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« STUDY ON SOME HYDRODYNAMIC PROCESSES IN WATER TREATMENT PLANTS »

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STUDY ON SOME HYDRODYNAMIC PROCESSES IN WATER TREATMENT PLANTS

- CONTRIBUTIONS TO THE OPTIMIZATION OF THE COAGULATION-FLOCCULATION AND WATER PURIFICATION PROCESSES -

FOREWORD

The research paper entitled *Study of some hydrodynamic processes in water treatment plants* includes an up-to-date issue on the treatment plants and is of an outstanding importance in the field of water treatment.

At the end of the paper research process, I would like to give special thanks to my scientific coordinator, *Mr.Prof.Univ.PhD.eng. Virgil Breabăn* and *Mr.Prof.Univ.PhD.eng. Gabriel Racoviţeanu* for the support they have given me during the period of study.

Through their high academic professionalism, understanding and shared knowledge, they had a very important contribution in the development of this paper.

Of particular importance in developing this doctoral thesis was the experimental research performed on the pilot plant of the Sanitary Engineering and Water Protection Department of Hydrotechnics Faculty of the Technical University of Civil Engineering from Bucharest. I want to thank the team of researchers, especially *Mr.Prof.Univ.PhD.eng. Gabriel Racoviţeanu* and *Mrs.Conf.Univ.Phd.eng.chim. Elena Vulpaşu* for the material and moral support, shared knowledge and advice they have given me throughout the period of the research.

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KEYWORD

Water, Treatment, Technological Flow, Pilot Plant, Coagulation, Flocculation, Filtration, Disinfection, Quality.

CONTENTS

1 INTRODUCTION - GENERAL ISSUES

Water is the most important nutrient. It can't be replaced. In extremis, one can give up water for other uses but one can't give up drinking water. One can resist long enough without food, but not without water. Man can find water in various types of food, but one can't do without liquid water. Therefore, drinking water has been, is and will always be the most important type of water. Water has a great importance in the human body, it is important for the human needs and it also has a special influence on the health of the human body.

Water is a fundamental and indispensable constituent of the human body. Small changes produce serious disorders and insufficient water intake is much less tolerated than the lack of other elements.

Water for human consumption is any kind of water in its natural state or after treatment, used for drinking, cooking, preparing the food or other domestic purposes, regardless of its origin.

The percentage of water in the body varies by age: from more than 97% for an embryo of 7 days, gradually decreasing to 80% for newborns, 60-65% for adults and 50-55% for the elderly. The percentage of water varies according to the intensity of the metabolic processes.

Bottled water can have different tastes according to the content of calcium, magnesium, sulfate or iron. Drinking water, like all substances, contains a certain quantity of bacteria. Most of these bacteria are common and they are not dangerous to human health. Water also contains minerals and other inorganic materials. [81]

1.1 Possible water problems

Water can contain various substances or microorganisms that threaten human health. It may contain pathigenic bacteria which can cause illnesses. It may contain protozoan parasites or viruses. The most popular parasites are Giardia and Cryptosporidium. Legionella is a bacterium that develops when water is kept for a long time at temperatures between 30 – 40 °C, which can lead to a disease called Legionella that can be deadly. The Nitrates in water can cause a disease called Cyanosis which reduces the ability of blood to carry oxygen. Lead also is a toxic substance easily assimilated by the body. Many people have second thoughts about the use of water from the public water supply system because they consider it be insufficiently clean and prefer to drink bottled water. Studies have shown that the general trend is to buy the cheapest water which means that people end up drinking a less clean type of water than tap water is. [82]

1.2 The influence of water on the health of the population

1.2.1 Hydric pathologies

A. The infectious hydric pathology

The most important threat of water consumption on people's health is the infectious hydric pathology. The infectious hydric pathology decreased significantly in the first part of the 20th century, but is statistically growing lately, mostly due to the inclusion of some viral and parasitic diseases in the category of diseases transmitted through water. Water-borne diseases continue to make 25 000 victims daily, in the whole world. In Romania, there were officially registered a total of 75 episodes of hydric outbreaks between 1985 and 1995, with a total of 10 238 people affected. The peak was reached in 1993. It is estimated, however, that these data are undervalued compared to the real situation, because of faulty reports. The main way of transmission is through ingestion (directly or by food contaminated by water), but also through washing and bathing (leptospirosis, schistosomiasis, tularemia) and inhalation (aerosols containing Legionella). The main water-borne diseases are: microbial diseases, viral diseases, parasitic diseases. Statistically, in order to get sick, a man must ingest on average (50 % of the infective dose) billions of Escherichia coli, hundreds of millions of Vibrio cholerae, tens of millions of Salmonella typhi, Shigella tens of thousands, but only a few hundreds of enteroviruses, a few dozens of Amoeba, Giardia or Balantidium, a few ascarids or leptospira and finally, only one Hymenolepis or Taenia (tapeworm). The dose depends on age, health, etc. [81], [84], [85], [86], [87], [94]

B. The noninfectious hydric pathology

1.2.2 The changes of the contents of micro and macro elements

Water is a relatively minor source of iodine (which is mostly taken from food) but this fact is due not only to the insufficient amount of ingested water, but also to the interference of the very high quantities of Ca, F, or Mn with the absorption of iodine.

Fluoride deficiency (characterizing most water sources in Romania) promotes tooth decay. Fluoride can counteract the methemoglobinizant effects of nitrates. Excess fluoride exists in many areas (because of natural or artificial reasons - pollution) and causes fluorosis, while in high doses it causes osteosclerosis and ankylosing osteofluorosis.

Water hardness negatively affects the washing process (including that of the human body), but it positively affects the cardiovascular disease, hard water being considered a protective factor. More recent studies consider that it is not the hardness itself that is beneficial, but calcium (Ca) and magnesium (Mg), whose compounds are major factors to cause water hardness.

Clinical studies indicate a favorable effect of calcium (Ca), magnesium (Mg), chromium (Cr), vanadium (Fr), manganese (Mn) and zinc (Zn), while sodium (Na), copper (Cu) and cobalt (Co) are blamed for their adverse effects. [81], [84], [85], [86], [87], [94]

1.2.3 Water contamination with toxic chemicals

Among all the toxins transmitted through water, some have a natural origin, but most of them come from groundwater pollution.

• **Nitrate** (NO3-) can be a major problem, and its concentration in drinking water is above the permissible limits in many places in our country. Nitrates are highly concentrated in vegetables.

• **Nitrite** (NO2-) results from nitrates either before consumption or in the lumen of the digestive system, when reduction elements in the intestine migrate, in different circumstances, to the stomach and the small intestine. This leads to methemoglobinemia, which usually affects the young and occasionally the adults (such as those with stomach problems). Nitrites are also blamed for and gastric cancer.

• **Arsenic** (As) has been reported in water at concentrations sometimes significantly above the accepted limits. As a metal, arsenic is less toxic. It can cause acute poisoning and skin cancer.

• **Selenium** (Se) is sometimes present in high concentrations in water sources. It is essential to the human being, the necessary quantity being of 0.05 – 0.2 mg per day. Selenium deficiency affects health. In excessive doses it causes skin problems, gastroduodenal diseases, respiratory diseases, etc.

• **Cadmium** (Cd) often exceeds the permissible limits and its accumulation is strong. It mainly affects the kidney. One of the sources of water contamination are the zinc pipes where zinc can be found under the form of impurities. Zinc is also suspected of causing cancer.

• **Mercury** (Hg), the inorganic mercury is absorbed from water in low quantities, but bacteria may methylate it and methylmercury is absorbed in the ratio of 95%. As well as other heavy metals, mercury accumulates in the body and can be indirectly absorbed by fluids by eating fish and other products.

• **Lead** (Pb) is frequently found among pollutants and can cause especially chronic poisoning due to the phenomenon of accumulation. The World Health Organization recommends children or pregnant women to avoid it. It is also suspected of causing cancer.

• **Chromium** (Cr) is an essential element for life in quantities of 0.05-0.2 mg per day for humans. In high concentrations, it is toxic. AS a metal it is nontoxic, but its salts are toxic. Hexavalent chromium is 100 times more toxic than the trivalent one.

• **Copper** (Cu) in very high concentrations in water is toxic. It does not accumulate in the human body. It can come from copper pipes that are damaged by acidic or soft water.

• **Cyanides** (CN-) are salts of hydrocyanic acid. Both the acid and its salts (cyanide, especially of sodium or potassium) are highly toxic to humans and animals. Their effect is acute such as the blocking of breathing at the biochemical level, i.e. the cellular level. The lethal dose for humans is 0.57 - 1 mg/ kg body weight.

• **Aluminium** (Al) in high volume is toxic for the central nervous system. In the human body there are about 300 mg of aluminum. Normally it is poorly soluble but with a highly acidic or alkaline pH the solubility increases notably.

• **Nickel** (Ni) is toxic in larger quantities. Nickel salts can cause allergies and even cancer.

• **Asbestos** is a group of silicate minerals with filamentary structure which are used to produce heat and fire resistant material and asbestos cement sheets and pipes, many of which are used for water. In many countries it is prohibited to use asbestos because asbestos fibers cause cancer.

Organic pollutants in water are various, according to the spectacular widening of the spectrum of substances synthesized by the current industry. There are over

10 million chemicals, over 100,000 of which are sold and so they are widespread. [81], [84], [85], [86], [87], [94]

1.2.4 Water contamination with radioactive elements

Radioactive contamination of water should be taken into account mainly because of the exposure of the inner body which occurs due to the absorption and fixation of radionuclides in the body. Water can contain uranium (U), present in many ore deposits accompanied by Radon (Rn). This noble gas can as well be found in radioactive contaminated water and from where it is emitted gradually, exposing people to the risk of inhaling it from the water used in shower or in vaporizers and humidifiers. Sea water is on average 100 times less radioactive than the river sediments, but some thermal waters are highly radioactive. [81], [84], [85], [86], [87], [94]

1.2.5 Eutrophication

High discharges of compounds containing phosphorus and nitrogen may cause the phenomenon of eutrophication. The excessive multiplication of algae lowers the oxygen concentration, produces toxic substances and brings about the creatures' death, with important indirect consequences (economic, environmental, etc.) on human communities. [81], [84], [85], [86], [87], [94]

1.2.6 The influence of other changes in water quality

Water suspensions (organic and inorganic), even in the absence of a direct negative action on human health, trouble the water usage (drinking, bathing, the use in industry, irrigation and recreation, etc.), accumulate clogs, affect navigation, etc.

Pollution with **floating suspended substances** (crude) and **tensioactive substances**/ surfactants (detergents, foaming substances) occurs because they are placed at the surface of the water and prevent oxygenation, causing the above-mentioned effects. Also, the **colorants** affect photosynthesis and the self-cleaning of the water, along with its aesthetic aspect. High water **hardness** results in multiple deposits in pipes and many other undesirable effects, causing the water to be improper for use without softening.

Highly **acidic** or **alkaline** substances affect water pH with multiple negative consequences. Fish usually die at 4.5 pH. [81], [84], [85], [86], [87], [94]

1.3 Standards and regulations

It is stated that water is the most well known and monitored environmental factor. Each country or region of a country has its own quality standards. Yet the world is tending towards a common set of standards, resulting from all the people's experience and needs. In this regard, the World Health Organization has issued and is periodically reissuing "Guidelines for Drinking Water Quality" and international organizations, such as the European Union, also promote common rules in detail or at least guidelines, such as the Directive 98/83/EC [38] regarding water quality for human consumption.

In Romania, the quality standard for drinking water in the 80s was STAS 1342/1984 [74] and in the last decade it was STAS 1342/1991 [75].

On 29th August 2002, the Law no. 458 [39] / 8 July 2002 on the quality of drinking water became effective and it was published in the Official Gazette of

Romania, Part I, no. 552 of 29th July 2002. Annex I of the law indicates another list of water quality parameters to be met. Some parameters in the new list are identical to those of STAS 1342-1991 [75], while others are different.

The quality of drinking water, according to the Directive 98/83/EC [38] of the European Union transposed in Romania by the Law 458/2002 [39] and amended by Law 311/2004 [72], must be free from microorganisms or substances which, depending on their number or concentration, constitute a potential danger to human health.

In the case of the drinking water supplied through the distribution system, the quality of the water must match the values settled for the quality parameters, at the exit from of the treatment plant and at the consumer's tap. [38]

1.4 Water sampling from different areas

1.4.1 Protection areas

There are three levels that are centered around the source of water: the area with severe regime of sanitary protection, the sanitary protection area with restriction regime, hydrogeological protection perimeter. [88]

1.4.2 Delimitation of protection area for groundwater abstractions

The dimensions of sanitary protection zones according to the above criteria have the following size requirements: minimum 50 meters upstream and 20 meters downstream of the abstraction area for the area with severe regime of sanitaryprotection.
For the deep groundwater for which the cover deposits give a good natural anti-pollution protection, sanitary protection zones can be limited to the areas with severe regime.

The area with severe regime must be fenced to stop uncontrolled access of the population, animals and plants of any kind. [88]

1.4.3 Delimitation of protection area for surface water abstraction

The minimum size of the area with severe regime will be of 100 meters upstream, 25 meters downstream and 25 meters of the outlet side. When the lateral size can’t be kept, constructive compensatory measures are taken. For abstractions from lakes, the area with severe regime will have a minimum radial size of 100 meters on the lake starting from the shore, and at least 25 meters on the shore. The area with severe protection is marked by fences on the shore and by buoys and other similar things while on the water mirror. [88]

1.4.4 The regime for land in the protected areas

• **In the protected area III B**, the following shall be prohibited: the evacuation of rainwater from urban areas or from areas of traffic; placing of nuclear or other units discharging radioactive water; placing industrial units discharging wastewater with a high risk of pollution. [88]

• **In the protected area III A** the following shall be prohibited: all restrictions mentioned for the protective areas type III B; placing livestock units and slaughterhouses; the storage on land and the use of growth stimulants, substances for plant protection and against the pests in agriculture and forestry; placing treatment and wastewater infiltration plants. [88]

• **In the protected area with restriction regime** agricultural activities are allowed while the following are prohibited: the use of natural fertilizers; the use of plant protection substances not degradable in less than 10 days; the irrigation with wastewater, even if it is completely treated; livestock units and the storage of animal waste. In addition, all the activities referred to as restricted in protection areas type III B and III A are prohibited. [88]

• **In the protected area with strict regime** all the activities referred to as restricted for the protection areas type III A and III B and for the restricted area are prohibited, as well as the any kind of construction or arrangements which are not directly related to the exploitation of the source of water and the use of (plants) the pieces of installation; making explosions and excavations of any kind; the storage of materials, except for those necessary for the exploitation of the source of water and of the plant. [88]

1.5 The objectives of the thesis

A.Improving the coagulation-flocculation physico-chemical processes in the surface water treatment process; B.Making theoretical and experimental studies to optimize the hydrodynamic processes of water filtration; C.Optimization of the water treatment processes in Palas Constanta Water Treatment Plant.

1.6 The contents of the thesis

The thesis comprises 141 pages, 57 pictures, a total of 41 tables and a bibliography of 100 titles.

Chapter 1 presents generalities about the water, the problems that water can have and its role in the human body and the influence on the health state of the population.

There are also presented the standards and regulations regarding drinking water quality, including the main objectives to be met in accordance with current legislation on the quality of water and intended for human use (Directive 98/83/EC [38], and the Drinkable Water Law 458/2002 [39], supplemented with Law 311/2004 [72]).

Thus, there are mentioned the key requirements:

• Providing drinking water without risk to human health;

• The need to ensure the optimization of the technological flow to keep to the required parameters.

The conclusions of the national reports regarding the monitoring of water quality in the water supply systems are presented in this thesis.

Water treatment processes, the schemes of water treatment plants and reagent dosing are presented in Chapter 2 of the thesis.

Also, in Chapter 2, a case study is presented (The Palas - Constanta Water Treatment Plant). It describes the current situation of the plant, the objects on the premises of the plant which is going to undergo rehabilitation and the water quality requirements in the plant after rehabilitation.

Chapter 3 contains a general description of laboratory experiments and the pilot plant where they were performed. Other items described in this chapter are: the quality of raw water, the quality of the water treated at the Palas Treatment Plant and the experimental plant of the Sanitary Engineering and

Water Protection Department in the of the Faculty of Hydrotechnics of the Technical University of Civil Engineering.

Chapter 4 of this paper presents an analysis of the experimental results made in the laboratory and the experimental cycles performed in the pilot plant. It describes the coagulation-flocculation tests which were performed with aluminum sulfate, basic poly aluminum (MOPAC, PAX 18), ferric chloride and advanced coagulation tests (low pH of 6.5) with aluminum sulfate and tests with sulfate aluminum and polymers (AN 910).

The experimental laboratory research led to establishing the most effective coagulation-flocculation reagents and the recommended doses, so that their effect on the water to be treated should be at its highest.

Also, in order to determine the optimal solution for water treatment from the Palas Constanta Water Treatment Plant four experimental cycles have been performed to analyse the degree of reduction power of following indicators: turbidity, total organic carbon, organic matter and pH. To this purpose, samples have been analyzed at intervals of 1 hour for settled water, filtered water through rapid sand filter and granular activated carbon filtered water.

At the end of Chapter 4 there are the conclusions and recommendations following the experimental research regarding the technological scheme for water treatment at the Palas Constanta Water Treatment Plant and general parameters for the proposed scheme of treatment.

Chapter 5 describes the items on the premises of Palas - Constanta treatment plant, which is going to be rehabilitated.

In Chapter 6 of this paper, there are presented the author's contributions and original elements, the perspective on ways of further developing this theme and achieving the objectives stated in this thesis.

2 THE CURRENT STATE OF THE TREATMENT PROCESSES

The interest in the process of water quality correction is very popular, with a significant impact on a substantial part of the population of Romania. A serious scientific research is made on water quality correction process because, on the one hand, the quality of surface water sources for drinking water has deteriorated because of the increased load of organic materials, and, on the other hand, the consumers' requirements have increased as it is reflected in the increasingly strict indicators imposed in the current legislation. [76], [77]

Present in relatively large numbers in Romania, water treatment plants must be adapted to the techniques, concepts and rules of the European Union. As a result, the rehabilitation, upgrading and optimization of water quality correction processes are an opportunity for the current scientific and technical research to increase drinking water quality with reasonable production costs. On the social level, the opportunity to increase the quality of drinking water produced, with reasonable production costs, represents a priority in order to ensure a decent living in decent sanitary conditions. [76], [77]

The exploitation of the treatment plant shall be done in such a way that the effluent plant, thus, the water delivered to consumers, should meet the imposed quality standards, which are sometimes very strict. This should be done considering the fact that source water has a very significant variation of its quality indicators (sometimes from hour to hour). [76], [77]

The product of a water treatment plant is a type of water of high quality that meets the requirements of use:

To obtain drinking water the treatment steps are:

Raw water

- Seawater
- surface water from lakes or rivers
- groundwater and spring water

Water treatment to obtain drinking water

- Flocculation
- Precipitation
- Filtration and Adsorption
- The removal of iron, manganese and arsenic
- Softening and stabilization
- Micro filtration and ultra filtration
- Desalination
- Hardening
- Neutralization and pH adjustment
- Oxidation

• Disinfection

2.1 The structure of the schemes of water treatment plants

The water supply system consists of all the buildings and facilities which are necessary to meet the water requirements for all the utilities of the population and industrial centers. [77], [78]

The treatment station (plant) is a component of the water supply system and it can be defined as all the buildings and installations in which the processes that ensure the correction of the water source, to meet the quality requirements of the consumer, take place.[44], [77], [79]

There are many treatment processes which are put in practice, but the general scheme of a water treatment plant (see the picture below) includes:

- Pre-oxidation is an ongoing process that should ensure the best subsequent processes;

- The water rinsing processes consisting of:

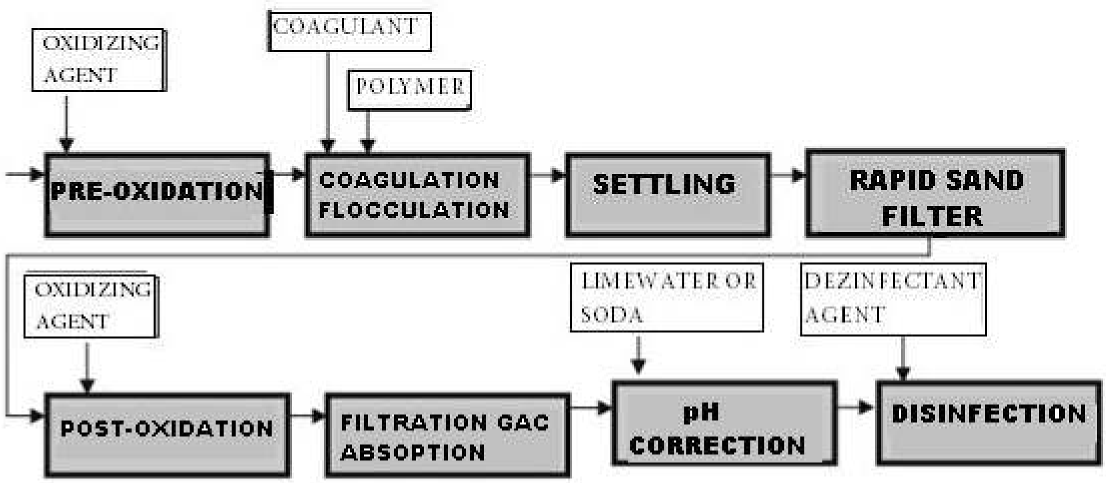
- Coagulation-flocculation is an independent process in this sector; in this process, choosing the compatible coagulant is crucial in order to obtain performance;

- Settling water for the retention of coagulated suspensions; retaining the great majority (90 to 95%) of suspensions in water by relative stationary process after the coagulation – flocculation phase;

- Filtering the water through a sand filter layer to complete the rinsing process;

- Loosening of the water obtained from oxidation with ozone followed by adsorption on granular activated carbon in order to remove certain toxic chemicals;

- The disinfection of water to completely remove all viruses, bacteria and other micro-organisms in water, a compulsory step in Romania, according to the Law on Drinking Water Quality, no. 458/2002. [39], [42], [77], [80]



The general scheme of a water treatment plant [42], [77], [80]

Any water treatment plant has its own maintenance facilities. Among these, there are:

- The chemical reactions station with the purpose of storing, preparing and measuring the the needed reagents for the treatment process (coagulants, flocculants, disinfectant agents, pH adjustment);

- Flushing filters, consisting of pumping stations and blowers;

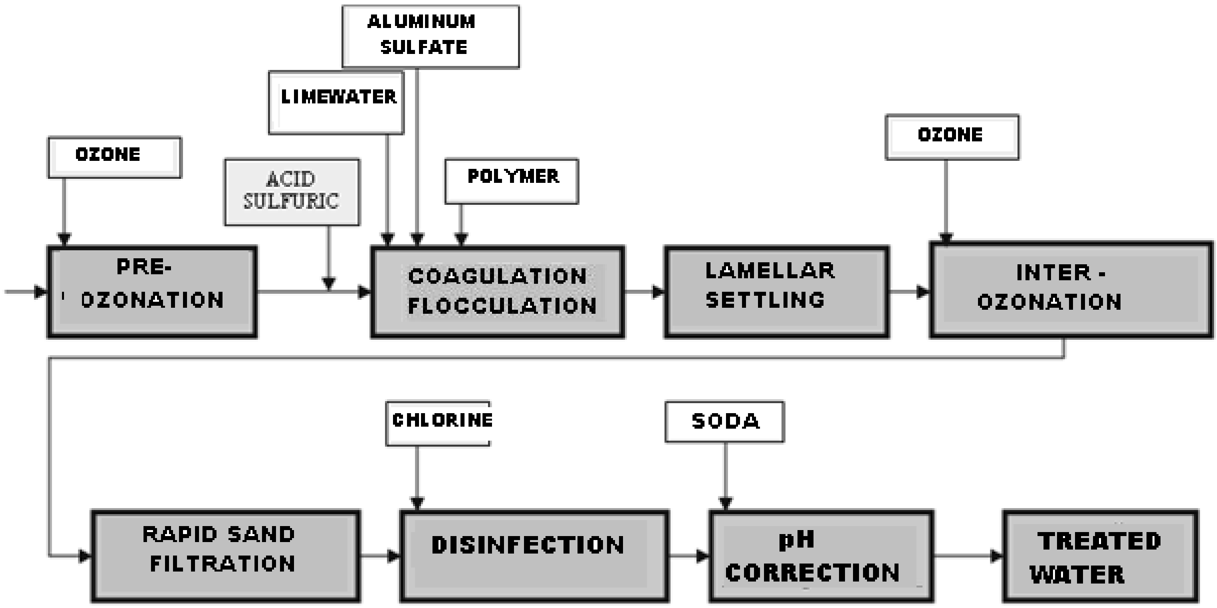
- A laboratory to determine the accuracy of the treatment process and the quality of the produced water;

- Other features include the recovery systems for the water used to clean the filters and the sludge from the settling filter. [42]

2.2 Dosing of reagent

An accurate dosage of reagents meant to establish the minimum quantities of reagent producing maximum rinsing effect in as short a period of time as possible.

The Jar-test method, considered to be the closest to reality, uses a device which performs systematic filling with different doses of coagulant. [77]



The diagram of a water treatment plant which describes how to determine the dosage of the reagent. [42], [77], [80]

Depending on the raw water quality parameters, especially turbidity and temperature, after performing a jar test the following are noted:

- The dose of aluminum sulfate, the reagent used for the coagulation of colloidal particles in the raw water (unsettled very small particles which are in balance in the stream of water and which give the water turbidity);

- The dose of sulfuric acid or whitewash, some reagents used to adjust the pH of the water during coagulation;

- The dose of polymer, which is an auxiliary of aluminum sulfate. [77]

2.3 Issues that must be considered in the exploitation of water treatment plants in winter

In water treatment processes, the temperature has a very important role. Thus, at low water temperatures (less than 4 ÷ 5 ° C) its viscosity increases, leading to a reduced capacity of the reagent to mix with water.

During winter, when the water temperature is low, for the same values of the turbidity of the raw water in spring, summer or autumn, in order to have comparable turbidities after water rinsing processes (settling and filtration) , the dose of reagents are larger (greater amounts of reagents). [77]

2.4 The current situation of the Palas treatment plant- Constanta city

The water treatment plant of Palas currently includes:

- A tank for mixing and distribution, in which the supply lines coming from Galesu are connected; a chlorine solution is introduced in the tank in such a way that through precloration the oysters brought in the plant should be destroyed. The tank along with the construction and the mechanical and plumbing system are in an advanced stage of degradation.
- 4 pulse settling filters, 3 of which are working;
- A plant for the preparation and dosing of reagents;
- A water plant for disinfection with chlorine;
- the plant for open fast filters with quartz sand, containing 20 filters arranged in two rows in four batteries of 5 dual cells;
- The pumping Station No. 4 (SP4) catering for the filters and directing water to the storage tank of 10 000 m3;
- A plant with blowers serving the filters plant;
- The tank of R6 000 m3 and pumping plant SP4;
- Electrical household for each item in the station;
- Transport networks on the premises (linking pipes to assure the water transport between the elements of the plant described above, pipelines for fluids such as chlorine, reagents, compressed air, a sewage system;
- Roadways on the premises of the Palas plant. [90]

2.4.1 The current technologic flow

At the surface water source at Galesu, on the banks of the Năvodari – Poarta Albă Chanel, there is a chlorination plant which performs a precloration of raw water before being pumped into the Palas plant.

From the source of surface water, water is transported to the plant by two pipes measuring 1000 mm each (Dn). The pipes are made of steel and PREMO, the two materials alternating along each pipe. These have the role of downloading their content in the mixing and distribution tank of the plant. These pipes merge into one before downloading their content in the mixing tank.

In the case of the Palas Constanta Water Treatment Plant, the water resulted from the surface water source at Galesu is mixed, after having been treated, with the water from groundwater sources, before being pumped to consumers.

The current technologic flow comprises: the mixing tank, four settling filters, 20 filters, blowers plant, the chlorine disinfection plant, the reagents dosing plant, the pumping plant no. 4 (SP4). [90]

2.5 Requirements on the quality of treated water in the Palas treatment plant-Constanta city

The quality of treated water delivered to the distribution system shall comply with the EU Directive 98/83/EEC [38] on the quality of water for household use (in loc de consumption)and the Romanian legislation on drinking water quality (Law 311/28.06.2004 [72], Law 458 / 2002 [39] and O.U.G. 1/19.01.2011 Ordinance amending and supplementing Law 458/2002 on drinking water quality [91]). Also, as a result of rehabilitation, the plant will be able to cater for the water supply system drinking water in the best quality parameters. [90], [95]

2.5.1 *Microbiological parameters*

Microbiological water quality at the monitoring point must meet the parametric values as defined by the legislation regarding the content of enterococci, coliform bacteria, Escherichia coli (E. coli) and Clostridium perfringens (including spores) according to Law 458/2002. [39], [90], [95]

2.5.2 *Chemical parameters*

Chemical parameters are in accordance with Law 458/2002 [39] and GEO (OUG) 1/19.01.2011 regarding the amendment and completion of Law 458/2002 on drinking water quality. [90], [91], [95]

2.5.3 *Parameter indicators*

Parameter indicators are in accordance with Law 458/2002. [39], [90], [95]

3 EXPERIMENTAL STUDIES

3.1 Objectives of experimental research

The research was conducted under a research contract through the Environment Operational Programme 2007-2013. [67]

The research was conducted by a research team which also included the author of the present PhD thesis.

A. Laboratory experimental research

Laboratory research was conducted in order to establish the necessity of using coagulation-flocculation reagents, the recommended doses and their effect on the treated water.

Thus, several tests of coagulation flocculation have been conducted with the following reagents: aluminum sulfate, alkaline aluminium polychloride: MOPAC, PAX 18 and ferric chloride. Also, advanced coagulation tests (pH reduced to 6.5) have been done with aluminum sulfate and tests with aluminum sulfate and polymers (AN 910). [95], [99], [100]

B. Experimental research on the pilot plant

In order to establish the best solution the treatment of the water that powers the Palas Constanta Water Treatment Plant four experimental cycles have been conducted. [95], [99], [100]

3.2 Water quality

In order to evaluate the quality of the raw water which supplies the Palas Constanta Water Treatment Plant the results of the observations made by the operator during the period 2009 - 2011 have been analyzed and there have been taken raw water samples both from the Danube - Black Sea Channel (from the Galesu area) and the from the entrance to the Palas Constanta Water Treatment Plant on 07.07.2011 and 28.07.2011. [95], [99], [100]

3.2.1 Physical – chemical analysis of the quality of raw water

The results obtained after the monitoring of the raw water quality during 2009 - 2011 by Palas Constanta drinking water testing laboratory are presented in this thesis.

The Analysis of the physico-chemical results highlights the following: water has an alkaline pH of an average value of 8.09 and a maximum value of 8.42; the raw water is relatively clear, its turbidity fits in the range 0.72 - 7.38 NTU; as far as the level of mineralization is concerned, there is a salt content of 236-397 mg / l which corresponds to a conductivity of 420-760 μS / cm; the total value of the hardness is fits the medium range of 10.18 - 15.8 degrees of hardness, most of it representing only temporary hardness caused by calcium bicarbonates; the organic load, assessed only by means of potassium permanganate reaches average values with permanganate consumption values in the range 1.49 - 4.32 mg O_2 / l; the level of nitrogen compounds in drinking water is under the required limit that is maximum 0.49 mg / l NH4 + and 15.8 mg / l NO_3^-.

In order to confirm water quality two sampling campaigns have been done on 07.07.2011 and 28.07.2011. The results are presented in this thesis.

The analysis of the data in the table reveal the following facts: the water is relatively clear with the level of turbidity ranging between 5.22 and 7.36 NTU for water in the duct, i.e. 2.88 - 9.34 NTU for the water entering the Palas Water Treatment Plant; in general, the water at the entrance in the plant is clearer than the water taken from the duct; water pH is alkaline (in domeniul bazic), with values ranging over 8, values that are favorable to the growth of Dreissena Polymorpha; the values of water mineralization is average with a total concentration of salts in the range 267-298; the mineralization is mostly given by the calcium bicarbonates and magnesium; nitrogen compounds reach low values, below the required limits for the surface water category A1; the concentration of heavy metals is reduced and from this point of view the water fits in the category A1 according to NTPA 013/2006 [92]; the concentration of organic pollutants (polycyclic aromatic hydrocarbons, Polychlorobiphenyls, absorbable halogenated organic compounds) is reduced below the limits imposed by the legislation in effect; the concentration of organic substances evaluated through the permanganate index is relatively low with values in the range 2.29 - 3.79 mg O_2 / l, but the values of the total organic carbon concentration were between 3.7 and 11 mg C / l. These concentrations are specific to surface waters with high organic load and indicate that most of the organic substances are poorly degradable. [95], [99], [100]

3.2.2 Biological and bacteriological analyses of the quality of raw water

Given the fact that the existence of the Dreissena polymorpha (Zebra Mussels) species is known from the history of the treatment plant, biological analyses and specific determinations of this species have been performed.

The most important factors that influence the ability of this mollusc to occupy new areas are: pH level, salinity level, temperature, the level of dissolved oxygen, the calcium content. pH significantly affects aquatic life.

Dreissena polymorpha adults survive at pH values between 6 and 9, but the optimum pH is 7.5 - over 8.

Dreissena polymorpha can’t survive if the calcium concentration in water is insufficient, which is essential for the formation of the shell; the optimal values of the calcium concentration is 25 - 35 mg /l.

The results of the biological tests revealed the following: considering Law nr.161/2006 [93], the analyzed raw water samples taken both from the Danube - Black Sea Channel (from Galesu section) and from the entrance in the Palas Constanta Water Treatment Plant fit in the following category of quality: oligo probes - β - mezosaprobe, water of low to moderate contamination, with high levels of dissolved oxygen without polisaprobe forms. Water shows a small number of bacteria and high numbers of insects and insect larvae, and the value of the saprobic index corresponds to the value determined for a “good” ecological status; the values of the concentration of chlorophyll "a" establishes the water quality class I – II, which corresponds to a “very good”- “good” ecological status; the measures on the presence of Dreissena polymorpha indicate a significant numerical abundance of both young and adult species; the results for the samples collected on 07.07.2011 from the entrance in the Palas Constanta Water Treatment Plant indicate the presence of Dreissena polymorpha in the veliger larva stage; on 28.07.2011 the latter was absent.

In terms of microbiological quality, the raw water from both the Galesu intake and the entrance in the Palas Water Treatment Plant fits in the A1 quality category according to NTPA 013/2006. [92], [95], [99], [100]

3.2.3 The quality of treated water in the Palas Constanta water treatment plant

Several analyses have been performed on treated water and the water distributed to consumers.

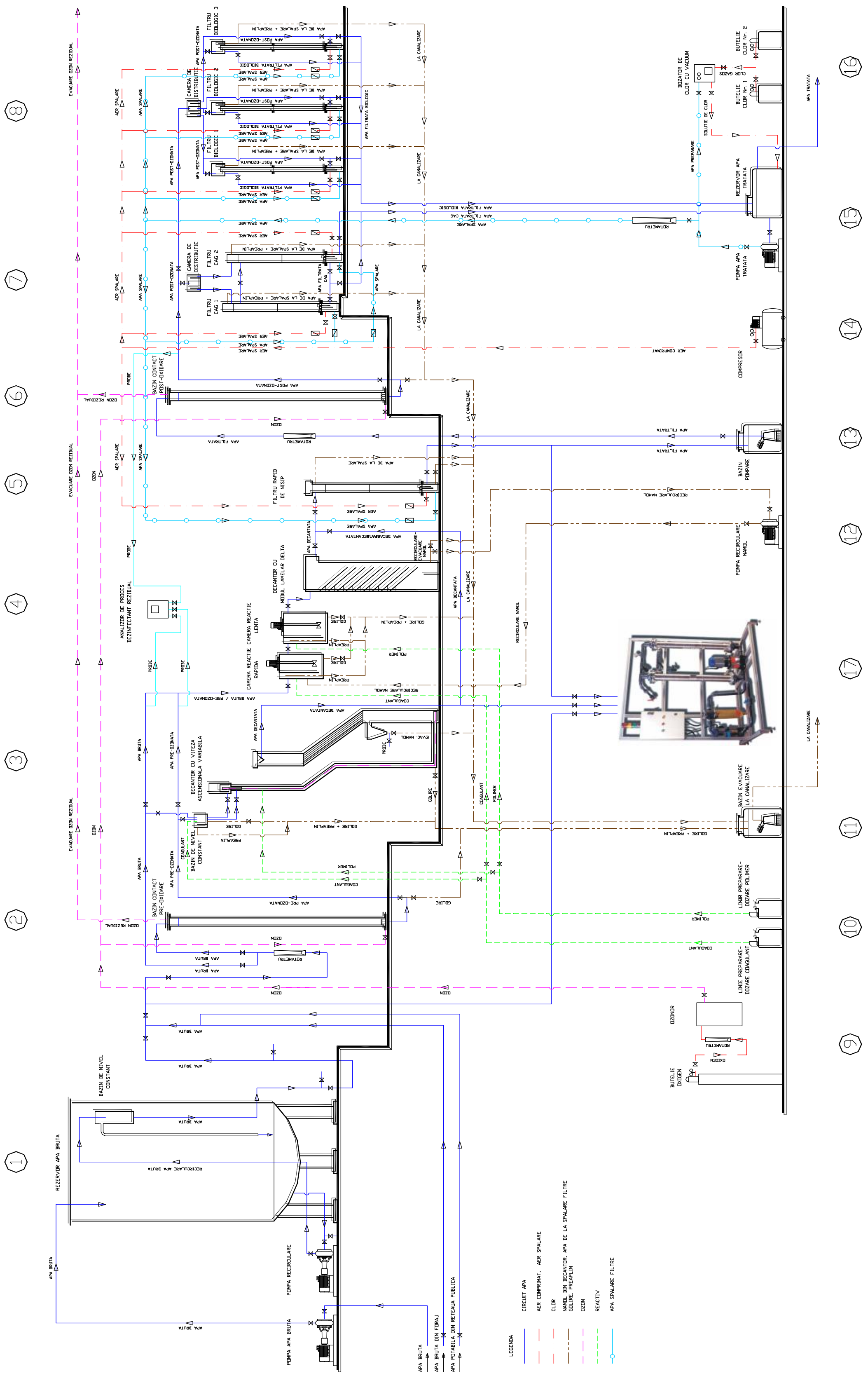
The results are presented in this thesis.

In terms of the analyzed parameters, the water fits the limits imposed by Law 458/2002 [39] as amended and supplemented. [95], [99], [100]

3.3 The pilot plant (The sanitary engineering and water protection department of Faculty of Hydrotechnics U.T.C.B.)

The experimental facility of the Sanitary Engineering and Water Protection Department of the Faculty of Hydrotechnics of the Technical University of Civil Engineering was designed to provide greater flexibility for a nominal flow rate Q = 0.36 - 0.72 m3 /h and it consists of the following technological items: pre-oxidation tank, with a height of 4 m of the column of water that ensures a contact time of 8-15 min.; ozone, chlorine and the sodium hypochlorite may be used as oxidizing agents; the settling stage is provided by two alternative technologies: a settler with variable ascending speed with upflow lamella modules or a settler with fast and slow reaction tank and Lamella module type "Δ"; a fast sand layer filter with a height of H = 1.2 m; post- oxidation contact tank with similar characteristics as the pre- oxidation contact tank; granular activated carbon filters (2 items) with an active layer height of H = 2 x 1.2 m, with the possibility of installation in series or in parallel , which provides a contact of 15-30 min.; a generator of ozone from oxygen; systems for reagent dosing, including metering pumps and reagent storage tanks; vacuum dosing equipment for chlorine, including chlorine containers, the circulation pump , the injector and dispenser itself; booster systems with a tank and a submersible pump; water facilities for filters wash with a water tank of V = 300 dm3 and wash water pump; air compressor for filters cleaning; raw water storage tank and recirculation and supplying pumps; fully automated facilities for ultrafiltration; laboratory and processing equipment. [95], [99], [100]

The following picture shows the technological design and photos of the pilot plant.



Picture - The Pilot Scheme for Water Treatment, Water Supply Laboratory – UTCB

Legend: 1. Raw water storage tank; 2. Pre-oxidation contact tank; 3. Settler with variable ascending speed; 4. Settler with reaction tanks and lamella modules type "Δ"; 5. Rapid sand filter; 6. post-oxidation contact tank; 7. Granular activated carbon filters; 8. Special filters; 9. Ozone generator; 10. Reagents preparation and dosing equipment; 11. Sludge disposal facility; 12. Sludge recirculation pump; 13. Booster systems 14. Compressor; 15. Pump and water tank for filter wash; 16. Facility for the chlorine preparation and dosing; 17. Membrane filtration system. [95]

4 EXPERIMENTAL RESEARCH RESULTS

4.1 Laboratory experimental research

Laboratory experimental research was conducted to determine the necessity of using coagulation-flocculation reagents, the required doses recommended and the final effect that reagents have on the water to be treated. [95]

4.1.1. Coagulation tests with aluminum sulfate

The results of coagulation tests with aluminum sulfate at the natural pH of the water are provided in this thesis.

There can be noticed a reduction in the turbidity to values of 0.44 NTU for an aluminum sulfate dose of 25-30 mg /l.

The concentration of organic substances corresponding to this dose was of 12.62 mg $KMnO_4$ /l (a reduction of 15.7%).

A coagulation test has been performed at pH = 6.7. Its results are presented in this thesis.

There could be noticed a reduction of turbidity at less than 1 NTU for aluminum sulfate doses of from 10 mg /l.

In terms of organic load reduction, the coagulation at low pH led to a better retention.

It was found that lowering the pH prior to coagulation reduces oxidizing organic substances with an efficiency of 41.69% for a dose of 25 mg /l compared to 16.75% for the same dose with coagulation at the natural pH of the water. The efficiency of organic carbon concentration reduction was also higher when lowering the pH before coagulation. [95], [99], [100]

4.1.2. Coagulation test with basic aluminum polychlorides - MOPAC

A coagulation test has been made with MOPAC, which is a basic aluminum polychloride used in water treatment processes. MOPAC coagulation test results are shown in this thesis.

It was noticed the reduction of the turbidity to values of 0.3 NTU for a MOPAC dose of 25 mg /l.

The concentration of organic substances corresponding to this dose was 11.69 mg $KMnO_4$/l $KMnO_4$ compared to 15.16 mg $KMnO_4$/l for raw water, and the total organic carbon concentration was of 3.92 mg C /l compared to 5.77 mg C/l for raw water (a reduction of 32%). [95], [99], [100]

4.1.3 Coagulation test with basic aluminum polychlorides - PAX18

A coagulation test has been made with the PAX 18, which is a basic aluminum polychloride used in water treatment processes. The results of the coagulation test with PAX 18 are presented in this thesis.

When using coagulation reagent PAX 18, turbidity values decreased to 0.26 NTU for a dose of 30 mg /l PAX 18 compared to 7.36 NTU for raw water.

The concentration of organic substances corresponding to this dose was 9.48 mg $KMnO_4$/l compared to 15.16 mg $KMnO_4$/l for raw water (a reduction efficiency of 37%).[95], [99], [100]

4.1.4 Coagulation test with ferric chloride

The results of the coagulation test with ferric chloride are presented in this thesis.

It was noticed a decrease in water turbidity to values below 1 NTU when using ferric chloride but the supernatant remains slightly colored. [95], [99], [100]

4.1.5 Coagulation test with the use of polyelectrolytes

In order to improve the process of coagulation, a jar test has been performed with aluminum sulfate and anionic polyelectrolyte AN 910 PWG.

It was found in terms of turbidity that an addition of 0.05 - 0.1 mg/l AN 910 PWG results in increased efficiency of the coagulation process. In terms of organic load, the addition of polymer isn't necessary more efficient than the coagulation with aluminum sulfate alone.

The analysis of the results of the coagulation - flocculation tests has revealed the following: the most effective reagent in reducing turbidity and for organic charging was MOPAC in doses of 5-15 mg /l (0.3 - 1 mg Al_3^+/l) but also PAX 18 in similar doses; in the picture below there is presented a comparison of the results; the organic load was reduced by 22% for oxidability and by 32% for the total organic carbon when using MOPAC and by 16% for oxidability and 13% for the total organic carbon when using aluminum sulfate. The concentration of total organic carbon in sediment water was of 3.92 mg C/l when using MOPAC. [95], [99], [100]

4.1.6 Oxidation tests

In order to determine the time required to neutralize the activity of the Dreissena Polymorpha species, a test has been conducted and it followed these steps: the quantitative determination of Dreissena Polymorpha larvae for a sample of raw water; the addition of a dose of 2 mg Cl_2 /l of sodium hypochlorite for the raw water sample (0.2 ml for a container of 1 liter or 0.4 ml for a 2 liter container); the quantitative determination of Dreissena Polymorpha larvae after 30 min. and an hour of contact with the dose of sodium hypochlorite.

The test results are presented in this thesis. They showed that a contact of 30 min. for a dose of 2 mg Cl_2 /l is insufficient to inactivate the larvae which can reach the treatment plant. After a contact of 1 hour, the Dreissena Polymorpha larvae were absent. [95], [99], [100]

4.2 Experimental research on the pilot plant

In order to establish an effective solution for the treatment of the water that powers the Palas Water Treatment Plant, four experimental cycles have been performed for the efficiency of reduction of the following indicators: turbidity, total organic carbon, organic matter and pH.

In this respect, analyzes were performed at intervals of 1 hour for the settled water, the water filtered through fast sand layer filter, water filtered with granular activated carbon. [95]

4.2.1 Experimental cycle No. 1

- a pre-oxidation with sodium hypochlorite;
- coagulation - flocculation with aluminum sulfate;
- settling;
- rapid sand filtration;
- post-oxidation with ozone;
- granular activated carbon adsorption.

This thesis shows the operation parameters of the plant for the experimental cycle no. 1 and the quality of the raw water.

The raw water had a turbidity of 7.67 NTU and an organic matter load of 7.06 mg C/l or 3.79 mg O_2 /l - a concentration of organic matter determined by the method with potassium permanganate.

The qualitative analysis of the phytoplankton component revealed the predominance of oligoprobe and betamezoprobe chlorophytes as well as that of oligo - betamezosaprobe diatoms. Quantitatively, the chlorophytes reached the highest percentage in both numerical abundance (85%) and biomass (98%). [95], [99], [100]

Considering the provisions of Order 161/2006 [93], water fits in the quality category of oligo probe, i.e. water with low contamination, with high quantities of dissolved oxygen, without polysaprobe forms, with low quantities of bacteria and large numbers of insects and insect larvae, while the saprobic index value corresponds to the value required for a "very good" ecological status.

The concentration of chlorophyll type "a" of 7.77 µg /l places the water sample in the category of quality No. 1 which corresponds to a "very good" ecological status.

The quantitative determinations for Dreissena polymorpha indicate the presence of this species in the veliger larval stage in the water sample.

From a microbiological point of view, the quality of the raw water is in category A1 according NTPA 013/2006. [92]

The dose of aluminum sulfate was determined through a coagulation-flocculation test. The optimal dose was established to 35-40 mg/l aluminum sulfate.

The reduction of turbidity was not significant after the settling stage (from 7.66 NTU for raw water to 6.89 NTU for settled water). It can be said that the settler did not work due to low turbidity of the raw water. After the filtration stage, the turbidity significantly decreased to values of 0.58 NTU, and after the granular activated carbon adsorption stage to 0.1 NTU.

The concentration of oxidizing organic substances with potassium permanganate reduced from 14.89 mg $KMnO_4$/l for raw water to 11.55 mg $KMnO_4$/l for settled water, respectively 9.2 mg $KMnO_4$/l for water filtered on sand layer (compared to the raw water, the efficiency of reduction was 38%). After boosting stage (post-oxidation with ozone and granular activated carbon adsorption), the concentration of organic substances significantly decreased reaching 1.19 mg $KMnO_4$/l (compared to the raw water, the efficiency of reduction was 92%). [95], [99], [100] The concentration of total organic carbon decreased from 7.96 mg/l for raw water to 7.1 mg/l for settled water and 5.92 mg/l for the water filtered on sand layer (reduction efficiency of 25%). After the boosting stage, the concentration of total organic carbon was of 2.46 mg /l (reduction efficiency of 69.1%).

It was noted that a significant reduction in turbidity occurred after the sand filtration stage, while the reduction of the organic load is done with the greatest efficiency after the stage of post-oxidation with ozone and granular activated carbon adsorption.

Measurements have been done on biodegradable dissolved organic carbon (BDOC) on raw water, rapid sand filtered water and on granular activated carbon filtered water.

It was noted that for the raw water the concentration of BDOC was of 2.67 mg C /l compared to the concentration of organic carbon of 7.96 mg C/l (33.6%); for the rapid sand filtered water the BDOC concentration was of 1.8 mg C/l compared to the total organic carbon concentration of 5.92 mg C/l (30.4%); for the charcoal filtered water the BDOC concentration was of 2.21 mg C/l compared to the total organic carbon concentration of 2.46 mg C/l (89.8%).

It was found that post-oxidation with ozone led to the increase in the level of biodegradability of organic substances. [95], [99], [100]

4.2.2 Experimental cycle no. 2

Given the fact that in the experimental cycle no. 1 it was found that the settling stage does not work, in the experimental cycle no. 2, the treatment strategy consists of the following processing steps:

- a pre-oxidation with sodium hypochlorite;
- coagulation - flocculation with aluminum sulfate and polyelectrolyte AN 910 PWG;
- rapid filtration on sand;
- post-oxidation with ozone;
- granular activated carbon adsorption.

The operating parameters of the plant for the experimental cycle no.2 and the quality of raw water quality are presented in this thesis.

The results presented place the quality of raw water in the category “oligosaprobe water" with low contamination levels.

The concentration of chlorophyll type "a", also places the water quality in the category no.1, which corresponds to a "very good" ecological status, according to the Order nr.161/2006. [93]

The Dreissena polymorpha species exists in the veliger larva stage in the water sample analyzed with a numerical density of 4000 individuals/l and a residual biomass of 3.11 mg /l. [95], [99], [100]

Water turbidity values decreased to 0.16 NTU for rapid filtered water on sand compared to 7.63 NTU for raw water. The picture below illustrates the variation of turbidity along the treatment process.

The organic load of water measured through the consumption of potassium permanganate was reduced to 8.33 mg $KMnO_4$/l after coagulation-flocculation and rapid filtration on sand (reduction efficiency of 50.27%) and to 0.71 $KMnO_4$/l after post-oxidation stage with ozone and granular activated carbon adsorption (compared to the raw water, the reduction efficiency was of 95.76%).

The concentration of total organic carbon decreased from values of 9.57 mg C/l for raw water to values of 4.86 mg C/l for filtered water (the retaining efficiency of 49.22%) and values of 1.68 mg C/l after the stage of post-oxidation with ozone and granular activated carbon adsorption (reduction efficiency of 82.45%).

The reduction of turbidity occurred with high efficiency because of the coagulation-flocculation processes and rapid filtration on sand, while reducing the organic load was done with great efficiency after the stage of post-oxidation with ozone and granular activated carbon adsorption.

Biodegradability tests have revealed the following: the BDOC concentration in raw water was of 2.67 mg C/l compared to the concentration of total organic carbon of 9.57 mg C/l; for the rapid filtered water on sand, the BDOC concentration was of 2.26 mg C/l compared to the concentration of total organic carbon of 4.86 mg C/l; after the stage of post-oxidation with ozone and granular activated carbon, the filtered water had a BDOC concentration of 1.05 mg C/l compared to 1.68 mg C/l, which was the total organic carbon concentration; while for the rapid filtered water on sand the biodegradable organic carbon concentration was of about 46.5% of the total organic carbon concentration, for the water filtered in the post-oxidation with ozone and for the charcoal filtered water, the concentration of biodegradable organic carbon was of 62.5%. Post-oxidation with ozone leads to an increase in the level of biodegradability of organic substances. [95], [99], [100]

4.2.3 Experimental cycle no. 3

Given the high organic load of water, the advanced coagulation process was chosen for in this experimental cycle.

Due to the need to reduce natural organic matter in water treatment systems where drinking water is produced, and considering the dependence of THM formation on total organic carbon concentration, the advanced coagulation process appeared. [95]

Experimental cycle no. 3:

- pre-oxidation with sodium hypochlorite;
- pH reduction to 6;
- coagulation - flocculation with aluminum sulfate;
- rapid filtration on sand;
- post-oxidation with ozone;
- granular activated carbon adsorption.

The thesis presents the operating parameters of the plant in the experimental cycle no. 3 and the quality of water.

Biological determinations placed water quality in the “oligosaprobe” category with reduced water contamination, while the saprobe index value corresponds to the value determined for a “very good” ecological status.

The chlorophyll type "a" concentration of 3.79 mg /l places water into the quality category 1 which corresponds to a "very good" ecological status. There were also identified veliger larvae of the Dreissena polymorpha species.

The injection of sulfuric acid to reduce the pH was performed in the rapid reaction tank, while the injection of aluminum sulfate was performed in the slow reaction tank.

Reducing the pH to 6.5 - 6.7 was achieved with 6% sulfuric acid concentration. The dose required was determined through potentiometric titration and it was of 140 mg /l. The average value of pH was of 6.6 compared to 8.2, the pH of the raw water.

In terms of turbidity, the coagulation-flocculation processes and rapid filtration on sand led to its reduction to the value of 0.06 NTU compared to 2.81 NTU, which was the turbidity of raw water (a reduction efficiency of 97.86%). [95], [99], [100]

The concentration of organic substances evaluated through the potassium permanganate consumption decreased from 11.69 mg $KMnO_4$/l for raw water to 6.36 mg $KMnO_4$/l for filtered water on sand (retaining efficiency of 45.59%), and respectively of 0.36 mg $KMnO_4$/l for filtered water on granular activated carbon (a reduction efficiency of over 95%).

The concentration of total organic carbon is shown in the following picture. It is shown a 56% reduction after the rapid filtration on the sand (from 5.67 mg C/l for raw water to 2.48 mg C/l for filtered water on sand, and respectively of 94.71% after post-oxidation and granular activated carbon adsorption. TOC concentration in the filtered water on granular activated carbon was of 0.3 mg C/l.

It was noticed that the efficiency of organic load reduction was of over 95% for both permanganate consumption and for total organic carbon.

Just like as in the previous cycles, the post-oxidation with ozone leads to an increased level of biodegradability of organic matter. To neutralize sulfuric acid, which is added to reduce the pH before coagulation, the dose of lime water needed for water balancing was determined through potentiometric titration. It was of 110 mg of $Ca(OH)_2$/l. [95], [99], [100]

4.2.4 Experimental cycle no. 4

The experimental cycle no. 4 focused on the influence of the addition of polymer on the efficiency of treatment processes. To this purpose, the technological scheme of the experimental cycle no. 1 was resumed, adding 0.1 mg/l of polyelectrolyte AN 910 PWG. [95]

Experimental cycle no. 4:

- pre-oxidation with sodium hypochlorite;
- coagulation - flocculation with aluminum sulfate and polyelectrolyte AN 910 PWG;
- settling;
- rapid filtration on sand;
- post-oxidation with ozone;
- granular activated carbon adsorption.

The quality of the raw water of this experiment was identical to that of the water in the experimental cycle no. 3. [95]

The operating parameters of the pilot plant are presented in this thesis.

Turbidity reduction was noticed after the settling stage up to values of 0.5 - 0.6 NTU compared to 3.53 NTU from raw water. Unlike the coagulation with aluminum sulfate without polymer leading to a decrease in the turbidity of 10%, the addition of the polymer led to a decrease in turbidity after the of settling stage to values of 82%.

In terms of the organic load assessed by permanganate consumption in the picture below, a reduction of approx. 35% can be noticed after the settling stage (from 11.69 mg $KMnO_4$/l for raw water, to 7.58 mg $KMnO_4$/l for settled water). The Filtering stage does not lead to further reduction of organic load, but after the stage of post-oxidation with ozone and granular activated carbon adsorption, organic load removal efficiency reaches 89.65% (1.21 mg $KMnO_4$/l for the activated charcoal filter effluent). [95], [99], [100]

The concentration of total organic carbon shows a variation similar to the permanganate consumption with reduction efficiency of 37% after the settling stage, and respectively of 91.71% after the stage of post-oxidation with ozone and activated carbon adsorption. The charcoal filter effluent has a total organic carbon concentration of 0.47 mg C /l, while the sand filters effluent of 3.13 mg C/l.

It was found a sudden increase of the retention efficiency of the organic load the stage of after post-oxidation with ozone and granular activated carbon adsorption.

The biodegradability tests have shown a very low concentration of biodegradable dissolved organic carbon in the water filtered through granular activated carbon.

The addition of polymer doses of 0.1 mg/l resulted in an increased efficiency of coagulation-flocculation process both in terms of reducing turbidity and in terms of reducing the organic load. [95], [99], [100]

4.3 Conclusions from the experimental research

In order to establish the optimal technology of the operating parameters as well as the types and doses of reagents for the Palas Constanta Water Treatment Plant, laboratory experimental determinations have been made to find the optimal coagulation-flocculation reagents, as well as four experimental cycles on the pilot plant.

To determine the quality of the raw and the treated water in the Palas Constanta Water Treatment Plant, complex analyzes have been performed in the laboratory of the Technical University of Construction in Bucharest, in the Sanitary Engineering and Water Protection Department.

The analysis of the results of raw and treated water quality has revealed the following: raw water which supplies the Palas Constanta Water Treatment Plant is relatively clear, but it has a relatively high organic load, likely to produce disinfection byproducts (trihalomethanes); from a biological point of view , the analyzed raw water samples, taken both from the Danube - Black Sea (Galesu section) and the entrance in Palas Constanta Water Treatment Plant, belong to the category of quality "oligosaprobe-β-mezosaprobe", i.e. water with low to moderate contamination levels, with high levels of dissolved oxygen and without polisaprobe forms. Water shows a small number of bacteria and high numbers of insects and insect larvae, and the saprobic index value corresponds to the value determined for a "good" ecological status; the concentration values of of chlorophyll type "a" place the water in the quality class I - II which corresponds to a "very good" -

"good" ecological status; the measurements done on Dreissena polymorpha indicate a significant numerical abundance of both young and adult species; the water treated in the Palas Constanta plant shows the turbidity exceeding in some cases the amount required by Law 458/2002 [39] for drinking water produced from surface sources (1 NTU); in terms of organic load, had the concentration of oxidizing organic matter with potassium permanganate in the treated water was of 11-12 mg $KMnO_4$/l and respectively a total organic carbon concentration of 3.5 - 6.2 mg C/l. According to the specialized literature, higher concentrations of total organic carbon in treated water (> 2 mg/l) leads to bacterial growth potential in the water distribution network, i.e. with trihalomethane formation potential when using high doses of chlorine for disinfection. [95], [99], [100]

Worldwide research (Chapra, Canale and Amy, 1997) [16], have shown a strong correlation between the potential formation of trihalomethanes and total organic carbon concentration in the raw water. Thus, it has been established following relation:

$$THMFP = 43.78 TOC^{1.248} \quad [16], [95] \qquad (1)$$

Where:

THMFP (μg /l) - trihalomethanes formation potential;

TOC (mg /l) - the concentration of total organic carbon.

According to this formula, for an average concentration of 8 mg C/l in raw water, trihalomethanes formation potential is of 586.58 μg/l, if the chlorine dose and contact duration are adequate.

The reduction of organic load after sand filtration stage was performed at concentrations of 3 mg/l, which leads to a trihalomethanes formation potential of 172.47 μg/l compared to of 100 μg/l, the maximum allowed by Law 458 / 2002 [39], which shows significant risk of cancer formation.

Therefore, in order to avoid the formation of these compounds and to retain the compound formed at the source in the pre-oxidation stage, the post-oxidation with ozone and the adsorption on active carbon are necessary. Although in the case of the samples in the experiments performed after the sand filtration stage the analyzed THM concentration was under the maximum allowed by applicable law (100 μg/l, according to Law 458/2002 [39]), the potential exists and it represents a human health risk. [95], [99], [100]

The results of the experimental cycles performed on the pilot plant are compared in this thesis.

The results of the experimental cycles results performed on the pilot plant have revealed the following: the need to achieve the pre-oxidation with a contact duration of minimum 1 hour, so as to assure the inactivation of Dreissena Polymorpha species and avoid entering the treatment plant; the need to achieve the coagulation process with as high efficiency as possible, to reduce turbidity on the one hand, and to reduce the organic load on the other hand; due to low turbidity of raw water, the settling stage does not lead to the desired results; using polyelectrolytes leads to an improvement in the coagulation-flocculation process; regarding the efficiency to reduce turbidity, direct filtration cycles led to the best results (cycle II and III); in terms of the organic load, the highest efficiencies have been obtained in the case of advanced coagulation (reduction efficiency of 56% for TOC after sand filtration, and 95% after post-oxidation ozone and GAC adsorption); it can be noticed that for all 4 experimental cycles experimental, efficiencies of over

90% in organic load retention were obtained only after post-oxidation with ozone and GAC adsorption. Total organic carbon concentrations less than 2 mg C/l for a bio-stable water can be obtained by post-oxidation and GAC adsorption. [95], [99], [100]

In this thesis, the advantages and disadvantages of the experienced technological schemes are presented.

All things considered, it is recommended the following technological scheme for water treatment at the Palas Constanta Water Treatment Plant: **pre-oxidation with chlorine** (1.5 - 2 mg /l) at Galesu intake point, providing a contact duration of at least 1 hour to inactivate the larvae of Dreissena Polymorphic before the water gets to the treatment plant; currently the chlorine injection is performed in the raw water pump discharge outlet at Galesu, which loads the headrace; the current technical solution can be kept, considering that the headrace works as a contact basin; the contact duration provided by the headrace is of 1.5 - 2.0 hours, enough for the complete inactivation of larvae or adult molluscs of Dreissena polymorpha; **coagulation-flocculation** in the presence of a coagulant and a polielectrolit. Tests have shown that aluminum sulfate behaves very well as a coagulant, but other reagents can also have results. The addition of polielectrolit as an adjuvant for coagulation will be done only in periods when it is really necessary (low temperature of raw water). In this case, an anionic polymer is recommend. The polielectrolit coagulant doses will be determined through laboratory tests (jar - test) whenever the raw water quality changes. The process will take place in well equipped rapid and slow reaction tanks. It is not recommended to use a settling stage, because raw water is generally very clear and the type of settler existent in the Palas Water Treatment Plant does not meet the quality of source water it can’t form the suspension layer, being practically ineffective. It is recommended the changing of the existing settlers in **rapid and slow reaction tanks**, through proper design and equipping them with mechanical agitators to ensure variable reaction gradients depending on the raw water characteristics. The coagulation-flocculation stage is absolutely necessary because it is necessary to significantly reduce natural organic matter and thus of the risk of THM formation and the risk to human health. Additionally, the water becomes bio-stable by reducing total organic carbon content and lengthens the period in which it keeps its qualities. Without the coagulation-flocculation process, the suspensions present in the water can’t be retained, basically going through the rapid sand filters; direct filtration- rapid sand filters. It is recommended the technological rehabilitation but also that of the facilities for rapid sand filters station within Palas Treatment Plant and its being equipped with modern equipment in terms of automation and process management. It should be noted that if polyelectrolyte be used as an adjuvant for coagulation, it may lead to more frequent clogging of filters and their need for frequent washing. In this respect, it is recommended to use the polyelectrolyte only in special situations, when the coagulant is inefficient (low temperatures, high turbidity, etc.), on limited periods; after the **direct filtration** stage, it is recommended to perform an intermediate filtered water pumping stations to ensure the technologic flow in following items: **post-oxidation with ozone**, this stage has the role to oxidise the orhanic compounds, especially those who are precursors to the formation of is to retain oxiding organic compounds from ozone; nature in general and especially those that are precursors to the formation of trihalomethanes (potentially carcinogenic substances); the post-oxidation with ozone will also achieve a significant improvement in water taste and smell as well as an increase in treated water bio-stability; it is advisable provide ozon contact tanks at a sufficient rate to provide gravity flow to the station of granular activated carbon filters; **adsorption by granular activated carbon filtration**; this stage is ,meant to retain oxidized ozone organic compounds; the stage works properly provided that the water is perfectly clear and if the organics\ substances are prior oxidized with ozone; the GAC filtration stage is dependent on the presence and effectiveness of prior treatment processes. (coagulation-flocculation, rapid/fast filtration on sand and post-oxidation with ozone); the granular activated carbon will be selected to match the retention of organic compounds; the hydraulic flow will be ensured by gravitational flow from post-oxidation with ozone tanks; **disinfection with chlorine** (0.5 mg/l) to ensure the dose of marking in accordance with Law 458/2002 [39] on drinking water quality with subsequent completions and additions. [95], [99], [100]

In this thesis, the recommended general parameters of the proposed scheme are presented.

5 PROPOSALS FOR REHABILITATION OF THE PALAS WATER TREATMENT PLANT-CONSTANTA CITY

These proposals aim at the rehabilitation of the Palas Constanta Water Treatment Plant so that it can provide quality drinking water, at a greater flow than today and allowing future expansion of consumption, according to the level of interest given to the surface water sources in the drinking water supply systems in Constanta.

5.1 Rehabilitation proposals at the Galesu source

At the Galesu Source it is going to be introduced a sodium hypochlorite **disinfection** (instead of chlorine treatment) - with production on the spot.

5.2 Rehabilitation proposals on the premises of the Palas water treatment plant

The operating current technological scheme will undergo the following changes: establishing a new water **distribution tank** at the entrance to the Palas Water Treatment Plant; settling filters will be built in **tanks of rapid and slow reaction**, through their proper hydraulic profiling; the introduction of a new **automated storage and dosing of reagents** to be introduced through the supply pipes before entering the distribution tank; the introduction of **granular activated carbon filters** as a finishing stage, with the main objective of improving the organoleptic qualities of the water; the filter pipe network will be completely rehabilitated and all the components will be replaced with corrosion resistant materials; the **sand filters** will be completely rehabilitated; **blowers** will be placed on concrete and the construction which is currently protecting them from the weather will be replaced with a light soundproof one; the rehabilitation of the **pumping plant Number 4 (SP4)** including soundproofing access ways; the restoration of indoor and outdoor painting and the restoration carpentry; building a **radial settler** for the takeover of the washing water filters, as well as a sludge and rinsed water pumping system; the rehabilitation and supplementation of the **network on the premises**, including the water transport pipelines which are no more made of acceptable materials and new water transport pipes transport to make the connection between the various elements of technology; also be reagents pipes, the air ducts and the air blowing pipes the will be rehabilitated; a drainage system will be properly designed to take new radial settler sludge produced in fast and slow reactions tank, as well as the other sewage flows from administrative buildings; **sodium hypochlorite production plant**, for an increased safety in operating inside the Palas Water Treatment Plant, with injection reservoirs leading to consumers; the disinfection will treat the entire flow of the Palas Water Treatment Plant; the **introduction of a SCADA system** with dispatcher; the rehabilitation **pathways** on the premises. [90]

6 CONCLUSIONS

6.1 Achieving the objectives of the thesis

The objectives proposed in this thesis were: 1.Improving the coagulation-flocculation physico-chemical processes in the surface water treatment process; 2.Making theoretical and experimental studies to optimize the hydrodynamic processes of water filtration; 3.Optimization of the water treatment processes in Palas Constanta Water Treatment Plant.

To achieve the objectives mentioned above, in this thesis there have been presented elements regarding water treatment processes, with special reference to the coagulation-flocculation processes.

There have also been presented schemes of water treatment plants, the situation of Palas - Constanta treatment plant beeing observed as a study case, talking into consideration the items on its premises.

This thesis presents the experimental research undergone in laboratory and on the pilot plant and an analysis of the experimental results obtained (see Chapter 3 and 4).

To achieve the objectives 1 and 2 of this thesis, the performed coagulation-flocculation tests have been presented in this thesis. They have been performed using: Aluminium Sulfate, Basic Aluminium Polychloride (MOPAC, PAX 18), Ferric Chloride and advanced coagulation tests (pH reduced to the value of 6.5) with Aluminum Sulfate and tests with Aluminum Sulfate and polymer (AN 910) (see Chapter 4).

Also, to achieve the first two onjectives of this thesis, the experimental laboratory research presented in the paper have revealed the following: the most effective coagulation-flocculation reagents and the recommended doses for reagents were established in order to obtain the strongest effect of reagents on the treated water (see Chapter 4).

To establish the optimal formula for water treatment at the Palas plant, the four performed experimental cycles have been described. They were indended to reduce the following indicators: turbidity, total organic carbon, organic matter, pH and samples have been analyzed for: settled water, rapid sand filtered water, granular activated carbon filtered water (see Chapter 4), thus achieving the the last two objectives on this thesis.

This thesis presents the findings of the experimental research, recommendations regarding the technological scheme of water treatment and also the rehabilitation proposals, taking into consideration the items on the premises of Palas Constanta Plant (see Chapters 4 and 5). Thus, the third proposed aim of the thesis has been achieved.

6.2 Original features and the author's contribution

The paper includes a number of theoretical and practical elements regarding water treatment processes, especially coagulation-flocculation processes used in water treatment to produce drinking water.

Lately, the coagulation-flocculation process has become independent in the technological flow of water treatment plants and is considered the most important in terms of water treatment efficiency.

The work consists of research conducted in the laboratory and pilot plant. The analysis of a large number of samples and the interpretation of results, in agreement with the most important discoveries in the field, guarantee the originality of this paper.

The paper provides the criteria for effective coagulation-flocculation reagents to reduce turbidity, total organic carbon, organic matter and pH. In this way, the operator has the choice of methodology for the most efficient reagents in order to obtain the desired results on the quality of the treated water in the plant and provided for the population.

The experimental research presented in the paper, conducted both in the laboratory and on the pilot plant, brings news regarding the choice of technological solutions on getting specific water quality indicators whose value must be within the limits set by the current legislation on the quality of water intended for human use.

Also, in addition to above, three scientific papers have been written, one of which is to be published in the Romanian Journal of Civil Engineering and the other in the "Ovidius" University Annals of Constanta - Series Civil Engineering.

6.3 Development perspectives of the topic

The retechnologization of a large number of treatment plants, including the Palas Constanta Treatment Plant requires the following steps: the development of extensive treatability studies that could lead to the choice of optimal treatment solutions; the implementation of pilot plants to all plants that have a water production over 10 000 m^3/day; designing and developing laboratories for analysis under the management of water operators and laboratories adequately equipped so as to constantly analyze the evolving water quality from the source and also the water supplied to consumers.

To ensure the quality of drinking water it is necessary that water operators constantly update the treatment technology by acquiring the latest equipment in the field and also take steps in terms of the training of the operating personnel.

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