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UNCONVENTIONAL, ECOLOGICAL METHODS OF WASTEWATER TREATMENT

- SUMMARY OF PhD THESIS -

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CONTENTS

Introduction

Natural water is a crucial source in route to a sustainable future. In the hydrologic cycle, water is the basis for food production, trade, human needs and the wealth of aquatic ecosystems. Natural source of water is finite, while water demand is steadily growing, thanks to human activity in the last decades.

Currently, one of the major problems of mankind is pollution. It is obvious that the natural environment is deteriorating gradually and that ecological systems can not adapt to anthropogenic factors pressure, and self-regulation of ecosphere is no longer possible.

The theme of this paper is part of current concern to assess and reduce the impact of pollutants on surface water, but also to develop and improve modern, unconventional, friendly, water treatment methods, as conventional treatment technologies are great energy consumers.

A comprehensive study (theoretical and experimental), systematization of information and develop viable solutions to address the wastewater would allow reuse of these waters.

The thesis contains 331 pages and is structured in two parts, as follows:

Part I, summarized in three chapters, display literature study, over 61 pages, 4 tables and 3 figures, describing the current state of knowledge about wastewater treatment options, the presence of various pollutants that affect the quality of surface water and the need to control them.

Part II presents, in its the three chapters and, respectively, 234 pages, the research conducted in order to achieve the objectives of present thesis. The experimental part includes a series of 50 tables and 75 figures.

I want to thank especially to Mrs. Prof. Univ. Dr. Biol. Letiţia Oprean, scientific advisor of this paper, for the given scientific support, as well as opening for all my proposals; I also express gratitude for the confidence, support and understanding given throughout the thesis development.

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I would like to thank Prof. Dr. Dr. habil. FH Frimmel, Head of Department at Engler-Bunte Institute, Water Chemistry Department, University "Fridericiana" in Karlsruhe (TH), for allowing me to participate in this research project.

I would like to express my gratitude and thank my parents with all my heart, for their love and understanding demonstrated throughout the thesis completion.

I thank to my friends for the precious moral support and to all those who were actively involved in all that meant to me during the PhD.

CURRENT STATUS OF KNOWLEDGE

Water – general characterization

Water, a chemical essential for life

There is an avid molecule sought by man in the universe: WATER, since its discovery in the atmosphere of some distant planet would be the embodiment of the craziest dreams of humanity. Water is the single substance whose properties define the biological and physiological characteristics of the Earth.

It is commonly accepted that absolutely pure water does not exist in nature, but its properties have to be known as they are set against the natural water quality, and of water taken from sources for different needs (PÎSLĂRAŞU şi colab., 1981).

Water, having molecular formula H_2O, is the only natural substance that exists in three states of aggregation: gaseous, liquid and solid, in the normal temperature range. At room temperature, water is colourless, odourless and tasteless. At normal atmospheric pressure (1 atm) it boils at 100 º C (212 º F) and freezes at 0 º C (32 ° F). Water is a very stable compound, but may be decomposed by electrolysis, releasing hydrogen and oxygen.

Water sources

For water supply of population centres and industries, one can use the following natural sources, which are distinguished between them by qualitative characteristics, flow regime and the capture and treatment possibilities (TEODOSIU, 2001): surface water sources, consisting of running water: rivers and tributaries, natural and artificial lakes, seas and oceans, groundwater sources.

Discharge of insufficiently treated effluents has led to the alteration of water courses and the emergence of a wide range of contaminants: heavy degradable organic substances, nitrogen compounds, phosphorus, sulphur, trace elements (copper, zinc, lead), pesticides, insecticides organo-chlorinated, detergents, etc. Also, in many cases one may notice exacerbated bacteriological contamination (ROJANSCHI şi OGNEAN, 1989).

A characteristic feature of water from rivers is self-cleaning capacity, due to natural a series of biochemical processes, favoured by the air - water contact.

Self-cleaning or natural treatment is all natural treatment processes by which water quality is restored to the level existing before being polluted and has, at natural scale, the role of contaminated water treatment plants, downstream of discharge point. Self-cleaning process is performed by the action of environmental factors (physical, chemical and biological), which can simultaneously occur or in a particular sequence (NEGULESCU, 1985). Same environmental factor may influence several processes; so temperature affects the speed of sedimentation of suspended materials, speed of some chemical reactions or intensity of metabolic processes of bacteria or aquatic organisms.

Water pollution

In the study of water pollution, *analytical chemistry* plays an important role. In terms of determining the pollutants components, water is a complex system. *Operation of measurement* is fundamental in the analysis. A simple measurement may involve properties such as: mass, intensity of current, voltage, volume and time (MARTIN et al., 2000; MUSSARI et al., 2000; DUNSTAN et al., 2000). Other properties, such as absorption or emission energy, optical rotation (PEDDLE et al., 1999), refractive index (KENDRICK et al., 2001), the equilibrium constant (ORTIZ et al., 2000), the reaction rate constant (DILLINGHAM et al., 2000; LAARHOVEN and MULDER, 1997), activation energy (MITCHELL et al., 2002), heat of reaction (CEDENO et al., 2000; DAI et al., 2000) requires complex assessments (PAULSEN et al., 1999).

Monitoring of water quality

For worldwide environmental monitoring, there is Integrated Global Background

Monitoring – IGBM and Global Monitoring for Environment and Security – GMES. The first one deal with background monitoring (before the intervention of pollution) and the second is for monitoring the impact (after the intervention of pollution).

GEMS component for water was launched in 1977, including more than 300 monitoring stations, spread throughout the world. GEMS have dozens of rules and monitors water quality parameters for various categories of water, including some such as: chlorophyll, boron, hydrogen sulphide, molybdenum, vanadium, many organic compounds that are not routinely analyzed in many countries.

By NTPA 002/2002 norm are established the conditions for discharge of wastewater in local sewerage networks or directly into treatment plants in order to ensure protection and proper functioning of receptors and protecting the environment from the harmful effects of accidental discharges of wastewater. NTPA provides the quality indicators to be used to characterize wastewaters and their maximum limits.

Wastewater

Wastewater comes from loading natural water with materials and substances which alter its quality indicators and pollutes it. Water is charged with polluting materials, becoming wasted by being used by humans in various practical purposes and storm water contact (rain, snow) with products of human activity found in air and soil. In the first case, since the areas of water use take the different forms (drinkable water, water supply to industry and agriculture, fisheries, urban and recreational purposes), possibilities of pollution are very high.

Large quantities of wastewater come from industrial units. Thus, to obtain a ton of paper results about 100 - 200 m^3 of wastewater; for a ton of rubber, 150 m^3; for processing one ton of fruit results about 10 to 20 m^3 wastewater, and wastewater that comes from household consumption (sewage) is large enough quantity. Thus, there was, for a non-industrialized district of Bucharest, a consumption rate of about 0.35 m^3/inhabitant/day (ROJANSCHI şi OGNEAN, 1997).

Municipal wastewater is a mixture of domestic sewage and industrial wastewater. Surface water quality – of emissaries, in which wastewater is discharged – is also influenced by the quality of wastewater, resulted by their more or less treatment in wastewater treatment plants.

For determining the composition of surface and waste water is determined, by laboratory tests, the physical, chemical, bacteriological and biological characteristics. Analyses aimed at:

÷ providing information on the degree of pollution of wastewater and surface water and on the conditions under which they should be treated and used;
÷ determining the efficiency of treatment plants and the conditions to produce self-cleaning;
÷ determining the impact of wastewater discharge in rivers.

Determinations (parameters will be detailed in the subchapter. 1.5.2.2) can be grouped into five broad categories (NEGULESCU, 1978):

÷ establishing the amount and condition of materials contained in water, and their appearance: total dissolved solids separable by decantation, colour, turbidity, etc.
÷ defining quantity, state and conditions in which organic materials are: suspended solids separable by decantation, organic-dissolved solids, biochemical oxygen demand in 5 days, chemical oxygen demand, total nitrogen etc.;
÷ establishing the presence of specific wastewater substances: nitrogen in all its forms, O_2, fat, chlorides, sulphides, pH;
÷ indicating wastewater or surface water decomposition: BOD_5, O_2, nitrogen in different forms, H_2S, smell, temperature;
÷ establishing the presence and type of organisms in the water, in order to find out the purification degree in different stages of the treatment plant, chlorine demand, degree of river pollution, etc.

2. Wastewater treatment

Industrial wastewater is a part, sometimes quite important, of urban wastewater, which is discharged in the sewage system, and in the treatment plant, respectively, only under certain conditions. Joint treatment of industrial wastewater and sewage is recommended by literature whenever water mixture does not degrade or impede the functioning of the sewerage system and does not prejudice the proper functioning of the wastewater treatment plant (MUNTEANU, 1960). Industrial wastewater discharge into municipal sewage system and their common treatment offers the following benefits (NEGULESCU, 1978):

- ensures an effective cooperation between industry and the city, both intended to reduce the cost of wastewater treatment;
- industrial wastewater sometimes contains nutrients necessary to develop optimum treatment process, which should be artificially added if separate treatment is applied;
- if there is one common treatment plant, wastewater treatment cost is lower; also the investment value of only one station is lower;
- an unique responsible for wastewater treatment for the entire city can better meet the wastewater treatment.

General principles of industrial wastewater treatment

Wastewater treatment includes all physical, chemical, biological and bacteriological processes, which reduces the load on organic or inorganic pollutants and bacteria, in order to protect the environment (air, soil, emissary etc.). It results in obtaining clean water in various degrees of purification, depending on the technology and equipment used, and also a mixture of objects and substances which are called, generically, mud.

Theoretical principles and basic reactions of wastewater treatment process

Principiile teoretice şi reacţiile chimice care stau la baza procesului de epurare sunt prezentate, pe scurt, în cele ce urmează. Asocierea celor trei faze de epurare, mecanică, chimică şi biologică a fost concepută în vederea obţinerii unui randament sporit de îndepărtare a impurităţilor existente în apele reziduale brute, pentru redarea lor în circuitul apelor de suprafaţă, la parametrii avizaţi de normele în vigoare. Astfel, treapta de epurare mecanică a fost introdusă în procesul tehnologic, în scopul reţinerii substanţelor grosiere care ar putea înfunda canalele conductelor şi bazinele existente sau care, prin acţiunea abrazivă, ar avea efecte negative asupra uvrajelor.

Theoretical principles and chemical reactions underlying purification process are summarized in this chapter. The association of the three phases of treatment, mechanical, chemical and biological was designed to achieve a high removal efficiency of existing impurities in raw sewage, in order to result surface water with parameters advised by the rules. Thus, the mechanical cleaning step was introduced in the technological process for retaining coarse substances that might clog existing pipes and tanks, or that would adversely affect the openings, by their abrasive action.

Description of wastewater treatment technological process

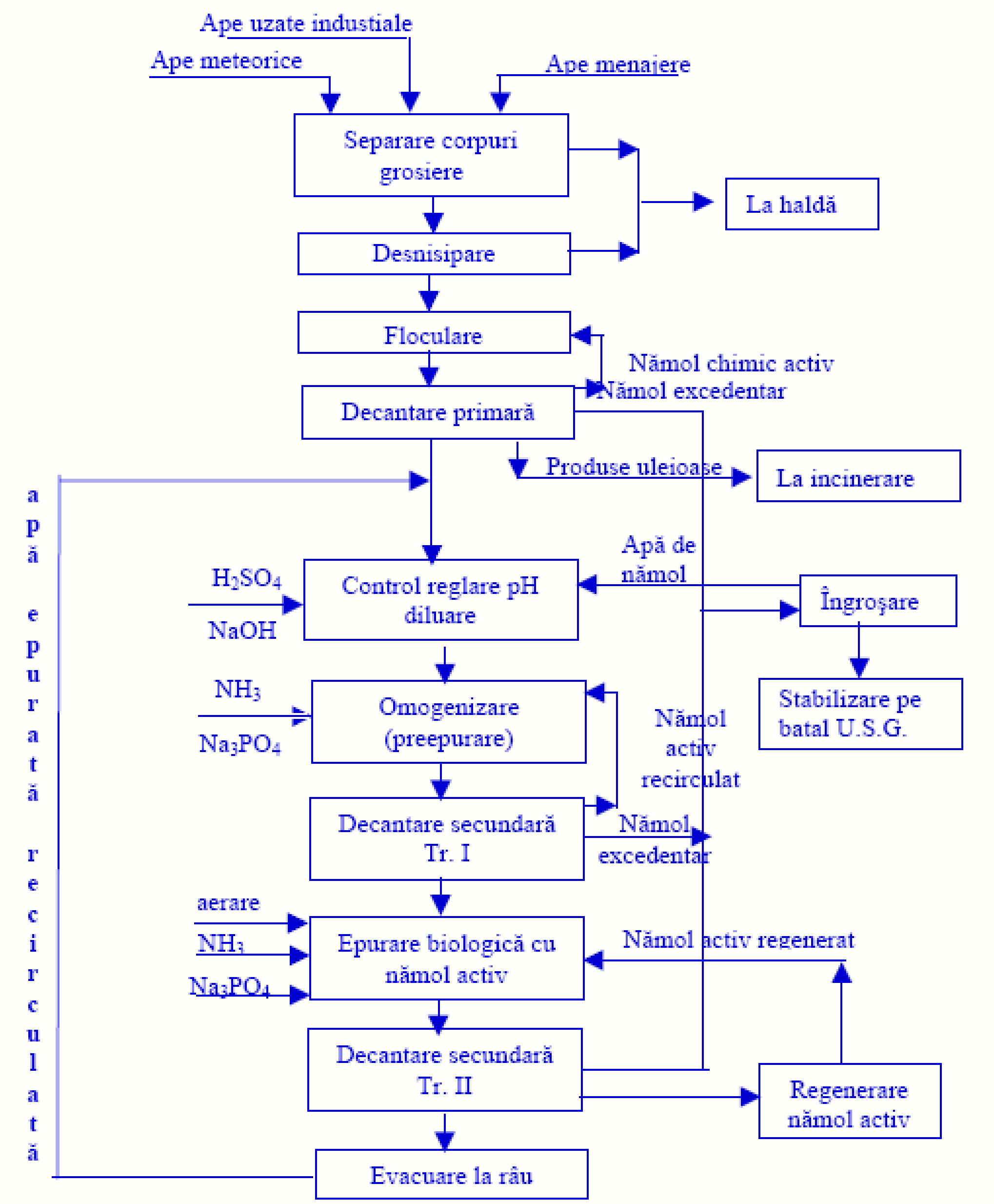
Operaţiile principale ale procesului tehnologic de epurare al unei staţii de epurare sunt prezentate schematic în fig. 2.1. Procedeele de epurare a apelor uzate, întâlnite în acest proces tehnologic, denumite după procesele care se bazează, sunt următoarele:

The main operations of the purification process of a treatment plant are shown schematically in Fig. 2.1. Wastewater treatment processes encountered in this technological process are:

- mechanical treatment – includes physical treatment processes;
- chemical treatment – includes physical and chemical treatment processes;
- biological treatment – includes physical and biochemical treatment processes.

The constructive principle of a wastewater treatment plant

Although different in size and technologies used, most of the stations of urban wastewater treatment have similar constructive scheme. Some of them are built vertically, as a tower, but most are horizontal. Occupies relatively more land, but part of facilities can be underground built, with green top. A primary stage is distinguished – mechanical; a secondary step – biological; and, at some stations (yet not at all) a tertiary level – biological, mechanical or chemical.



Primary stage consists of several successive elements: grids retain floating bodies and coarse suspensions (pieces of wood, textile, plastic, stone, etc.). Usually, there are successive grids, with spaces between the blades becoming more often. Cleaning of retained materials is mechanically done. They are handled as household waste, and taken to landfill or incinerator. Sieves have identical role with grids, but denser mesh, retaining small diameter solids. On the bottom of their pools, desanding tanks or decanters for providing coarse particles deposit sand and gravel and other fine particles that passed the sieves, but do not remain in still water more than a few minutes. Deposited sand is mechanically collected from the bottom of pools and managed as waste, together with the results of previous stages, because it contains many organic impurities.

Primary decanters are longitudinal or circular and provide longer water remaining, for settling fine suspensions. Various chemicals might be added in water as coagulation or flocculation agents; sometimes filters are interfered. Foams and other floating substances collected at surface (grease, oil substances, etc.) are also retained and removed ("despumation"), and mud deposited on the bottom is collected and removed from the pool (e.g. scraper blades backed by bridge crane) and sent to methane tanks.

Secondary level also consists of several stages: aeration tanks are pools where the water is mixed with "activated sludge", which contains microorganisms that aerobically decompose organic substances. Air is introduced continuously to accelerate biochemical processes. Secondary decanters are tanks where are settled suspended materials formed by complex processes in aeration tanks. This sludge is sent to methane tanks, and gas (containing more methane) is used as fuel, for example, in boilers.

Tertiary stage does not exist at all treatment plants. It is usually designed to remove excess compounds and to ensure water disinfection (e.g. by chlorination). This step may be: biological, mechanical or chemical or combined, using conventional technologies such as filtering, or some special ones such as activated carbon adsorption, chemical precipitation, etc. Eliminating nitrogen excess is a biological process, through nitrification (transformation of ammonium into nitrite and then nitrate) followed by denitrification, which converts nitrate to nitrogen discharged into the atmosphere. Elimination of phosphorus is made through biological or chemical process. After going through these stages, water quality must be acceptable according to the standards for treated wastewater. If the river receiving treated water can not provide a strong dilution, purified water must be very clean.

Ideal is to have a quality that make them no longer worthy to be called "wastewater", but in practice is rarely seen such a happy situation. On the one hand, treatment technologies are improving, but on the other hand, faeces domestic water contains more and more substances that should not be in it and that treatment plants can not remove from the water.

In the end, purified water is returned to the emissary – usually the river from which was taken, upstream from the city. It obviously still contains traces of pollutants, so it is advantageous to be large emissary flow, to ensure proper dilution.

Other solutions propose using of wastewater for irrigation, after secondary treatment because they have a high content of nutrients. This procedure is applicable if those waters do not contain specific toxic substances, exceeding permitted limits and resulted agricultural products are not directly consumed. In this case there is no need to stage III and no longer discharged waters into the emissary (actually negative in terms of flow, but good for the quality, because treated water is never really close to the natural, anthropogenic unpolluted water).

In experimental stage is the use of wastewater as a source of drinking water, of course subjected to advanced cleaning treatments. Sludge from primary and secondary settling tanks is inserted into the fermentation tower, called methane tanks. They are usually large concrete tanks, providing relatively constant and high temperature, and anaerobic conditions, in which bacteria ferment sludge and decompose organic matter, to inorganic substances, resulting in a sludge rich in nutrients and gases, used as fuel due to high content of methane.

Characterization of surface and waste water in Mediaş area

Geographically Mediaş is situated in the heart of the country, at about 54 km from Sibiu. Located in Transylvania Plateau in the central part of Târnave Plateau, namely framed by the hills between Târnava Mare and Târnava Mică, Mediaş is placed on the middle course of Târnava Mare in an area with features specific of valley corridors, with forests of oak, hornbeam, holm and beech, with meadows and farmlands. Region is presented as a depression corridor facing E-V, limited in north by Târnava Mică hills and in south by Hârtibaci Plateau.

Mediaş has found an ideal location in the physical natural frame, in the depression corridor of Târnava Mare and the surrounding hills, observing the site configuration and morphology of the landscape, emphasizing permanent housing in the St. Margaret Church in the major river beds and field of the young terraces of Gura Câmpului area, and mouth of valleys edge – Wewern, Greweln, Moşnei and gentle slopes.

Mediaş area is part of the Mureş river basin; the surface hydrographic network is composed of Târnava Mare River, which is the main surface water course which crosses the city from east to west over a length of 7.5 km, with variable flow fall - spring, multi-annual flow being 13.8 m^3/s, along which occur streams like Buzd, Moşna, Ighişul, tributaries of the left and Curciu, Păucea and Blăjel, tributaries of the right side that have small length and size. Their length varies between 8 and 15 km. Direct tributaries on both sides are short, aggressive, moody and dynamic only during prolonged periods of heavy rain and especially of those with torrential character. In these situations, they discharge into Târnava Mare River the amount of water and a impressive solid flow, which is deposited in the main riverbed, at the mouth and the small meadow. Moşna Valley has most significant contribution. It occupies the largest water capture area of the tributary valleys of Mediaş area. It has a permanent course and drains the southern and south-eastern part of the city. The others (Wewern, Greweln, Ighişul, Buzd) only simulate continuous leakage.

AIM AND OBJECTIVES OF THE THESIS

The purpose of the present thesis is to evaluate the water status of Mediaş area and to develop unconventional, ecological methods of wastewater treatment.

The objectives of thesis are:

1. Setting the wastewater load in pollutants in the Mediaş area.
2. Identification of microbiological hazards of wastewater from the Mediaş area.
3. Quantifying the contribution of economic industrial agents to the pollution level of wastewater from Mediaş area.
4. Estimating the efficiency of Mediaş's treatment plant.
5. Impact assessment of the Mediaş's wastewater discharge into Târnava Mare River which crosses the region.
6. Achieving a mathematical model able to illustrate the extent to which the treatment produced differences in the values of environmental parameters that influence untreated, respectively, treated water quality.
7. Developing of an unconventional, non-polluting method for wastewater treatment using zeolite volcanic tuff.
8. Comparing the degree of purification achieved in applying the two treatment methods (conventional and unconventional).
9. Achieving an experimental design of octylphenol degradation under the influence of natural and artificial ultraviolet radiation.
10. Evaluation of dependence between octylphenol photodegradation and the presence/absence of the common water constituents.
11. Evaluation dependence between octylphenol photodegradation and effects of various reaction parameters.
12. Validating a statistically significant model of action of UV radiation on octylphenol.
13. Evaluating the expression degree of estrogenic activity after octylphenol irradiation with natural and artificial ultraviolets.

EXPERIMENTAL PART

4. Physico-chemical and microbiological monitoring of water in Mediaş area

Materials, methods and tools used in determinations

In tests conducted on surface water and wastewater were monitored the following parameters: pH, electrical conductivity, filterable residue dried at 105 °C, chemical oxygen demand (COD), biochemical oxygen demand (BOD_5), ammonia nitrogen, nitrates, nitrites, orthophosphates, total phosphorus, phenol, detergents, sulphides, sulphates, petroleum ether extractable substances, suspended solids, iron, heavy metals.

Standardized methods of analysis were used, and are given in the table below.

Analysis methods

Nr.	Determination	Standard	Nr.	Determination	Standard
1.	pH / pH	SR ISO 10523/1997	9.	Filterable residue dried at 105 °C	STAS 9187/1984
2.	Electrical conductivity	SR EN 27888/1997	10.	Total suspended materials	STAS 6953/1981
3.	CODMn	STAS 9887/1974	11.	Nitrates	SR ISO 7890-3/2000
4.	CODCr	SR ISO 6060/1996	12.	Nitrites	SR ISO 6777/1996
5.	Solvent extractable substances	SR 7587/1996	13.	Phenol	SR ISO 6439/2001
6.	Ammonium	SR ISO 7150-1/2001	14.	Phosphorus	SR EN 1189/2000
7.	BOD_5	SR ISO 5815/1991	15.	Metals	SR EN ISO 11885/2004
8.	Iron	SR ISO 6332/1996			

Physico-chemical and microbiological monitoring of wastewater at entrance and exit of Mediaş wastewater treatment plant

The results of monthly monitoring of physico-chemical parameters of wastewater at the entrance and, respectively, exit of Mediaş's treatment plant, during the 2009 - 2011, are presented in the following three tables. Mention that exceeded values are written in bolded characters.

Evolution of wastewater parameters at Mediaş's treatment plant, in 2009

Month	pH		TSM		BOD_5		CODCr		NH_4^+	
	in	out	in	out	in	out	in	out	in	out
Jan	7,17	7,29	110,0	4,6	89	**37**	240,3	106,4	**55,7**	**39,0**
Feb	7,36	7,56	140,6	14,0	118	18	322,8	62,4	**80,7**	**30,0**
Mar	7,39	7,34	204,0	16,6	108	22	287,6	72,1	**74,9**	**30,7**
Apr	7,25	7,29	104,0	19,3	69,0	22	296,5	68,6	**76,9**	**50,0**
Mai	7,21	7,43	113,0	6,0	129	**38**	396,6	118,2	**70,2**	**32,0**
Jun	7,31	7,28	53,2	12,3	72	**30**	210,6	92,7	**56,0**	**27,3**
Jul	7,36	7,34	60,4	29,6	107	**34**	286,2	111,4	**61,1**	**33,4**
Aug	7,27	7,33	124,4	**58,0**	118	**38**	316,1	108,6	**65,6**	**37,0**
Sep	7,26	7,27	122,0	26,4	110	**41**	320,2	118,6	**63,0**	**33,0**
Oct	7,17	7,29	179,0	21,3	208	**30**	426,6	107,7	**74,8**	**31,0**
Noi	7,32	7,22	105,0	**43,2**	112	**33**	320,2	118,0	**63,1**	**31,3**
Dec	7,34	7,25	90,4	29,6	92	**39**	323,0	102,4	**68,3**	**33,3**

Evolution of wastewater parameters at Mediaş's treatment plant, in 2010

Month	pH		TSM		BOD_5		CODCr		NH_4^+	
	in	out	in	out	in		in	out	in	out
Jan	7,35	7,28	126,0	10,4	154,0	11,0	387,3	52,4	**37,40**	**22,60**
Feb	7,35	7,07	100,8	16,4	87,2	10,0	343,4	49,0	**31,60**	**24,50**
Mar	7,41	7,07	136,4	17,6	104,0	9,0	324,2	51,6	**37,20**	**28,70**
Apr	7,47	7,01	110,8	13,2	94,0	5,5	263,0	39,8	**43,70**	**32,30**
Mai	7,47	7,23	118,0	20,7	127,0	6,0	315,6	28,2	25,80	**25,30**
Jun	7,41	7,28	102,8	4,0	124,0	7,0	276,5	47,7	28,40	**25,00**
Jul	7,29	7,06	102,8	10,0	92,0	5,0	248,4	36,6	29,30	**26,70**
Aug	7,41	7,31	115,6	13,3	86,0	11,0	340,3	49,6	**33,30**	**30,50**
Sep	7,23	7,13	119,2	6,0	92,0	15,0	329,6	61,4	**31,10**	**29,20**
Oct	7,36	7,02	120,5	16,8	76,0	**26,0**	348,0	82,8	**32,70**	**26,40**
Noi	7,36	7,05	109,0	18,0	110,0	8,0	272,5	28,8	**32,65**	**26,35**
Dec	7,50	7,07	62,0	30,8	64,0	4,0	273,0	49,8	27,25	**25,95**

Evolution of wastewater parameters at Mediaş's treatment plant, in 2011

Month	pH		TSM		BOD_5		CODCr		NH_4^+	
	in	out	in	out	in		in	out	in	out
Jan	7,17	7,27	128,0	30,0	90	**26**	282,3	94,2	**35,5**	**27,4**
Feb	7,37	7,30	122,0	30,8	126	**28**	280,4	91,3	**33,0**	**29,2**
Mar	7,28	7,25	109,2	32,4	95	20	283,5	94,4	**32,0**	**29,1**
Apr	7,31	7,25	86,8	35,5	80	18	235,0	72,6	29,2	**27,5**
Mai	7,29	7,33	76,4	34,4	78	15	226,6	64,4	**30,8**	**27,7**
Jun	7,32	7,03	153,2	6,8	176	16	426,5	53,4	**39,4**	**29,8**

The analysis of data obtained during 2009 - 2011, emerges the conclusion that the conventional treatment method applied in the Mediaş's wastewater treatment plant is not efficient enough to obtain purified water, especially in terms of ammonium, parameter that has the highest overshoot to the limits set by NTPA 001/2002 which lays down limit values for pollutant loading of industrial and municipal wastewater discharged into natural receivers, complemented by NTPA 011/2002 containing prescriptions for discharges from municipal wastewater treatment plants.

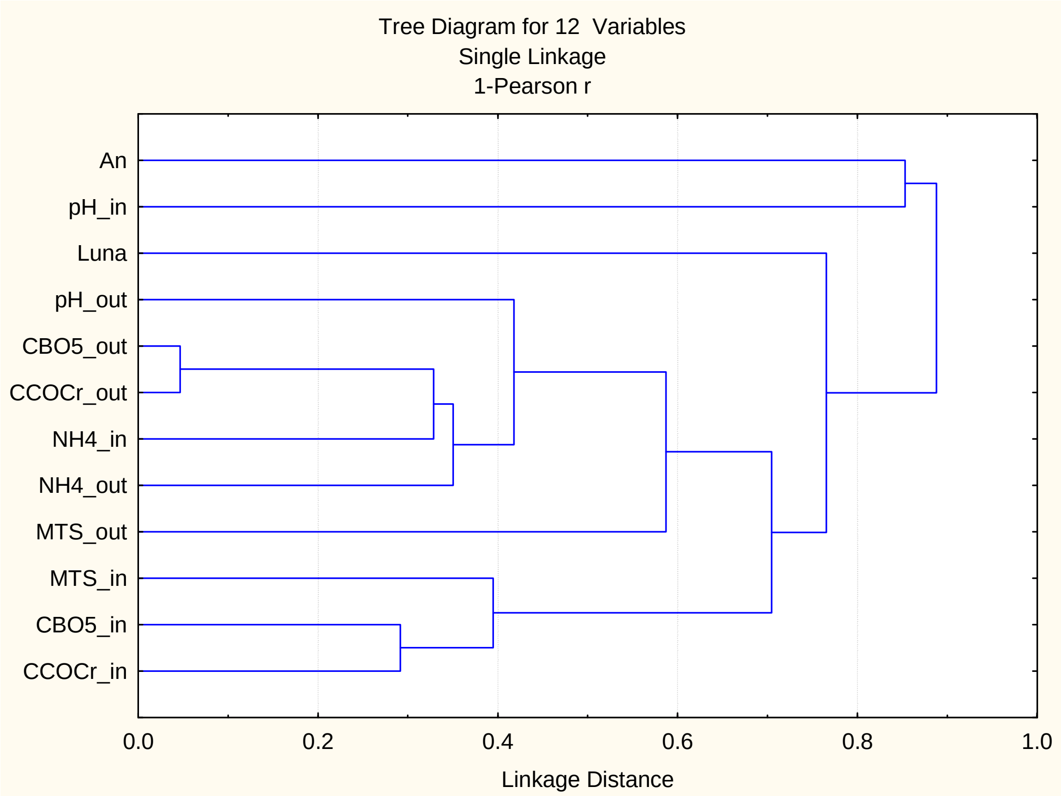
In order to determine more precisely the degree of sewage purification achieved by the conventional method used, efficiency (β) for each monitored parameter was calculated.

The highest treatment degree is found for biochemical oxygen demand in 5 days and an average of about 80 % during the three years of monitoring, in 2010 achieving a purification of up to 90 %, which is, in fact, the maximum efficiency obtained for all parameters monitored throughout the period of conducting this study.

At removal of material in suspension similar values were obtained, meaning an average of about 79 % during 2009 - 2011, while in 2010 even 85 %. A good performance was achieved in terms of chemical oxygen demand that is 75 %, respectively.

The most acute problem is the removal of ammonia nitrogen from wastewater. Influent comes with a high intake of NH_4^+, while efficiency of treatment method ranges from 14 to 29 %, a very small percentage compared to the requirements imposed by regulations, which causes high loads of effluent in ammonia nitrogen.

Measure of association between indicator values is obtained throughout cluster analysis (dendrogram); figure below is an association diagram obtained by representing 1-Pearson_r difference that yields a greater association while 1-Pearson_r difference is smaller; thus the strongest associations are those that are connected closest to 0 (that have the smallest difference from one another – the difference becomes 0 for a perfect correlation).



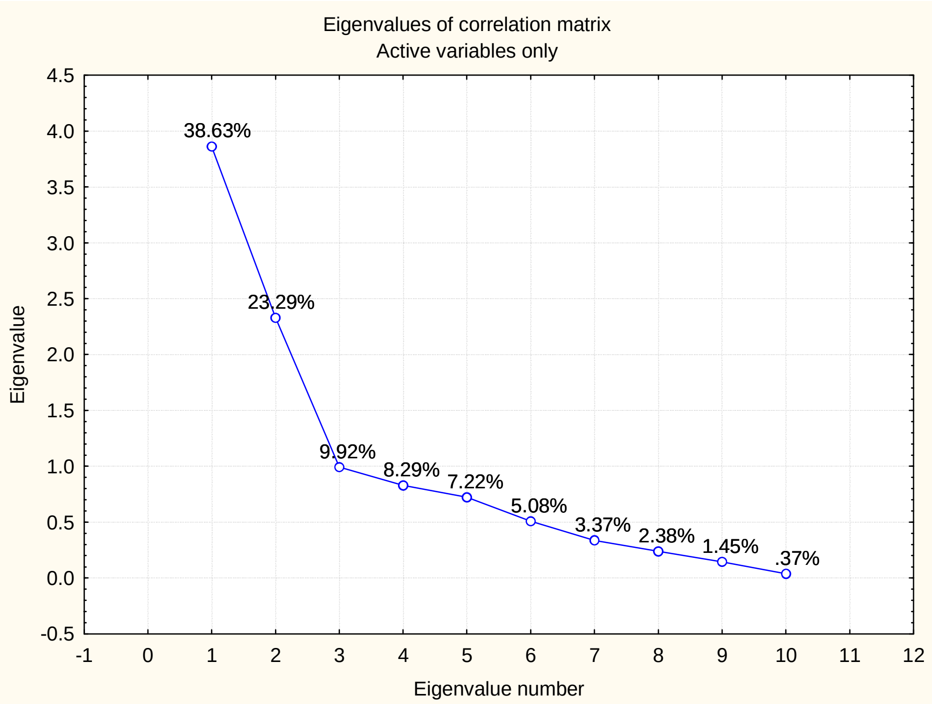
Cluster tree based on the change of physical-chemical indicators over the period 2009 - 2011 (grouping based on average values of parameters, by means of 1-Pearson r, using simple linkage)

As can be seen, the strongest association, located at a distance of about less than 0.1 (a correlation coefficient above 0.9) is established between biochemical and, respectively, chemical oxygen demand, at the output of the treatment station (CBO5_out and CCOCr_out). Efficiency of COD and BOD_5 reduction is a criterion for assessing water treatability.

It is notable the association of ammonium at the entrance and exit with BOD_5 and COD at the exit, indicating a possible nefarious relation of NH_4^+, affecting the efficiency of biological treatment, especially since content of NH_4^+ in Mediaş region exceeds the legal permitted limits prescribed by regulations.

Analysis of covariance can be led using Principal Component Analysis. It is known that the Principal Component Analysis (http://en.wikipedia.org/wiki/Principal_component_analysis) sequentially decomposes variance, in many components (factors), in each sequence the unexplained amount becoming less and having a development approximated by an exponential curve with negative exponent.

As shown in the figure, sequential separation of the main factors accounting for evolution data over 3 years (2009 - 2011) of environmental parameters is subjected to this variation model, taking place a rapid decrease in unexplained variance in the number of main factors (from 38.6 % of variance explained by a single factor, to another 23.3 % explained using the second, with another 9.9 % through the third). Moreover, as shown in the next figure, beginning with the fourth factor, explained variance varies approximately linearly with the number of factors, which is attributed to overfitting, this model tending to start estimating the error (http://www.stat.cmu.edu). This shows that the best analysis model based on principal component analysis has three main factors and variance is explained by factors (the three factors identified by the model) is not greater than 72 %, the remaining variation is due to random events (such as rain, drought, etc.).



Eigenvalues of correlation matrix for active variables

To highlight the correlations between physical-chemical parameters monitored during the period 2009 - 2011, the main sources of variation in the observations are identified and organized in three main components (factor 1, factor 2, and factor 3). The same association seen in the figure between the outputs of the two variables is highlighted by the values -0.8793 and -0.9083, corresponding to factor 1. Observed variables are modelled as linear combinations of potential factors, plus the terms "error". Information obtained on the interrelationships between observed variables can be further used to reduce the set of variables. Factor analysis estimates the proportion in which variability is due to common factors.

Factor analysis based on correlations. Active and Supplementary variables

Variables	Factor 1	Factor 2	Factor 3
pH_in	0.6767	0.0088	0.0669
pH_out	-0.6441	0.0781	-0.0796
MTS_in	-0.2497	-0.7797	-0.0780
MTS_out	-0.2924	0.4590	0.6585
CBO5_in	-0.2815	-0.8300	0.2621
CBO5_out	-0.9083	0.1974	0.1534
CCOCr_in	-0.2608	-0.8146	0.1613
CCOCr_out	-0.8793	0.2254	0.2696
NH4_in	-0.8352	-0.0780	-0.2908
NH4_out	-0.6319	0.2372	-0.5156
***An**	0.5774	-0.0096	0.3389
***Luna**	-0.0142	0.0752	0.2647
* supplementary variables			

Comparing the values observed at different observation points (entrance and exit), at the same time (month, year) or at the same point of observation (input or output), at different times (same month, different year), are able to show, on the one hand the extent to which the treatment produced differences in average values of parameters under the control and monitoring of the treatment plant and, on the other hand, how much from year to year changes have occurred systematically to influence untreated, and respectively, treated water quality.

These comparisons refer paired data (observations during a year performed in the same time of year – month – in different locations or years) and can thus make a comparison using "t" student test for paired values. Comparative analysis can refer, obviously, differences in the same size.

Thus, Table (a) gives the comparison of data pairs of pH, (b) for ammonium, (c) for biochemical oxygen demand, (d) for chemical oxygen demand and (e) for material in suspension.

Paired Two Sample for Means Test comparing variables during 2009 - 2011 years

(a) pH

Difference (significance)	pH_in_2009	pH_out_2009	pH_in_2010	pH_out_2010	pH_in_2011	pH_out_2011
pH_in_2009		0.0400(2.2E-1)	0.1000(8.2E-3)		0.0083(7.7E-1)	
pH_out_2009				0.1925(6.3E-4)		0.1267(3.1E-2)
pH_in_2010				0.2525(3.5E-5)	0.1200(1.2E-2)	
pH_out_2010						0.0817(3.3E-1)
pH_in_2011						0.0517(3.9E-1)
pH_out_2011						

(b) NH_4^+

Difference (significance)	NH4_in2009	NH4_out2009	NH4_in2010	NH4_out2010	NH4_in2011	NH4_out2011
NH4_in2009		33.525(8.19E-08)	34.9916(1.6E-08)		35.75(1.5E-3)	
NH4_out2009				7.0416(4.7E-4)		6.3833(1.5E-1)
NH4_in2010				5.575(1.0E-3)	0.7(8.5E-1)	
NH4_out2010						2.05(2.4E-1)
NH4_in2011						4.8667(1.4E-2)
NH4_out2011						

(c) BOD

Difference (significance)	CBO5_in2009	CBO5_out2009	CBO5_in2010	CBO5_out2010	CBO5_in2011	CBO5_out2011
CBO5_in2009		79.1667(1.1E-5)	10.15(4.9E-1)		3.35(9.5E-1)	
CBO5_out2009				22.0417(7.0E-6)		7.3333 (1.7E-1)
CBO5_in2010				91.0583(1.3E-7)	29.2833(4.7E-1)	
CBO5_out2010						33.6(2.2E-3)
CBO5_in2011						87(2.6E-3)
CBO5_out2011						

(d) COD

Difference (significance)	CCOCr_in2009	CCOCr_out2009	CCOCr_in2010	CCOCr-out2010	CCOCr_in2011	CCOCr_out2011
CCOCr_in2009		213.3(4.74E-08)	2.075(9.2E-1)		3.35(9.5E-1)	
CCOCr_out2009				50.78(2.69E-05)		8.35(5.7E-1)
CCOCr_in2010				262.0(5.72E-11)	29.283(4.7E-1)	
CCOCr_out2010						33.6(2.2E-3)
CCOCr_in2011						210.67(1.4E-3)
CCOCr_out2011						

(e) TSM

Difference (significance)	MTS_in2009	MTS_out2009	MTS_in2010	MTS_out2010	MTS_in2011	MTS_out2011
MTS_in2009		93.7583(2.4E-5)	6.8417(5.3E-1)		8.2(7.7E-1)	
MTS_out2009				8.6417(9.3E-2)		16.1833(2.1E-2)
MTS_in2010				95.5583(1.5E-8)	3.2(8.3E-1)	
MTS_out2010						14.6(3.1E-3)
MTS_in2011						84.2833(2.7E-3)
MTS_out2011						

Contribution of industrial economic agents on pollution of wastewater in the city of Mediaş

Establishing the origin and quality of the wastewater requires knowledge of the technological industrial process for judicious design of wastewater treatment plants. So is necessary to know the origin of the main tributaries and their main characteristics for defining the method of treatment (POPA, 2011c). Reduction of wastewater flows requires the use of new technologies.

Monitoring economic agents connected to the sewerage is based on a sampling program, taking into account the following criteria:

÷ nature of the economic agent in question, which determines the nature of pollutants in wastewater discharged into the system;

÷ discharged wastewater;

÷ history of discharges by the economic agent in question.

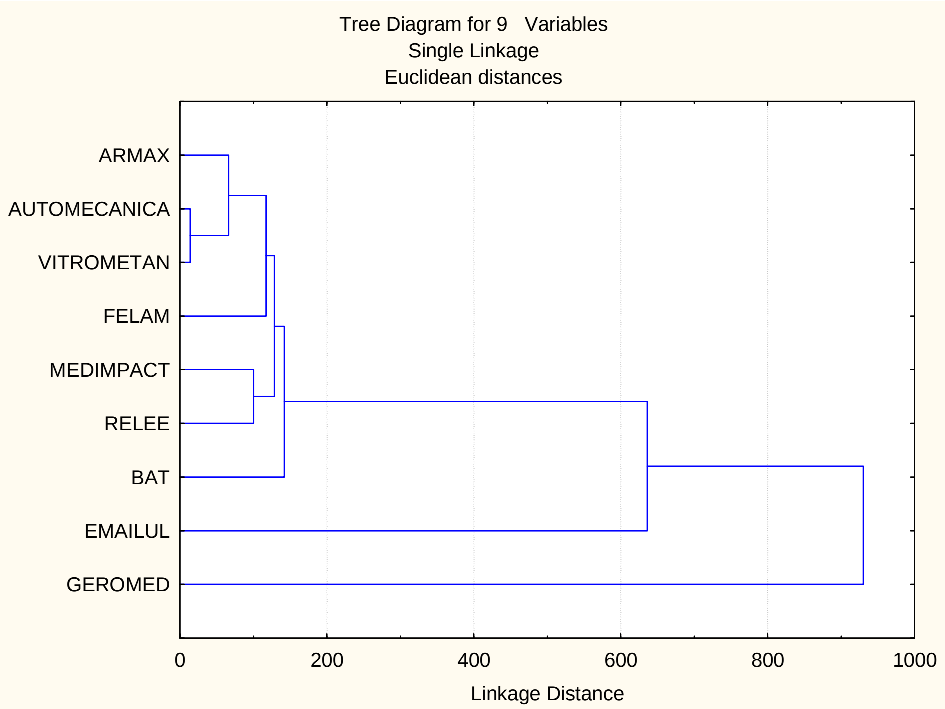
The main economic agents which, by their wastewater discharges, contribute to the pollutant load of the Mediaş's wastewater treatment plant influent are presented in the table below.

Monitored economic agents - dynamics of their work

No.	Economic agent	Domain of activity	Wastewater discharge
1.	Armax Gaz	Machining, pneumatic fitting, burners' assembly, metal coatings, plating, painting.	Târnava Mare River
2.	Automecanica	Design, manufacture and sale of equipment-automobiles-special vehicles, spare parts.	Târnava Mare River
3.	B.A.T.	Motor transport of goods and people, repair and periodic inspection of vehicles endowment.	Ighiş Rill
4.	Emailul	Production and marketing of enamelled vessels.	Târnava Mare River
5.	Felam	Production and marketing of fasteners and strip wire.	Târnava Mare River
6.	Geromed	Production of drawn glass, safety glazing materials and duplex windows, mirrors.	Sewage of Mediaş
7.	Medimpact	Dyeing and finishing leathers, making leather: footwear, riding.	Târnava Mare River
8.	Relee	Production of apparatus for distribution and power control.	Moşna Rill
9.	Vitrometan	Production and marketing of glassware (common household), glassware (crystal) and glassware for lighting fixtures.	Târnava Mare River

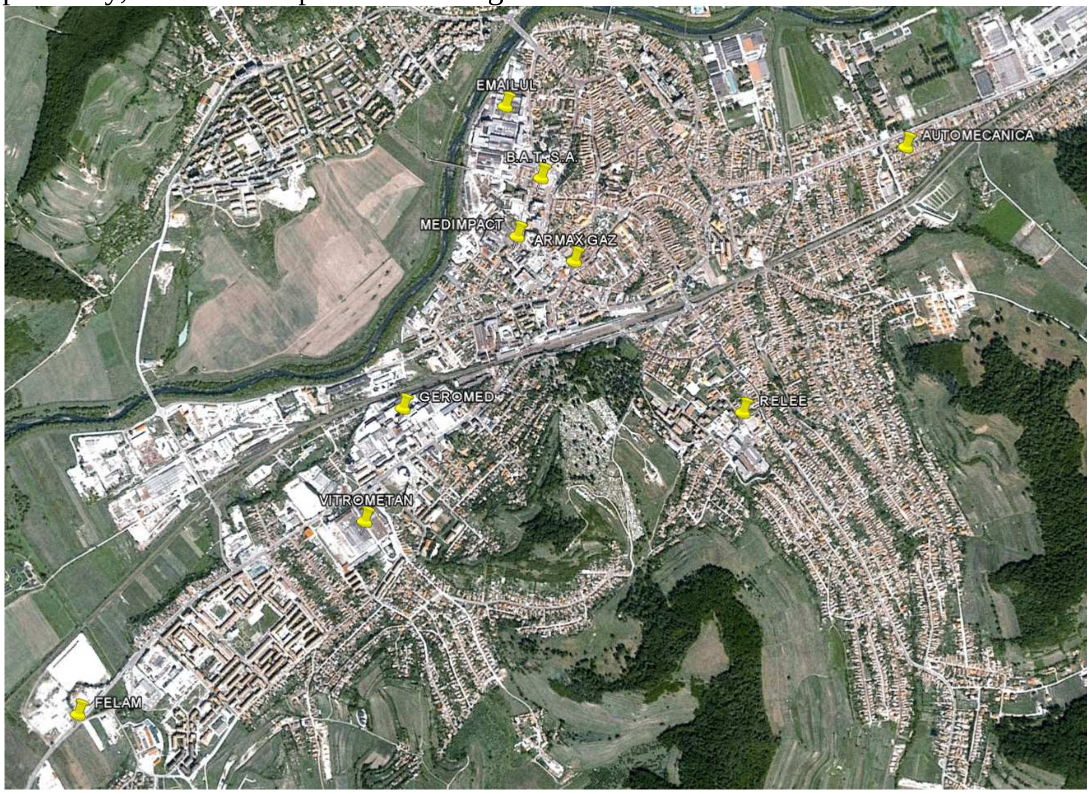
Impact assessment of Mediaş's wastewater discharges on Târnava Mare River

The following figure shows that, in terms of pollutants (those marked by recorded analysis), the strongest association is between AUTOMECANICA and VITROMETAN and decided (based on data analysis tables) mainly due to similar amounts of electrical conductivity and dry residue present in the waters analyzed from these two companies.



Cluster tree based on the change of physical-chemical indicators monitored for each economic agent (grouping based on average values of parameters, by means of Euclidean distances, using simple linkage)

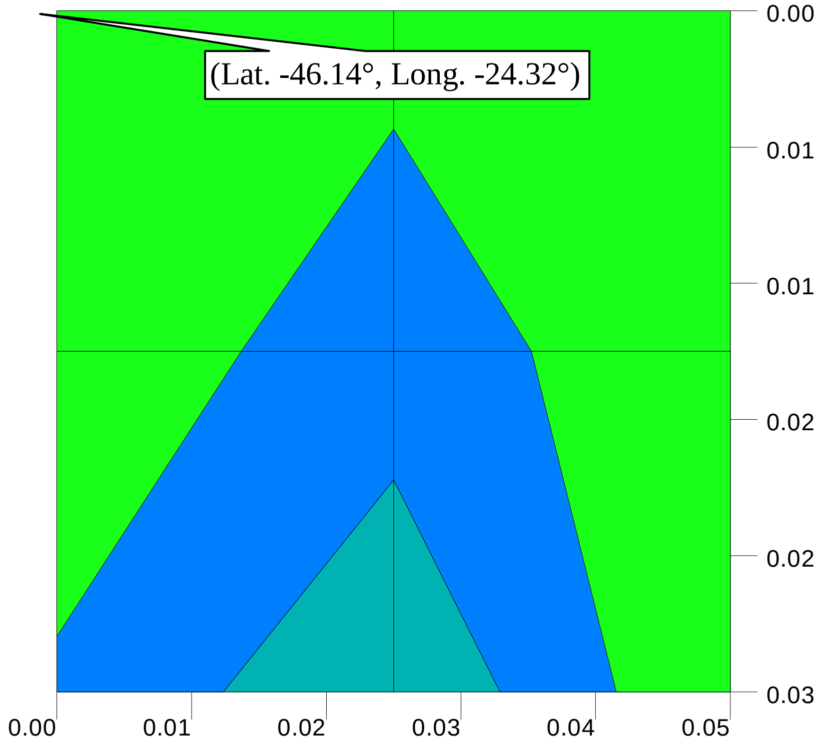
Estimation method (SUCIU şi colab., 2008) is able to build a grid to estimate water quality similar to that used in the analysis, characterization and taxonomization of soil used by USDA (http://soils.usda.gov) and can provide information on which to take decisions on the location of different types of economic agents, crops and residential areas, decisions that maximize resources and, respectively, to minimize potential damage due to unfavourable environmental conditions.



Mediaş City map with the location of observation points (Google Map)

In each of the nine observation points marked in the figure were measured physico-chemical indicators relevant to each specific company. Depending on the values recorded and given the spatial coordinates were graphically represented the following parameters: pH, total suspended material, filterable residue dried at 105 °C, electrical conductivity and chemical oxygen demand, using interpolation by spline functions.

Level map of materials in suspension, resulted by interpolating spline functions, the values measured in the nine observation points was drawn taking into account the limits set by regulations. It can be observed a minimum level of pollution in the south-eastern area of Mediaş.



Legend of values: Red - [200 - 500]; Green - [500 - 800]; Blue - [800 - 1100]; Cyan - [1100 - 1400]; Magenta - [1400 - 1700]

Surface level of filterable residue dried at 105 °C

In general, exceeded maximum permitted levels laid down in regulations were registered, depending on the specific activity profile of each unit, but most commonly exceedings arise in determining biochemical oxygen demand in five days (BOD_5), which correlated with the values found for organic matter content (CODCr) indicates an intense microbiological activity in the wastewater. These increases in water parameters are due to uncontrolled domestic and industrial wastewater discharges.

5. Research on using zeolite tuff in unconventional wastewater treatment technologies

Mineralized volcanic zeolite tuff of Rupea is obtained from volcanic rocks (from Perşani massive), rich in natural zeolites, in which clinoptilolite (real volcanic tuff with special properties) represents 70 %.

Tuff samples from Rupea were examined special laboratories in Germany and Netherlands, by the most modern methods, highlighting the following major components: aluminum oxide (11.58 %), titanium oxide (0.25 %), ferric oxide (1.40 %), manganese oxide (0.01 %), calcium oxide (2.72 %), magnesium oxide (0.79 %), sodium oxide (0.45 %) potassium oxide (2.18 %), phosphorus pentoxide (6.02 %), sulfur (0.01 %) (PODAR, 2007).

Volcanic zeolite tuff used in the present experimental research has been sampled globally (10 samples) from the top, basal and central career located in Rupea area.

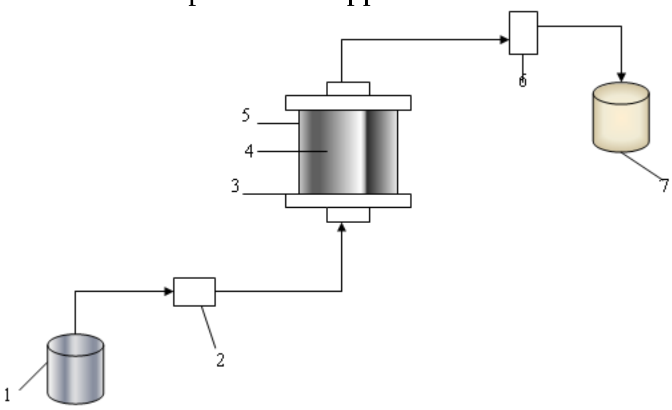
Tuff crumbling consisted in crushing zeolite tuff samples up to sizes of about 1 - 2 cm, followed by grinding in ball mill and, finally, classification was done on sieves in dry state, using Retsch A220 basic sieves (Germany), achieving thus a global, homogeneous tuff sample. Samples were processed in several cycles. After each cycle, 2 mm fraction was removed by a dry sieve, to prevent overtrituration.

Sieves Retsch A220

For the final product (grain size of 1 mm) a much lower grinding cycle was performed, about 3 minutes, because the materials are characterized by low resistance to fracture and compression. Material overtrituration is avoided by using much less grinding time.

Experimental appliance used

The figure below describes experimental appliance used in determinations.



Legend: 1 – wastewater storage tank; 2 – peristaltic pump; 3 – plastic sieve; 4 – natural zeolite bed; 5 – plexiglas column; 6 – sample collector; 7 – resulting solution container.
Schematic representation of the column and fixed bed adsorption installation

Volumes and corresponding quantities of used zeolite materials are listed in the table below.

Mention that bulk density is considered 0.9693 g/ml of zeolite used with average particle diameter of 1 mm.

Quantities of zeolite material used in experiments

	Zeolite bed height, cm			Column diameter, cm
	1	2	3	
Volume of zeolite material, ml	78,50	157,00	235,50	10
Mass of zeolite material, g	76,09	152,18	228,27	

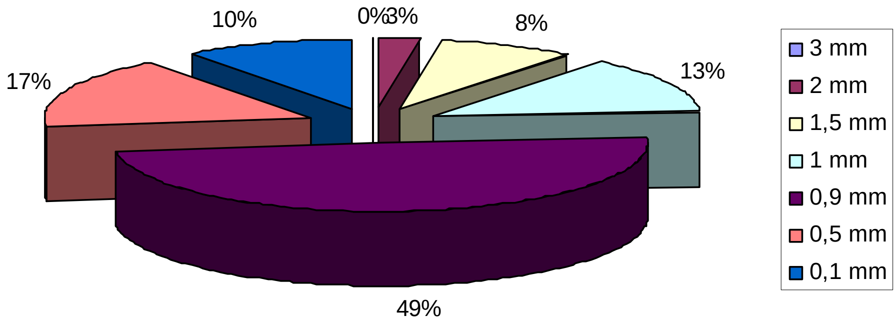
Determination methods are presented in table below.

Methods for determining the physico-chemical parameters of wastewater

No.	Determination	Standard
1.	pH	SR ISO 10523/1997
2.	CODCr	SR ISO 6060/1996
3.	Total suspended solids	STAS 6953/1981
4.	Ammonium	SR ISO 7150-1/2001
5.	BOD_5	SR ISO 5815/1991

To test the efficiency of the applied method, were determined physico-chemical parameters that are routinely monitored in wastewater treatment plants in order to characterize their level of treatment, namely: pH, total suspended matter, ammonium, chemical and biochemical oxygen demand in 5 days. Measurements were performed according to standard methods (Table 5.2), described in detail in Chapter 4.1.2 of the sentence.

The primary zeolite tuff, the amount of crystals to be removed is very small (GHERGARI şi colab., 1989). By grinding, fine clay and calcite material, due to low hardness, is eliminated in fraction of 0.10 mm. After grinding, the sample was classified on the sieves of 3 mm, 2 mm, 1.5 mm, 1 mm, 0.90 mm, 0.50 mm and 0.10 mm. The results obtained by ranking on sieves are represented in the figure below.



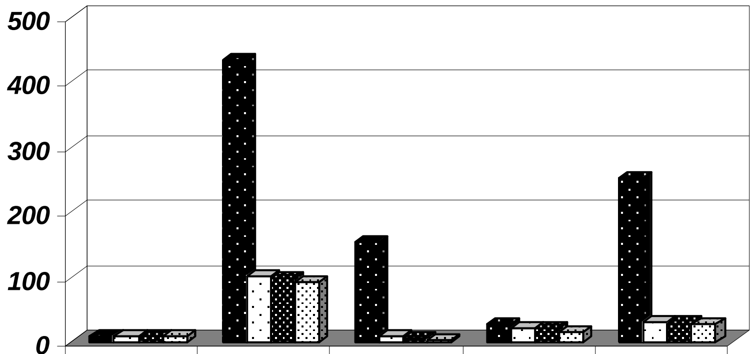
Ranking on the sieves of zeolite particles fraction

Once finished product of zeolite tuff was obtained, the experiment itself was performed.

Tests focused on the use of zeolites in layers of different thicknesses, so that the cost/efficiency ratio can be accurately determined. Layers had the following thicknesses: 1 cm, 2 cm, respectively, 3 cm.

The variation of relevant parameters was studied to characterize the wastewater, namely: pH, chemical oxygen demand (COD), biochemical oxygen demand (BOD_5), ammonium (NH_4^+), total suspended matter (TSM).

Measurements were initially made both for wastewater, and in the end, purified water, by applying the unconventional method using zeolite tuff in beds of different thicknesses. The following figure illustrates the comparative results as described above.



	pH	CCOCr	CBO5	NH4	MTS
intrare / inflow	*7,4*	*434,6*	*152*	*27,05*	*252*
iesire / outflow (1 cm)	*7,39*	*99,2*	*7,6*	*21,4*	*29,5*
iesire / outflow (2 cm)	*7,38*	*96,3*	*4,9*	*19,4*	*28,2*
iesire / outflow (3 cm)	*7,38*	*90,7*	*1*	*13,2*	*25,4*

Variation of monitored parameters, depending on the thickness of the used zeolite bed

6. Analysis of octylphenol degradation under natural and artificial ultraviolet radiation

Based on the environmental significance of alkylphenolethoxylates and their low biodegradability, in this work are investigated octylphenol's transformations in surface waters, under the influence of solar radiation. The objective of this investigation is to prove that OP photodegradation degree varies significantly depending on the common constituents of water. Therefore, photochemical behaviour of OP is pursued in ultrapure water (synthetic medium – Figure 1) and in natural waters (natural medium – Figure 2), exposed to UV real and simulated solar radiation, determining the fundamental parameters related to the transformation of OP under UV action and using raw water characteristics to forecast the degradation rate.

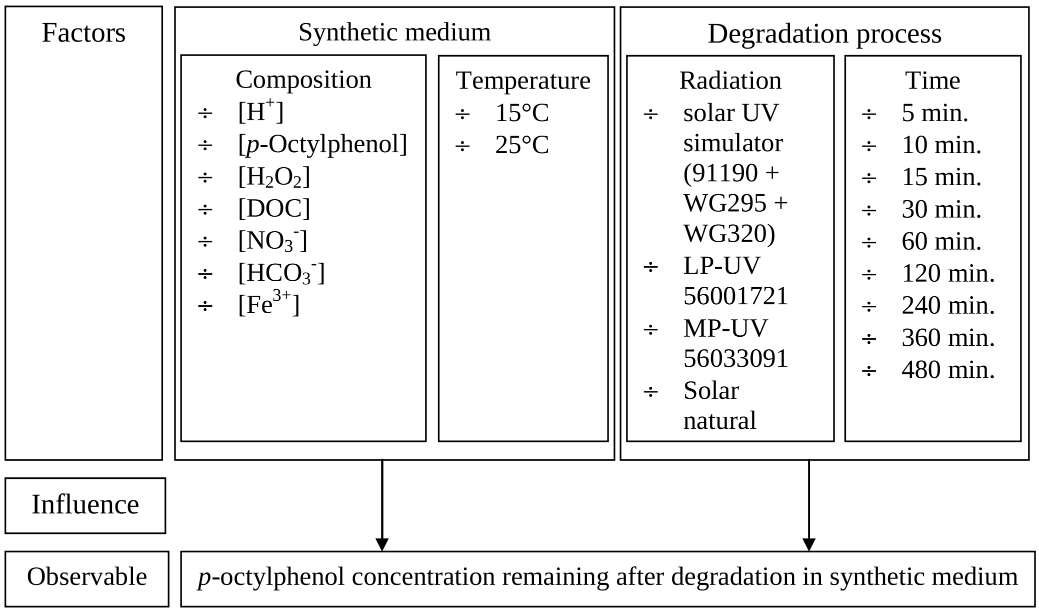


Figure 1. Experimental design for photochemical removal of OP in synthetic medium

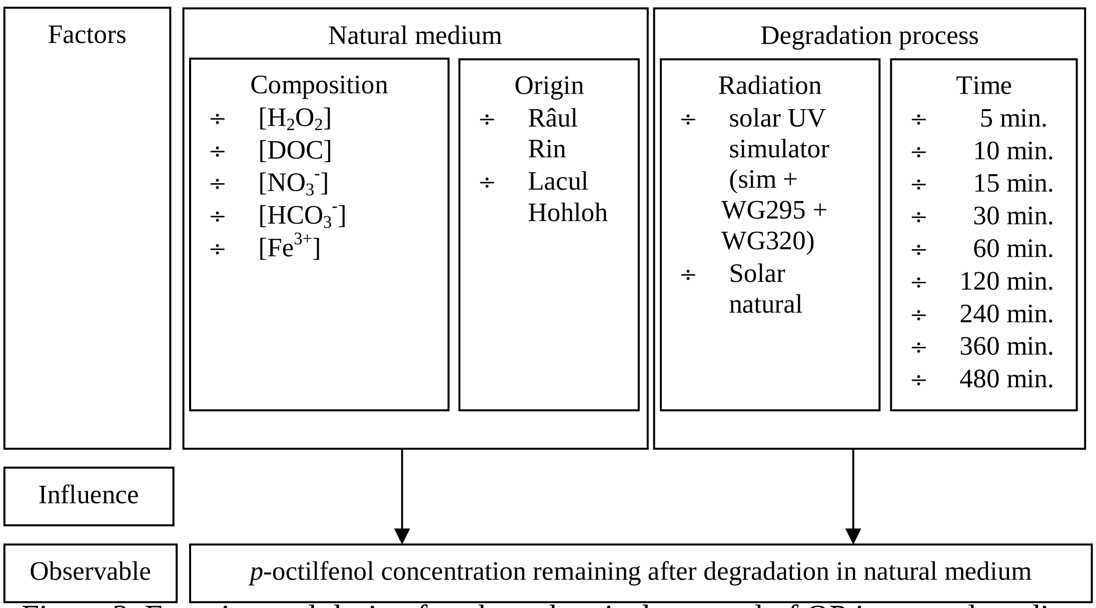


Figure 2. Experimental design for photochemical removal of OP in natural medium

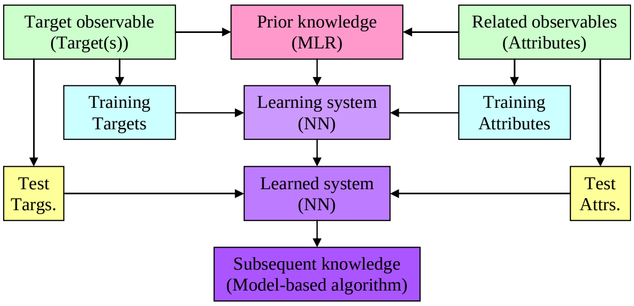
OP photochemical degradation is induced by laboratory-scale experiments, using real and simulated sunlight for samples irradiation. In establishing the experimental design (Figures 1 and 2) factors involved in OP photodegradation were considered, and influence of each of them on the observable of the process, namely the concentration of *p*-octylphenol; thus, the effect of different reaction parameters, such as pH, initial substrate concentration, reaction temperature and the concentration of hydrogen peroxide on octylphenol photodegradation in aqueous solutions were assessed. Octylphenol photolysis is also investigated in the presence, respectively absence of organic matter and dissolved ions HCO_3^-, NO_3^- and Fe(III).

Octylphenol degradation results under different exposure conditions

Source	$[H_2O_2]$	$[NO_3^-]$	$[HCO_3^-]$	$[Fe^{3+}]$	Temperature (°C)	pH	Time (h)	$[OP]_{initial}$	$[OP]_{final}$	$[OP]_{ratio}$
sUVs	0	0	0	0	10	8	0	2.05e-5	2.05e-5	1.000
sUVs	0	0	0	0	10	8	0.166	2.05e-5	1.86e-5	0.907
sUVs	0	0	0	0	10	8	0.333	2.05e-5	1.86e-5	0.906
sUVs	0	0	0	0	10	8	1	2.05e-5	1.81e-5	0.880
sUVs	0	0	0	0	10	8	2	2.05e-5	1.78e-5	0.866
sUVs	0	0	0	0	10	8	4	2.05e-5	1.72e-5	0.837
sUVs	0	0	0	0	10	8	8	2.05e-5	1.71e-5	0.833
sUVs	0	0	0	0	25	6.58	0	2.39e-5	2.39e-5	1.000
sUVs	0	0	0	0	25	6.58	0.166	2.39e-5	2.17e-5	0.907
sUVs	0	0	0	0	25	6.58	0.333	2.39e-5	2.14e-5	0.894
sUVs	0	0	0	0	25	6.58	1	2.39e-5	2.12e-5	0.885
sUVs	0	0	0	0	25	6.58	1.5	2.39e-5	2.11e-5	0.881
sUVs	0	0	0	0	25	6.58	2	2.39e-5	2.07e-5	0.864
sUVs	0	0	0	0	25	6.58	4	2.39e-5	2.01e-5	0.838
sUVs	0	0	0	0	25	6.58	6	2.39e-5	1.92e-5	0.800
sUVs	0	0	0	0	25	6.58	8	2.39e-5	1.69e-5	0.705
LPUV	0	0	0	0	15	6.58	0	1.96e-5	1.96e-5	1.000
LPUV	0	0	0	0	15	6.58	0.166	1.96e-5	1.76e-5	0.899
LPUV	0	0	0	0	15	6.58	0.25	1.96e-5	1.70e-5	0.867
LPUV	0	0	0	0	15	6.58	0.5	1.96e-5	1.44e-5	0.733
LPUV	0	0	0	0	15	6.58	1	1.96e-5	8.12e-6	0.415
LPUV	0	0	0	0	15	6.58	1.5	1.96e-5	6.51e-6	0.332
LPUV	0	0	0	0	15	6.58	2	1.96e-5	3.76e-6	0.192
LPUV	0	0	0	0	15	6.58	0	2.00e-5	2.00e-5	1.000
LPUV	0	0	0	0	15	6.58	0.5	2.00e-5	1.20e-5	0.601
LPUV	0	0	0	0	15	6.58	1	2.00e-5	7.59e-6	0.379
LPUV	0	0	0	0	15	6.58	1.5	2.00e-5	5.11e-6	0.255
LPUV	0	0	0	0	15	6.58	2	2.00e-5	3.69e-6	0.184
LPUV	0	0	0	0	15	6.58	4	2.00e-5	7.56e-7	0.038
LPUV	0	0	0	0	15	6.58	5	2.00e-5	1.79e-7	0.009
LPUV	0	0	0	0	15	6.58	6	2.00e-5	0.00e+0	0.000
Sun	0	0	0	0	15	6.58	0	2.00e-5	2.00e-5	1.000
Sun	0	0	0	0	15	6.58	0.166	2.00e-5	1.97e-5	0.984
Sun	0	0	0	0	15	6.58	0.333	2.00e-5	1.80e-5	0.902
Sun	0	0	0	0	15	6.58	0.5	2.00e-5	1.80e-5	0.901
Sun	0	0	0	0	15	6.58	1	2.00e-5	1.71e-5	0.854
Sun	0	0	0	0	15	6.58	1.5	2.00e-5	1.55e-5	0.775
Sun	0	0	0	0	15	6.58	2	2.00e-5	1.51e-5	0.756
Sun	0	0	0	0	15	6.58	4	2.00e-5	9.78e-6	0.489
Sun	0	0	0	0	15	6.58	6	2.00e-5	5.56e-6	0.279
Sun	0	0	0	0	15	6.58	8	2.00e-5	3.54e-6	0.177
MPUV	0	0	0	0	15	6.58	0	1.38e-5	1.38e-5	1.000
MPUV	0	0	0	0	15	6.58	0.083	1.38e-5	8.63e-6	0.627
MPUV	0	0	0	0	15	6.58	0.167	1.38e-5	6.89e-6	0.501
MPUV	0	0	0	0	15	6.58	0.25	1.38e-5	5.28e-6	0.384
MPUV	0	0	0	0	15	6.58	0.333	1.38e-5	3.62e-6	0.263
MPUV	0	0	0	0	15	6.58	0.417	1.38e-5	3.22e-6	0.234
MPUV	0	0	0	0	15	6.58	0.5	1.38e-5	2.31e-6	0.168
MPUV	0	0	0	0	15	6.58	1	1.38e-5	7.45e-7	0.054
sUVs	10	0	0	0	15	6.58	0	1.83e-5	1.83e-5	1.000
sUVs	10	0	0	0	15	6.58	0.166	1.83e-5	1.81e-5	0.994
sUVs	10	0	0	0	15	6.58	0.333	1.83e-5	1.69e-5	0.927
sUVs	10	0	0	0	15	6.58	4	1.83e-5	1.65e-5	0.903
sUVs	10	0	0	0	15	6.58	8	1.83e-5	1.35e-5	0.741
sUVs	50	0	0	0	15	6.58	0	2.03e-5	2.03e-5	1.000
sUVs	50	0	0	0	15	6.58	0.333	2.03e-5	1.58e-5	0.780
sUVs	50	0	0	0	15	6.58	1	2.03e-5	1.49e-5	0.737
sUVs	50	0	0	0	15	6.58	1.5	2.03e-5	1.32e-5	0.650
sUVs	50	0	0	0	15	6.58	2	2.03e-5	1.20e-5	0.593
sUVs	50	0	0	0	15	6.58	4	2.03e-5	1.02e-5	0.502
sUVs	50	0	0	0	15	6.58	6	2.03e-5	8.01e-6	0.395

sUVs	50	0	0	0	15	6.58	8	2.03e-5	3.92e-6	0.193
sUVs	0	0	0	100	15	6.58	0	1.91e-5	1.91e-5	1.000
sUVs	0	0	0	100	15	6.58	4	1.91e-5	1.77e-5	0.923
sUVs	0	0	0	100	15	6.58	6	1.91e-5	1.65e-5	0.861
sUVs	0	0	0	100	15	6.58	8	1.91e-5	1.60e-5	0.834
sUVs	0	0	0	0	15	6.58	0	1.54e-5	1.54e-5	1.000
sUVs	0	0	0	0	15	6.58	0.166	1.54e-5	1.48e-5	0.958
sUVs	0	0	0	0	15	6.58	0.5	1.54e-5	1.45e-5	0.940
sUVs	0	0	0	0	15	6.58	2	1.54e-5	1.41e-5	0.912
sUVs	0	0	0	0	15	6.58	4	1.54e-5	1.36e-5	0.885
sUVs	0	0	0	0	15	6.58	6	1.54e-5	1.35e-5	0.873
Sun	0	0	0	100	15	6.58	0	2.03e-5	2.03e-5	1.000
Sun	0	0	0	100	15	6.58	0.333	2.03e-5	1.94e-5	0.952
Sun	0	0	0	100	15	6.58	0.5	2.03e-5	1.87e-5	0.920
Sun	0	0	0	100	15	6.58	2	2.03e-5	1.52e-5	0.748
Sun	0	0	0	100	15	6.58	4	2.03e-5	1.17e-5	0.576
Sun	0	0	0	100	15	6.58	6	2.03e-5	7.74e-6	0.380
Sun	0	0	0	100	15	6.58	8	2.03e-5	3.41e-6	0.167
Sun	0	0	725	0	15	6.58	0	2.18e-5	2.18e-5	1.000
Sun	0	0	725	0	15	6.58	0.166	2.18e-5	2.15e-5	0.982
Sun	0	0	725	0	15	6.58	0.333	2.18e-5	2.09e-5	0.959
Sun	0	0	725	0	15	6.58	0.5	2.18e-5	2.02e-5	0.927
Sun	0	0	725	0	15	6.58	1	2.18e-5	1.96e-5	0.895
Sun	0	0	725	0	15	6.58	1.5	2.18e-5	1.92e-5	0.880
Sun	0	0	725	0	15	6.58	2	2.18e-5	1.89e-5	0.864
Sun	0	0	725	0	15	6.58	4	2.18e-5	1.46e-5	0.667
Sun	0	0	725	0	15	6.58	6	2.18e-5	9.68e-6	0.443
Sun	0	0	725	0	15	6.58	8	2.18e-5	4.80e-6	0.220
sUVs	0	0	725	0	15	6.58	0	2.10e-5	2.10e-5	1.000
sUVs	0	0	725	0	15	6.58	0.333	2.10e-5	2.10e-5	0.998
sUVs	0	0	725	0	15	6.58	1.5	2.10e-5	2.05e-5	0.975
sUVs	0	0	725	0	15	6.58	2	2.10e-5	2.00e-5	0.952
sUVs	0	0	725	0	15	6.58	4	2.10e-5	1.92e-5	0.916
sUVs	0	0	725	0	15	6.58	6	2.10e-5	1.77e-5	0.842
sUVs	0	0	725	0	15	6.58	8	2.10e-5	1.71e-5	0.813
Sun	0	61	0	0	15	6.58	0	2.13e-5	2.13e-5	1.000
Sun	0	61	0	0	15	6.58	0.166	2.13e-5	2.05e-5	0.960
Sun	0	61	0	0	15	6.58	0.5	2.13e-5	1.95e-5	0.913
Sun	0	61	0	0	15	6.58	1	2.13e-5	1.82e-5	0.853
Sun	0	61	0	0	15	6.58	1.5	2.13e-5	1.75e-5	0.821
Sun	0	61	0	0	15	6.58	2	2.13e-5	1.64e-5	0.767
Sun	0	61	0	0	15	6.58	4	2.13e-5	1.18e-5	0.554
Sun	0	61	0	0	15	6.58	6	2.13e-5	7.00e-6	0.328
Sun	0	61	0	0	15	6.58	8	2.13e-5	3.62e-6	0.170
sUVs	0	61	0	0	15	6.58	0	2.06e-5	2.06e-5	1.000
sUVs	0	61	0	0	15	6.58	0.333	2.06e-5	1.92e-5	0.934
sUVs	0	61	0	0	15	6.58	0.5	2.06e-5	1.88e-5	0.916
sUVs	0	61	0	0	15	6.58	1	2.06e-5	1.85e-5	0.898
sUVs	0	61	0	0	15	6.58	1.5	2.06e-5	1.80e-5	0.876
sUVs	0	61	0	0	15	6.58	2	2.06e-5	1.73e-5	0.841
sUVs	0	61	0	0	15	6.58	6	2.06e-5	1.66e-5	0.806
sUVs	0	61	0	0	15	6.58	8	2.06e-5	1.67e-5	0.809
sUVs	0	0	0	100	15	6.58	0	1.43e-5	1.43e-5	1.000
sUVs	0	0	0	100	15	6.58	0.166	1.43e-5	1.33e-5	0.926
sUVs	0	0	0	100	15	6.58	0.333	1.43e-5	1.26e-5	0.878
sUVs	0	0	0	100	15	6.58	4	1.43e-5	1.06e-5	0.738
sUVs	50	0	0	0	15	6.58	0	2.36e-5	2.36e-5	1.000
sUVs	50	0	0	0	15	6.58	0.5	2.36e-5	1.68e-5	0.713
sUVs	50	0	0	0	15	6.58	1	2.36e-5	1.51e-5	0.639
sUVs	50	0	0	0	15	6.58	4	2.36e-5	1.35e-5	0.574
sUVs	50	0	0	0	15	6.58	8	2.36e-5	1.19e-5	0.503
sUVs	50	0	0	0	15	6.58	72	2.36e-5	1.43e-7	0.006
sUVs	50	0	0	0	15	6.58	87	2.36e-5	1.24e-7	0.005
sUVs	0	61	0	0	15	6.58	0	2.17e-5	2.17e-5	1.000
sUVs	0	61	0	0	15	6.58	0.5	2.17e-5	1.99e-5	0.921
sUVs	0	61	0	0	15	6.58	1	2.17e-5	1.94e-5	0.898
sUVs	0	61	0	0	15	6.58	1.5	2.17e-5	1.74e-5	0.802
sUVs	0	61	0	0	15	6.58	2	2.17e-5	1.72e-5	0.795
sUVs	0	61	0	0	15	6.58	4	2.17e-5	1.61e-5	0.743
Sun	50	0	0	0	15	6.58	0	2.72e-5	2.72e-5	1.000
Sun	50	0	0	0	15	6.58	0.5	2.72e-5	2.08e-5	0.767
Sun	50	0	0	0	15	6.58	1	2.72e-5	1.96e-5	0.720

Sun	50	0	0	0	15	6.58	2	2.72e-5	1.86e-5	0.685
Sun	50	0	0	0	15	6.58	4	2.72e-5	1.17e-5	0.432
Sun	50	0	0	0	15	6.58	6	2.72e-5	4.51e-6	0.166
Sun	50	0	0	0	15	6.58	8	2.72e-5	3.01e-6	0.111
sUVs: Simulator solar Oriel Corp.; LPUV: low pressure lamp 56001721; MPUV: medium pressure lamp 56033091										



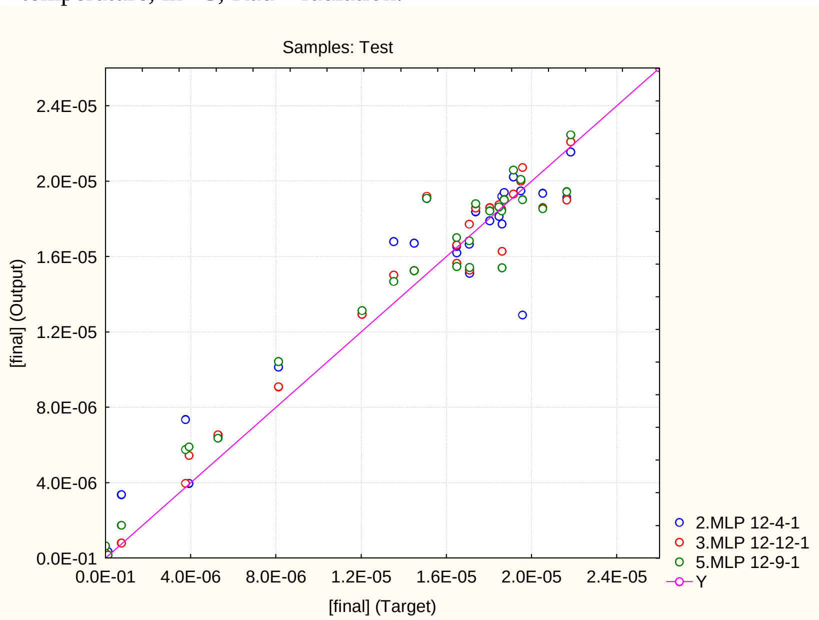
Experimental design for model-based learning

Analysis of data obtained in irradiation experiments was performed using multiple regression followed by construction of a neural network (see figure above). In the neural network, each node of a layer is connected with a certain weight to each node in the next layer. As can be seen, all four hidden neurons come with equal contributions to the output, which is checked by applying the sensitivity analysis, which quantitatively assesses the impact of input variables on output change (final concentration). Sensitivity analysis is also applied to investigate the robustness of model predictions (table below).

Sensitivity analysis for output (final concentration) to learning

	tim[h]	**pH**	**[init]**	**H_2O_2**	**NO_3^-**	**HCO_3^-**	**Fe^{3+}**	**tem[°C]**	**Rad**
2.MLP 12-4-1	7.45508	1.014023	9.65632	3.80291	1.051974	1.021354	0.992547	1.034736	10.7779
3.MLP 12-12-1	26.43648	1.025004	5.50293	5.37208	1.456305	2.297923	1.493637	1.403912	62.2158
4.MLP 12-6-1	18.38192	1.268011	19.41200	4.64322	1.146919	1.196185	1.332593	1.021057	20.5749
5.MLP 12-9-1	19.23526	1.062013	34.09111	10.52477	1.098256	1.356908	3.526223	1.297325	228.4584

Legend: MLP – Multilayer Perceptron; tim[h] – time, in hours; [init] – initial concentration; tem[°C] – temperature, in °C; Rad – radiation.



Output vs. target on testing set for the selected networks

Choosing one of the four obtained neural networks depends on their behaviour at testing (figure above).

CONCLUSIONS

1. The comprehensive study conducted during 2009 - 2011 for physico-chemical characterization and evaluation of wastewater at entrance and exit of Mediaş's treatment plant revealed pollution level of the area. The following physico-chemical indicators were monitored: pH, total suspended matter (TSM), chemical oxygen demand (COD), biochemical oxygen demand (BOD_5) and containing ammonium (NH_4^+).

The highest purification degree (80 %) was found for BOD_5, which in 2010 reached 90 % maximum efficiency at the station during supervised treatment. Good yields were obtained in terms of materials in suspension (~ 79 %) and COD (75 %).

The most acute problem is the removal of ammonium from wastewater, the effluent leaving with large load of NH_4^+, whereas the rate of treatment in this case varies between 14 - 29 %, much lower than for other parameters.

By the difference of obtained values for the influent and effluent, the efficiency of the wastewater treatment plant was estimated (an average of about 73 % for the 30 months of monitoring) and also of the conventional method used for purification.

2. Given the large number of experimental data obtained, a mathematical analysis model was build to determine correlations between parameters and the influence they exert on the treatment process. Additional variables "year" and "month" were also included in the analysis, to record the extent to which seasonality affects wastewater.

Originality in obtaining the mathematical model consists in applying and comparing the following statistical methods: analysis of association (in which a cluster tree was built using simple linkage and representing the difference 1-r, where r is the Pearson coefficient), principal component analysis, multiple regression analysis (involving the strongest association observed between variables) and a comparison based on averages of paired data (t-test Student).

The association analysis shows that the strongest relationship is established between BOD_5 and COD (correlation coefficient of 0.9) at exit of treatment plant, followed by the same combination of variables (correlation coefficient of 0.7), this time at entrance in the station. The relationship between NH_4^+ at entrance and BOD_5 and COD group at exit, shows that the efficiency of biological treatment is affected by ammonium content.

Results obtained by association analysis were confirmed by principal component analysis (the first three factors explaining 70 % of variance). Projection of the variables on the factor-plane is able to highlight more detailed around which observable are identified variation factors.

Multiple regression analysis allowed more accurate setting of interdependence between BOD_5 and COD at the entrance to the treatment plant, respectively a regression equation explaining about 48 % of CCOCr_in variance in dependence of CBO5_in variance.

Comparing paired values of parameters averages (Paired Two Sample for Means Test) statistically significant differences between them were highlighted, in order to estimate the extent to which the treatment produced differences in the values of environmental parameters under control and monitoring of treatment plant and, on the other hand, how much from one year to another systematic changes appeared, likely to affect quality of untreated and, respectively, treated water.

3. The original model, statistically significant, thus obtained, allows the analytical expression of the intrinsic link established between the determined physical and chemical parameters, but also the analysis of trends over time. This forecasting method has a significant contribution to modeling and thus improving the efficiency of treatment.

4. Microbiological monitoring of wastewater at entrance and exit of the Mediaş's treatment station was directed to determine the following hygienic and sanitary indicators: mesophilic aerobic total bacteria at 22 °C and 37 °C, the probable number of coliform bacteria (total coliforms), the probable number of thermotolerant coliform bacteria (faecal coliforms), the probable number of faecal streptococci and the probable number of *E. coli*. Following the treatment, in 2010 decreases in microbial load up to four magnitude orders were recorded.

5. To determine the dynamics of pollution in the city of Mediaş, major polluters were identified, while making a review of their own pre-treatment and purification stations.

Using simple linkage and Euclidean distance while grouping average values of the parameters, a cluster tree was built in order to illustrate the associations established between companies, making an analysis of similarity based on finished products but at the same time the environmental significance lies in similarity which they possess regarding the pollutants they are producing.

6. For the first time water quality factors were estimated based on measured values at economic agents' checkpoints using interpolation by spline functions. The originality of the method lies in trying to assess water quality by applying a similar estimation grid used in the analysis, characterization and soil taxonomization used by USDA to provide information on which to take decisions for locating various types of economic agents, crops, and residential areas, decisions that maximize resources and, respectively, to minimize potential damage due to unfavorable environmental conditions.

The applied method allowed spot visualization of pollution level in the city of Mediaş.

7. To assess the impact of Mediaş's wastewater discharge on Târnava Mare River (which crosses the region) the effluents from municipal sewage treatment plant and three sections located on river's course (Mediaş, Copşa Mică, Micăsasa) were physico-chemically monitored, while the river upstream and downstream of Mediaş was microbiologically supervised.

The comprehensive study done on the course of Târnava Mare River concluded that its water falls to a steady and satisfactory level, respectively in the second category of quality.

Hygienic-sanitary quality of Târnava Mare River was determined on eight groups of bacteria: total mesophilic bacteria (NTGM), total coliforms (TC), faecal coliforms (FC), faecal enterococci (streptococci) (EF), *Escherichia coli* (EC), sulphite-reducing clostridium (CSR), coagulase-positive staphylococci (SCP), *Pseudomonas aeruginosa* (PA). All species were found in the river, downstream microbial load is higher than upstream, which demonstrates the need to modernize Mediaş's treatment plant, due to possible presence of pathogens, necessity justified by the presence of the genus *Escherichia*.

Purification degree of downstream Târnava Mare is 60 %, the category II of quality, while upstream drops to 50 % (in category III).

8. In the section downstream of Mediaş's WWTP there is a considerable increase in ammonifying bacteria, thus confirming the results set by the mathematical model presented in the conclusion 2, meaning that poor NH_4^+ treatment (conclusion 1) is justified and also its negative influence of ammonium on the treatment process.

9. A personal contribution is applying of the unconventional, ecological method, of wastewater treatment using zeolite tuff of Rupea, thus following the optimization of cost/efficiency ratio of the treatment method. In Romania, the use of of zeolite tuff in alternative applications for retention of pollutants in the environment is in shy development stage.

From low efficiency (14 - 29 % for ammonium) of the conventional method of wastewater treatment applied to Mediaş's municipal station, linked to the clinoptilolite's property of representing an excellent selective exchanger for ammonium cations, experiments of wastewater treatment using zeolite layers of different thickness (1, 2 and respectively 3 cm) were performed. They same physical and chemical parameters as for the conventional method of treatment were analyzed.

An excellent removal of organic substances and suspended materials was achieved. Ammonium removal efficiency reached values of 50 %. Overall, the degree of purification of the zeolite method was placed around the mean value of 90 %.

10. It has been shown by experiments, that even if a small height of zeolite bed (1 cm) is used, purification yield is still very important, heavily weighing in quantifying operational cost/efficiency of application ratio, as well as in large scale application of the proposed method.

11. Comparing the conventional and unconventional methods of wastewater treatment, there can be seen a net improvement in the efficiency of the latter. Thus, in the case of biochemical oxygen demand, the purification degree increases from 80 % (conventional method of treatment) til about 100 % (unconventional method), suspended materials are removed at a rate of 79 % classically and 90 % with zeolite, the yield of chemical oxygen demand improved from 75 % to 80 %.

Increase of efficiency has been spectacular in terms of ammonium; removal efficiency has doubled, from 14 - 29 % to 50 % by using a zeolite bed 3 cm thick.

12. Since the presence of pollutants such as alkylphenols and their derivatives poses a threat to aquatic life due to their toxic and estrogenic effects, but also their reduced biodegradability, it is necessary to continuously monitor their removal and seeking removal solutions. Octylphenol reach the aquatic environment mainly by effluents discharged from wastewater treatment plants.

In Romania, until now, has not been expressed a concern in terms of identifying and removing these compounds from wastewater and surface water.

Therefore, an experimental design was built for the first time in this paper, in order to reveal factors involved in OP photodegradation and each of their influence upon the observable of the process (*p*-octylphenol concentration) during changes that OP suffers in surface water under the influence of solar radiation.

13. In case of experiments conducted on synthetic medium of OP, increased pH and temperature, low initial concentration, presence of hydrogen peroxide, of nitrate ion and dissolved organic carbon are factors leading to accelerating OP photodegradation. Instead, carbonate ions and iron (III) decrease the reaction rate.

14. Kinetic models were developed for processes that occur under the influence of solar radiation, depending on the chemical processes that occur and the frequency or speed at which they are carried out in order to describe analytically the process of decay under the UV action.

15. Experiments conducted in natural environment (water from the Rhine River and Lake Hohloh) led to lower yields of octylphenol degradation than in synthetic solutions of OP, which is explained by shielding light in aquatic systems by natural dissolved materials (DNOM) present in natural waters.

16. Experiments management aimed to compare the effects of different radiation sources. Thus, it was found that in all cases, the real solar radiation is more effective in removal of OP than UV solar simulator, which is explained by the different spectra of radiation sources used.

Best OP degradation, both in terms of efficiency and the duration is achieved by medium pressure mercury lamp (MP-UV).

17. By using HPLC some intermediate compounds of octylphenol decomposition were determined, but they have not yet been identified, representing a challenge for future research.

18. It was designed and developed a mathematical model to set the action of UV radiation on synthetic solutions of octylphenol in ultrapure water; the model's originality consists in applying, in parallel, two types of statistical analysis: multiple regression analysis and analysis using neural networks.

Using multiple regression analysis an additive model was obtained in which the statistically insignificant parameters were removed using **Backward Stepwise Method** and is able to explain about 50 % of the variance, which means that all factors have an important contribution with additive effect.

For supervised learning method (backpropagation) examples based, a neural network Multilayer Perceptron (MLP) type was used. Learning was done on 80 % of the total 138 factors (chosen randomly), while testing was applied to the remaining 20 % of the factors.

Neural network was able to illustrate the continuity of dependence between initial radiation and the octylphenol expected and estimated concentration/quantity, continuity raised by systematic observations at different radiation and under different experimental conditions that neural network was learned to, an effect that, on the other hand, is very difficult if not impossible to rebuild by other means, because of the complexity of experimental instrumentation to filter different radiation wavelengths and intensities divided often enough so that similar result can get from the experiment as the result of proposed neural network model.

The result obtained by neural network is significantly higher than the one achieved by multiple regression analysis. Determination of the neural network is 89 % compared with a determination of only 50 % for multiple regression analysis.

19. To evaluate the OP remaining estrogenic effect after the natural and artificial ultraviolet irradiation, YES test (Yeast Estrogen Screen) was applied. From all varied conditions applied in experimental protocols, the most effective concentration was found to be initially 50 mM H_2O_2 added to OP solution, when estrogenic activity practically disappeared.

20. All experiments aimed to determine octylphenol decreasing monotony, but that may take place at different rates, given by kinetics of degradation processes (under the influence of various substances in the analyzed medium under influence of UV radiation used for this purpose).

21. The present study demonstrates that the degradation of octylphenol aqueous solutions under influence of real and simulated solar radiation is quite slow.

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