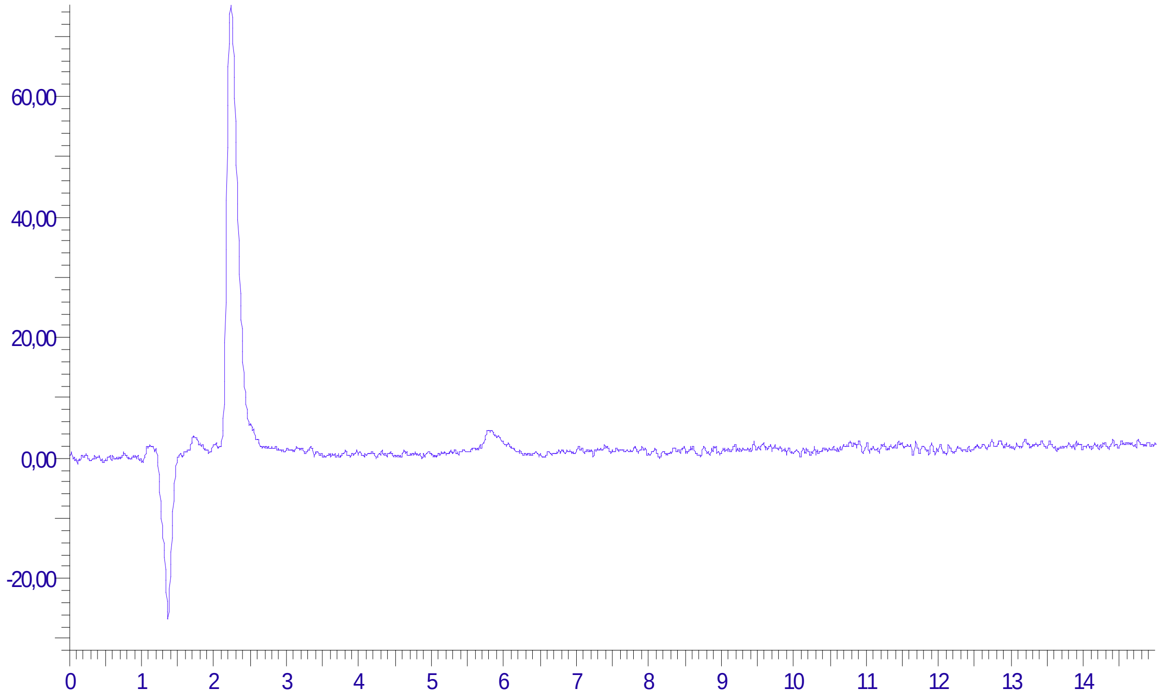


Fig. 3.39. A solution of phenol photocatalyzed for 60 minutes with 10 mg TiO_2/CNTs

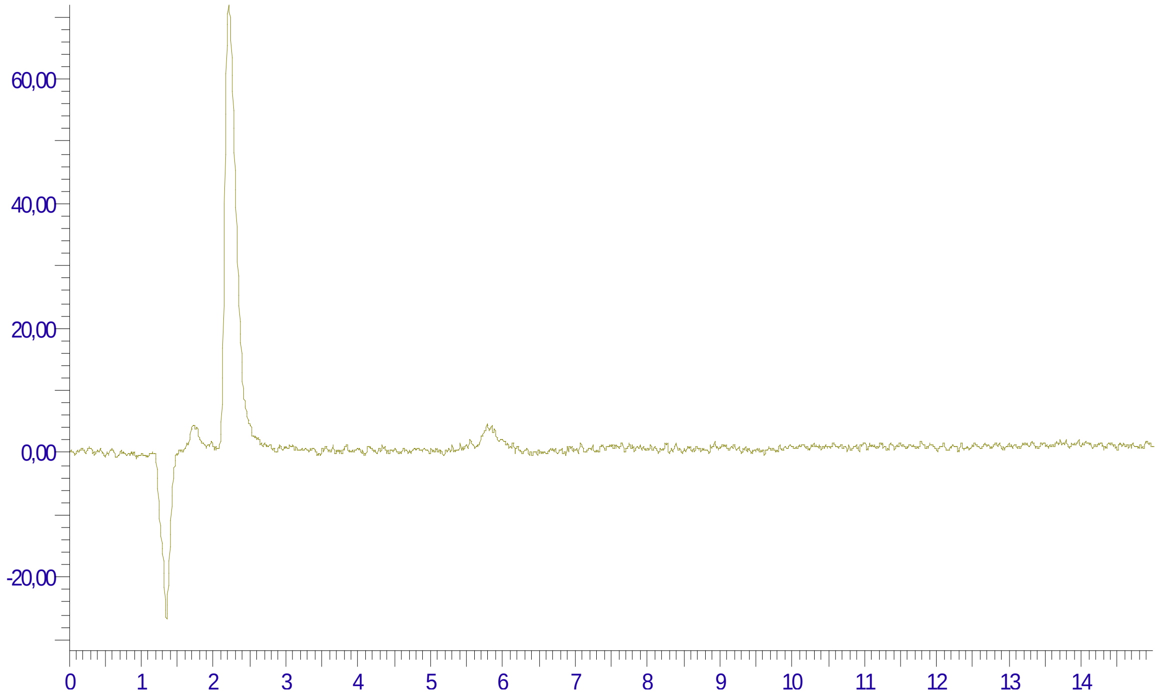


Fig. 3.40. A solution of phenol photocatalyzed for 120 minutes with 10 mg TiO_2/CNTs

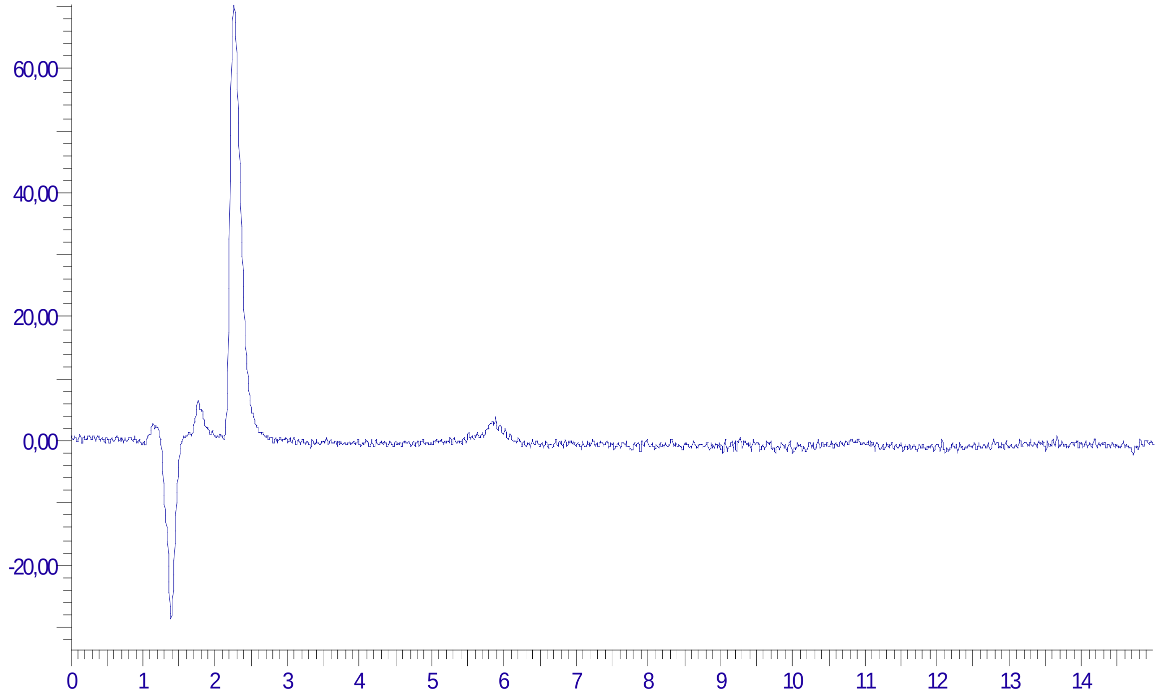


Fig. 3.41. A solution of phenol photocatalyzed for 240 minutes with 10 mg TiO_2/CNTs

Conversion in 15 minutes - 10.25%; 30 - 9.34%; 60 - 17.84%; 120 - 19.09%; 240 - 19.78%, which shows average efficiency for both small and longtime intervals.

Table 3.3

Results of experiments with determining the amount of photocatalyst

Phenol concentration (g/l)	Photocatalyst	Time (minutes)	Amount of photocatalyst (mg) Conversion (%)		
0.8	TiO2 (rutile)	30	50 20.57	75 29.42	100 20.74

In this experiment, we took a different amount of photocatalyst, which acts on phenol, with a concentration of 0.8 g / L. The result (table 3.3) showed that the most optimal amount of catalyst (TiO2 (with a rutile structure)) is 75 mg.

Table 3.4

Results of experiments with different photocatalysts, phenol concentration and amount of photocatalyst

Phenol concentration (g/l)	Photocatalyst	Amount of photocatalyst (mg)	Time (minutes) Conversion (%)				
0.8	Pt/TiO_2	10	30 24.56	60 12.99	120 19.35		
0.16	TiO_2/Pt	10	15 5.86	30 6.03	60 8.37	120 29.33	240 28.33
0.16	TiO2/CNTs	10	15 10.25	30 9.34	60 17.84	120 19.09	240 19.78
0.16	BiFe0.8Mn0.2O3	15	15 5.94	30 8.87	60 17.45	120 26.46	240 28.08
0.16	TiO2 (Ni)	100	30 48.14				
4	TiO2 (rutile)	100	30 11.37	60 11.43	120 5.89		
0.8	TiO2 (rutile)	5	5 35.19	10 23.17	20 24.32	30 25.96	
0.16	TiO2 (rutile)	100	30 63.33	60 70.62	120 75.9		

Table 3.4 shows the results of experiments, in which we changed the concentration of phenol, the photocatalyst and its quality, as well as the residence time of the phenol solution under the lamp. The best photocatalyst proved to be TiO2 (with a rutile structure) in an amount of 100 mg. Nickel supported on titanium dioxide can compete with it in efficiency. We also determined that the optimal concentration of phenol for experiments is 0.16 g/l. The concentration of 4 g/l is too high, the concentration of 0.8 g/l is also high with respect to photocatalysis, and the reaction proceeds with low efficiency.

3.3. Conclusions to Chapter

A series of experiments was conducted to choose the best catalyst and treatment conditions. The experiments involved such independent variables as the concentration of phenol, the photocatalyst and its quality, as well as the residence time of the phenol solution under the lamp. The output of the experiment was the change of phenol concentration, measured by High-performance liquid chromatography.

The obtained experimental results demonstrated that TiO2 with the rutile structure, which was obtained in a furnace by firing at high temperatures, works best as a catalyst.

In the future, our studies can be used as a reference point for the study of phenol photocatalysis and the analysis of some photocatalysts. The results should be also accounted in planning and implementation of environmental monitoring for aromatic substances presence in natural waters.

CHAPTER 4
RECOMMENDATIONS FOR THE CONTROL OF AROMATIC SUBSTANCES IN WATER FOR UKRAINE

4.1. Foreign experience in tracking organic pollutants in water.

Persistent organic pollutants are a fairly serious global problem. Monitoring of these substances in water is currently under development and is part of the UN Environment Chemicals and Health Branch program. This program is based on the assessment of monitoring potential, analysis of its quality in different countries of the world, as well as its development.

Global monitoring plan implementation includes several points:

- analysis and sampling of persistent organic contaminants

-national capacity building for the analysis and sampling of POPs and secure conditions for POPs sustainable monitoring, guidelines for POPs analysis and sampling, training in national laboratories, workshops and expert consultation meetings to plan for the POPs monitoring in the future;

- updating and establishment of the POPs Laboratory Databank, which identifies operational laboratories worldwide and provides information on their capabilities to analyze classes of POPs in different matrices;
- awareness and outreaching raising;
- UNEP Databank of Laboratories analyzing POPs and Mercury;
- POPs Interlaboratory Assessments, which have become an internationally accepted global standard and the network of POPs monitoring specialists and POPs laboratories should be considered to serve as a key component in creating the conditions for sustainable monitoring of POPs in the participating countries and globally in the future. [29]

4.2. Bioindication methods of phenols content monitoring in water

Bioindication methods are used to assess the quality of the environment and its individual components by the state of organisms affected by pollution. Bioindication methods are usually quite simple; they do not require special equipment and high costs.

The effect of phenols on aquatic ecosystems has been studied in sufficient detail. In water bodies, under the influence of various physicochemical processes and the life of aquatic organisms, the destruction and transformation of phenols are carried out, and the resulting metabolites (for example, pyrocatechol) may be more toxic than the original compound. [37] The lethal concentrations, which in 15 minutes after the action stop the movement of protoplasm in charoh algae, are $2 * 10^{-3}$ mg/l for pyrocatechol, $2.5 * 10^{-3}$ mg/l for hydroquinone, $5 * 10^{-3}$ mg/l for resorcinol. [45] l. An indicator of the toxic effect of phenols is a change in the intensity of gas exchange of aquatic organisms. In this case, the respiration rate of organisms and the change in the concentration of dissolved oxygen can also be estimated. So, at a concentration of phenol in water of 1-2 mg/l, suppression of the vital activity of yeast is noted and after 10-30 minutes a decrease in the concentration of dissolved oxygen is observed. [10] Under the influence of phenol, 60% of the salmon Micropterus salmoides showed an increase in respiration rate in 2-4 hours. [11] The indicators of the toxic effect of compounds of this group on Daphnia magna are respiratory rate, heart rate and activity of the thoracic legs.

The number of phenol-destroying bacteria, colorless flagellates, ciliates, fungi, and algae is used as indicators of phenol pollution. Phenol destructors include bacteria of the genus Pseudomonas and Azotobacter. Small doses (1 mg/l) have no significant effect on the processes of water nitrification. Intensive development of denitrifiers is observed in reservoirs with phenol content up to 500 mg/l. At high concentrations of phenol, the nitrification process is inhibited. [44]

In water bodies with intensive decomposition of phenols, the maximum amount of sulfate-reducing bacteria was also found. [1]

In the presence of the ciliate Paramecium caudatum, the destruction of phenol slows down due to the ingestion of bacteria by the ciliates. [76] It is noted that the thermophilic bacillus Bacillus stearothemophilus can use phenol as a source of energy and carbon. [84] The maximum content of phenols at which bacteria development is possible is 0.3%.

The destruction of phenols in water bodies causes a change in the bacterial periphyton. At a phenol concentration of 500 mg / l, the intensity of bacterial overgrowth is high, but the species composition is uniform; with a decrease in the concentration of the pollutant, the species abundance of microflora increases, and the number decreases. It was noticed that phenol in small amounts provokes photosynthesis of the unicellular greenish alga *Chlorella sp.* Simultaneously with an increase in the release of oxygen by chlorella cells, a decrease in the content of phenol in the aquatic environment is observed. [7]

The effect of phenol on the grouping of algae is also manifested in a change in the composition of the biocenosis and a change in dominants. Yes, green algae (*Protococcales*) are the most resistant to phenol. Some inhibition of growth was noted at a phenol content of 30-60 mg/l, while a complete inhibition of the growth of representatives of golden algae occurs at a concentration of 8-15 mg/l. Complete suppression of photosynthesis of Protococcales sp. observed in the range of pollutant concentrations from 700 to 1400 mg/l [85]

Phenols are actively absorbed by aquatic plants: water hyacinth *Eichhornia*, reeds *Phragmites australis*, reeds r. Scirpus. So, for example, in 8 days the reed removes up to 10 mg/l of phenol from the water. [14] In plants, some of the phenols undergo detoxification, and some that are not included in the metabolism are released through the stomata into the atmosphere.

Living organisms differ in sensitivity to phenols. Highly sensitive species include, for example, the cancer of the amphipod *Acanthogammarus victoria*, in which an increase in oxygen consumption begins at 1 mg/l of phenol. Medium-sensitive species include *Eulimnogammarus verricosus* and *Gammarus lacustris*. In the minnow *Phoxinus phoxinus*, which is not sensitive to phenols, a significant increase in oxygen consumption was found only in solutions with a concentration of more than 2 mg/l. [6]

High content of phenols in water is manifested in aquatic insects and arachnids by a complex of general symptoms, such as: increased general motor activity; impaired coordination of movements; convulsions; paralysis of organs and parts of the body that perform a locomotor function; complete loss of motor activity; death. [25]

Fish have been successfully used to indicate phenolic contamination. Acute phenol intoxication is accompanied primarily by damage to their gills, skin, kidneys and heart. At a phenol concentration in water of 20 mg/l, perches die in 4 hours, roach and carps in 1-5 days. A concentration of 10 mg/l for 1-3 days is toxic to young carp, roach, perch, and trout. The maximum tolerated concentration of phenol for fish is 17 mg/l. In experiments on eggs and larvae of bream and bruise, it was found that phenol disrupts the normal course of embryogenesis, leading to the appearance of various types of injuries - body curvature, disturbances in the structure of the cardiovascular system and other. [86]

Chronic exposure to phenolic compounds leads to pathological changes in the gills of bony fish. They include both changes in the structure of the integumentary epithelium (inflammatory reactions with swelling of the epithelium, detachment of the epithelium from the underlying connective tissue, dystrophic changes and necrosis of the epithelial tissue of the branchial lobes and secondary plates), and local circulatory disorders - hyperemia, hemorrhage. [38]

Phenols give fish its characteristic taste and smell. For example, the content of 0.1 mg/l of phenol in the body of sterlet on the sixth day leads to a change in its organoleptic qualities. The general symptoms of phenol poisoning in fish are manifested in a sharp motor excitability with a short-term collapse on the side, loss of balance, convulsive convulsions, resulting in a complete loss of motor activity, respiratory distress and death. [87]

In Netherlands present online monitoring of water intake, using water fleas, trout, mussels in a continous sytem, electronically sounding the alarm when the animals start behaving aberrant. In case of negative changes, the water intake is stopted and testing for potential toxic substances is initiated.

There are many methods for tracing phenol in water. All methods have their own advantages and disadvantages. High resolution monitoring equipment and the removal of phenols in water is not cheap. You also need to consider the cost of repairing the equipment and maintaining it in working order. Therefore, we recommend bioindication as a method of continuous control over the level of wastewater quality control. The most appropriate bioindication systems for the control of phenols in water are fish species, as they show the highest level of sensitivity and clearly detectable symptoms of poisoning.

Bioindication methods also have a number of disadvantages, since it is necessary to constantly monitor the state of living organisms, as well as the conditions of their habitat. The clarity of all conditions must be strictly observed, since a change in just one parameter can affect further results.

To increase the efficiency of the process of controlling phenol in water after phenol is discharged with effluents, it is necessary to include them into the regular water monitoring system.

4.3. Recommendations for the organic water pollutants control in Ukraine.

In Ukraine, water monitoring is an integral part of state monitoring. One can check the quality of the water online through the websites "OpenEnvironment" (http://openenvironment.org.ua/water/) and "Clean Water" (https://texty.org.ua/water/).

But the water monitoring system is not 100% effective since it includes limited indicators monitored: turbidity; color; nitrates; chemical absorption of oxygen; biochemical oxygen uptake; nitrites; dissolved oxygen; ammonium nitrogen (NH4-N); potassium; pH value; water temperature; conductivity; suspended solids. As we can see, there is no such indicator as "pollution with organic substances" in the monitoring program currently running. This means that for Ukraine the international experience of monitoring this indicator, taken from foreign countries, will be very useful. The experience of the Netherlands and their biomonitoring of water quality can be used to improve the quality of monitoring.

The control of POP in Ukrainian water is generally scarce and includes only research results obtained in different parts of Ukraine. There are no regulations about the control of these substances and the situation causes concerns about the possible negative human and biota health effects [3]. Thus, there is a need to amend the programs of state monitoring and include at least some POPs into compulsory program. The choice of the specific POPs must be based on the presence of substance specific sources of pollution. In particular, phenols should be controlled at the water bodies located in the proximity of chemical, woodworking, pharmaceutical, leather processing industries, as well as landfills. And the major focus should be made on rivers, since lakes are able to self-purification from phenols by natural photochemical reactions running over their wide standing open water surface.

4.4. Conclusions to Chapter

After analyzing the literature and foreign experience, we can say that the water monitoring system in Ukraine is currently imperfect and needs to be improved. There is clear need to incorporate monitoring of POPs into the state monitoring programs and define target pollutants to be controlled depending on the dominant source of POPs in water with the highest attention to be paid to flowing waters, as they are primary sources of water supply, but do not allow for natural photochemical degradation of POPs.

CHAPTER 5
LABOR PRECAUTION

Each enterprise is obliged to develop instructions and precautions for labor protection, in accordance with the requirements and in accordance with the Regulation on the development of guidelines for safety, approved by the Committee for Supervision of Compliance with Safety Rules of the Ministry of Labor and Social Policy of Ukraine dated January 29, 1998 No. No. 9 (NPAOP 0.00-4.15-98). Thus, the subject of this chapter is a specialist - a scientist (an environmentalist) who works in a laboratory in the field of studying photocatalysis of solutions of organic substances in water. The work of such a specialist combines a unique set of working conditions, since his workplace is in the laboratory of organic chemistry.

5.1. Analysis of hazard and dangerous factors at the working place

The required level of safety and harmlessness of labor in the field of science and production is designed to ensure the system of labor protection.

Hazardous production factors - production factors, the impact of which on the worker in certain conditions leads to injury, burns or other sudden sharp deterioration in health.

Harmful production factors - production factors, the impact of which on a worker in certain conditions leads to illness or decreased performance. [36]

In accordance with GOST 12.0.003-74, hazardous and harmful production factors are divided by the nature of the action into the following groups:

- physical; chemical; biological; psychological.

Physical hazardous and harmful production factors in a chemical laboratory include the increased or decreased temperature of the surfaces of equipment, materials, the source of which can be heating devices, as well as the possibility of electric shock to personnel.

The saturation of modern laboratories with electrical equipment is extremely high. First of all, it should be noted that various electric heating devices used as the main heat sources, including electric stoves, drying cabinets and thermostats, electric furnaces, devices for evaporation, distillation and drying with electric heating, etc. electricity is also consumed by various light sources, numerous instruments for optical, spectral, X-ray structural, chromatographic and other types of analysis, instruments and machines for mechanical testing.

The most common heating devices are electric hot plates. From the point of view of fire safety, according to the type of heating element, it is customary to subdivide them into tiles with an open spiral and with a closed heating element.

The increased danger of tiles with an open spiral is a consequence of the high temperature to which the spiral is heated. Most combustible materials will immediately ignite on contact with a hot coil. A significant number of fires, caused by careless handling of such tiles, have led to the ban on their use in laboratories.

Electric water, sand and steam baths, which are used to heat flasks and test tubes to 100 ° C, are safe heaters. The absence of highly heated surfaces excludes the possibility of ignition of hot oil or vapors. However, it is undesirable to heat glass flasks with the help of sand baths, due to the fact that grains of sand scratch the glass surface, significantly reducing the strength.

Dangerous factors for a fire are flames and sparks, high ambient temperatures, toxic products of combustion and thermal decomposition, smoke, etc.

Secondary manifestations of hazardous fire factors include: fragments, parts of destroyed vehicles, structures; toxic substances and materials released from destroyed devices and installations; electric current arising as a result of high voltage carrying out to conductive parts of structures and devices.

Organizational and technical measures should include:

- organization of fire protection; certification of substances, materials, technological processes, buildings, structures in terms of ensuring fire safety; organization, training of workers in the rules of fire safety at work; development and implementation of fire safety norms and rules, instructions on the procedure for handling fire hazardous substances and materials; the procedure for storing substances and materials, extinguishing of which is unacceptable by the same means, depending on their physicochemical and fire hazardous substances; development of measures for the actions of the administration, workers, employees and the population in the event of a fire and the organization of the evacuation of people; the applied firefighting equipment must ensure effective fire extinguishing, be safe for nature and people.

Protection against electric shock. The main measures to prevent electric shock in laboratories are protection against touching live electrical equipment and the use of protective grounding. Other protection measures - protective shutdown, the use of low voltages - are of limited use.

Chemical hazardous and harmful production factors are subdivided:

By the nature of the impact on the human body on: toxic; annoying; sensitizing; carcinogenic; mutagenic; affecting reproductive function;

Along the path of penetration into the human body through: respiratory system; the gastrointestinal tract; skin and mucous membranes.

When working in a chemical laboratory, one should proceed from the fact that all chemicals are poisonous to one degree or another. According to the degree of exposure to the body, harmful substances are divided into four hazard classes: extremely dangerous; highly dangerous; moderately dangerous; low hazard.

A prerequisite for safe work with chemicals is not only knowledge of the hazard class of all reagents and solvents, but also knowledge of the characteristics of their toxic effect, the main measures for the prevention of poisoning, symptoms of poisoning and methods of first aid.

When working with chemicals, the possibility of their penetration into the human body through the lungs, skin and through the mouth should be prevented.

General precautions. Any work with gaseous, volatile or dusty liquids and solids may only be carried out in a fume hood with ventilation on. Drying cabinets should also be placed under the draft, in which substances are dried from organic solvents. All laboratory employees, even those who do not work directly with chemicals, must have personal protective equipment in their personal use - goggles or a mask to protect the eyes and face, respirators for working with dusty substances, a gas mask pre-fitted and tested for tightness, rubber gloves, and overalls - a robe, and in some cases a hat and a rubberized apron. Do not store bathrobes and personal clothing together. If any substances come into contact with the skin, they must be removed immediately. It is strictly forbidden to suck liquids into the pipette by mouth. Laboratory supplies of reagents should be stored in specially equipped, well-ventilated dry rooms in strict order. Joint storage of reagents capable of reacting with each other with the release of heat or flammable gases is not permitted. Do not store bathrobes and personal clothing together. If any substances come into contact with the skin, they must be removed immediately. It is strictly forbidden to suck liquids into the pipette by mouth. Laboratory supplies of reagents should be stored in specially equipped, well-ventilated dry rooms in strict order. Joint storage of reagents capable of reacting with each other with the release of heat or flammable gases is not permitted.

In emergency situations, when the atmosphere of the laboratory suddenly becomes contaminated with poisonous vapors and gases, you can only stay in the room to eliminate the consequences of the accident in a gas mask. Personal gas masks of each employee should always be in a visible place in the workroom and be ready for immediate use.

Working with glassware and appliances. From the point of view of safety measures, glass has a number of serious drawbacks, the main of which are fragility and low resistance to sudden changes in temperature.

Most of the accidents in violation of the rules for working with glass belong to the category of microtraumas (after which you can continue to work) and minor injuries (loss of ability to work for one or several days). First of all, these are cuts of hands due to breakage of glassware, instrument parts, etc., as well as burns of hands due to careless handling of glass parts heated to high temperatures. Particularly dangerous are cuts by fragments of dishes contaminated with chemical compounds, since in such cases toxic substances can enter directly into the blood.

In addition to injuries in the event of breakage of glass equipment and dishes, other types of accidents and accidents are possible - fires and explosions (with the spill of combustible liquids, oxidants, etc.), poisoning and chemical burns (when toxic and caustic substances enter the atmosphere or on the skin).

Psychological dangerous and harmful production factors by the nature of the action are divided into the following: physical overloads (dynamic and static); neuropsychic overload (overstrain of analyzers, monotony of work, emotionality of overload).

When working in a chemical laboratory, there is always the possibility of a hazardous situation. Any research work that does not cause complications can cause an accident.

You should not work in a chemical laboratory if you feel unwell, in a sick state, or if you are very tired. Any work must be done carefully, without haste.

Hazardous operations include any work with toxic, caustic, flammable and explosive substances, with moving equipment, using high temperatures, strong cooling, electric current, as well as all non-standard operations. Therefore, a shorter working day is established for workers in the chemical laboratory, and milk or other equivalent food products are provided free of charge according to established norms. [46]

5.2. Development of labor precaution measures

Requirements for lighting of industrial premises

Lighting as light from any source, which creates illumination of the surfaces of objects and provides visual perception of these objects, is: natural; artificial; combined.

1. Natural lighting - lighting of premises with light emanating from the sky (direct or reflected), penetrating through light openings in external enclosing structures. It is subdivided into side, top and combined. The normalized characteristic is the coefficient of natural illumination. Side-by-side natural light - the natural light of the room through skylights in the outer walls. Upper natural lighting - natural lighting of the room through lanterns, light openings in the walls (in places where the heights of the building differ). Combined Daylight - A combination of top and side natural lighting.

2. Artificial lighting - lighting of rooms and other places where there is not enough natural light. It is subdivided into a) working, b) emergency, c) security, d) duty, e)

general, f) local and g) combined. If necessary, part of the luminaires for working or emergency lighting is used for emergency lighting.

3. Combined lighting - lighting in which insufficient natural lighting is complemented by artificial lighting.

Sources of artificial lighting are gas-discharge lamps and incandescent lamps. Discharge lamps are preferred for artificial lighting applications. The spectral composition of the luminous flux from gas-discharge lamps is close to natural illumination and therefore is more favorable for vision.

Industrial lighting systems use fluorescent gas-discharge lamps in the form of a cylindrical glass tube. The inner surface of the tube is covered with a thin layer of phosphor, which converts the ultraviolet radiation of an electric gas discharge into visible light. Fluorescent gas-discharge lamps, depending on the phosphor used in them, create a different spectral composition of light. There are several types of lamps: daylight, daylight with improved color rendering, cold white, warm white and white light.

The quality indicators of lighting in industrial premises are largely determined by the correct choice of lamps, which are a combination of a light source and lighting fixtures. The main purpose of the luminaires is to redistribute the luminous flux of light sources in the directions required for illumination, to mechanically attach light sources and supply electricity to them, as well as to protect lamps, optical and electrical elements from environmental influences.

Requirements for ventilation of industrial premises

The basic sanitary and hygienic requirements for ventilation of industrial premises are determined by hygiene standards, as well as building codes and regulations. For the efficient operation of ventilation, it is important that a number of sanitary and hygienic and technical requirements be met even at the design stage.

The amount of air required for ventilation of industrial premises and ensuring the required parameters of the air environment in the working area is set by calculation. The calculation is based on excess heat, moisture, or the amount of harmful substances (dust, gases, vapors) emitted. With the simultaneous release of heat, moisture and harmful substances in the room, the required air exchange should be established according to the prevailing hazard.

The ventilation system should not be a source of noise and environmental pollution. During operation, ventilation systems must be serviced, cleaned of contamination, repaired in accordance with the established schedule by trained personnel.

5.3. Verification calculation of natural lighting of the production room (laboratory).

According to the international lighting standard DSTU GOST ISO 8995: 2003 Principles of visual ergonomics. Lighting of working systems indoors, laboratory lighting must be 500 Lux. On the territory of Ukraine, there are lighting standards DBN V.2.5-28-2006. , according to this standard, lighting should be 300 Lux.

In order to calculate artificial lighting, we need to multiply the number of square meters of our room by the value of illumination specified in the standard and divide the result by the luminous flux of one LED bulb in lumens.

We need to calculate the lighting of the laboratory (L). The size of the laboratory (S) is 119 m2. The luminous flux of one LED bulb that is installed in the laboratory (i) is 2850 lumens (Lm). The standard for Ukraine (N1) is 300 lx. The standard according to the international standard (N2) is equal to 500 lx. From what our calculations look as follows.

Formula 5.1 - calculation for Ukrainian standards:

$$L = \frac{S \cdot N_1}{i} \tag{5.1.}$$

Formula 5.2 - calculation for international standards:

$$L = \frac{S \cdot N_2}{i} \tag{5.2.}$$

Based on calculations, for Ukrainian standards (formula 5.1.), The number of lamps of such power in the room should be 13. According to European standards (formula 5.2.), The number of lamps should be 21. It means that we can say that the laboratory meets both Ukrainian and European standards, because the number of lamps in the laboratory is 36.

5.4. Fire safety

The working surfaces of tables, shelves, fume hoods designed to work with fire-explosive liquids and substances, as well as with the use of open fire, must be covered with non-combustible materials.

To work with acids, alkalis and other chemically active substances, cabinets and tables must be made of materials resistant to their impact, with the device of the sides made of non-combustible material.

The laboratory room should be equipped with general ventilation and local suction from fume hoods.

Fume hoods in which work is carried out, accompanied by the release of combustible vapors and gases, must be equipped with upper suction.

All work in the laboratory related to the possibility of the release of toxic or fire-explosive vapors and gases should be performed only in fume hoods, which must be maintained in good condition.

Do not use fume hoods with broken glass or faulty local extractors.

It is not allowed to clutter up the fume cupboards with dishes, instruments and laboratory equipment not related to the work being carried out.

Flammable and combustible liquids should be stored in a special non-combustible cabinet labeled "Flammable", and labels with the name of the substance contained in them should be glued on vessels and flasks.

In the workplace, flammable liquids may only be present in quantities necessary for the job.

Glassware with flammable liquids, acids, alkalis and other caustic substances may only be carried in special metal or wooden boxes lined with asbestos inside. For sulfuric and nitric acids, the use of wooden boxes, baskets and shavings is allowed provided they are treated with a fire retardant.

Alkali metals should be stored in dry, carefully sealed containers.

When using electric stoves, electric heaters with baths, as well as other electrical equipment, do not use them immediately after being exposed to chemicals or water.

It is not allowed to use open tiles in fume hoods, as well as keep combustible materials near switched on electric heaters.

It is forbidden to leave the workplace and leave lighted burners and other heating devices unattended.

It is strictly forbidden to heat vessels containing low-boiling flammable liquids over an open fire, as well as on electric heating devices.

Heating of flammable low-boiling substances / acetone, benzene, ethers, alcohols, etc. / should be carried out only in round-bottom flasks made of refractory glass, in baths filled with an appropriate heat carrier / water, etc. /.

It is strictly forbidden to discharge flammable liquids, as well as contaminated water containing flammable and combustible liquids into the sewer.

Washing of dishes from under flammable and combustible liquids should be carried out only in a specially designated room for this purpose.

In the laboratory premises it is strictly forbidden to: wash the floor, tables and laboratory equipment with gasoline, kerosene and other flammable liquids; store rags, ends, towels, clothing and other items soaked in flammable liquids; dry anything on steam pipelines and batteries of steam and water heating; Leave spilled flammable liquids uncleaned.

When using spirit lamps, the following rules must be observed: the spirit lamp must be closed with a cap before lighting it; it is necessary to light the spirit lamp only with a match or a splinter; you cannot light the spirit lamp with another burning spirit lamp or paper; it is necessary to extinguish the spirit lamp by putting a cap on the wick.

It is forbidden to blow on the flame.

After finishing work in the laboratory, the person responsible for the fire condition of the premises is obliged to check: whether the burners and other fire devices are extinguished and whether the electric heating devices are turned off; are bottles and jars with reagents and other liquids closed with corks; are lighting and ventilation turned off; whether the work of all devices and apparatus is stopped; whether the remnants of flammable liquids have been removed. [26]

5.5. Conclusions to chapter

Having analyzed all the provisions of labor protection for work in the laboratory, we can say that all safety rules were observed when working in the laboratory. Also, the lighting in the laboratory complies with the standardized DBN V.2.5-28-2006.

CONCLUSIONS

The problem of organic water pollution is alarming in all parts of the world and Ukraine is not the exception. The conducted study presents the analysis of the treatment potential of phtocatalytic processes in relation to phenols as precursors of POPs formation. The results could be formulated as follows:

1) The sources of water pollution with organic compounds are very diverse and include almost all branches of industry. An important issue related to this form of pollution is that it undergoes intensive transformation in natural waters and may output even more toxic compounds. Among the most important precursors of highly toxic POPs are aromatic substances, which were chosen for further research, conducted on the example of phenol.

2) The methods of phenols analysis in waters were considered and the method of high resolution liquid chromatography was chosen for the analysis. The comparative analysis of the methods of waters treatment to remove phenols was conducted, including biodegradation, photooxidation, degradation using potassium zinc, hexacyanoferrate nanocubes, photochemical degradation, and electrochemical degradation. The method of photocatalytic degradation was the basis of the experiment, as it is cost and time efficient and needs minor intrusion into technological processes at the enterprises, where wastewaters polluted with phenol are generated. It also works without complicated equipment.

3) The experimental part of the work was aimed at choosing the most efficient conditions of photocatalysis in terms of duration of the processes and catalyst used. Experiments have shown that titanium dioxide with the rutile structure copes better than others with phenol.

4) The foreign experience and Ukrainian system in tracking organic pollutants in water were studied, and it was shown that the monitoring system in Ukraine is imperfect and needs to be improved by incorporating POPs into the regular monitoring programs.

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