Babeş-Bolyai University Cluj-Napoca

Faculty of Physics

Doctoral Thesis Summary

CONTRIBUTIONS TO THE STUDY OF THE ADVANCED OXIDATION PROCESSES WITH APPLICATIONS IN WATER DECONTAMINATION

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INTRODUCTION

The utilisation of the water resources as drinkable water sources or as raw material in the industry field, in the health field or in the analytical one, given the enhancement of the pollution and contamination degree, is a real challenge for the processes and technologies developers. The classic decontamination processes and technologies have become obsolete, notably in connection to species and groups of chemical pollutants that are refractory to the degradation processes used at present: humic acids, dioxans, phenols, phtalated substances, perchlorates, secondary disinfection products, pharmaceutical products (including the endocrine disruptors), fluorinated surfactant substances. The physical-chemical processes known under the generic name of *'Advanced Oxidation Processes'* (AOP) constitute a current field of interdisciplinary scientific research, enabling the oxidative, non-selective and strong degradation of the organic and inorganic substances from the aqueous environment in the presence of the highly reactive ^{o}OH radical species. We may speak about the action of the low temperature plasmas, about advanced oxidation processes with O_3 in an aqueous environment, about advanced oxidation processes in O_3/UV, H_2O_2/UV, H_2O_2/O_3, H_2O_2/O_3/UV systems, about Fenton processes, about heterogeneous photocatalysis processes, about electro-hydraulic cavitation and sonolysis, about water hyper-critical oxidation processes and about the action of the γ radiation and of the cathode beams.

The thesis sets out the author's contributions to the theoretical and practical study of a particular family of advanced oxidation processes, namely the advanced oxidation processes with ozone (O_3) and O_3/UV advanced oxidation. The approaches are theoretical and applicative in nature, including the elaboration and the implementation of certain numerical models, experimental studies, the design, the creation and the implementation of advanced oxidation processes at real scale. The former part of the thesis represents a thorough study and a synthesis of the literature in the field, with the author's own interpretations and structurations. The latter part comprises his own original contributions in the field. O_3/aqueous solution contacting processes and systems, O_3/UV advanced oxidation processes in photolysis reactors, O_3/UV advanced oxidation systems in a pressurized flow are tackled with theoretically and from the numerical modeling and the practical implementation standpoint. The numerical models have involved the utilisation of concepts and methods taken over from fluid dynamics (CFD - Computational Fluid Dynamics), combined with physical and chemical models linked to processes of convection, diffusion, energetical irradiation and reaction.

The applicative researches carried out could be done thanks to the financing granted by the Ministry of Education and Research for as many as 4 research projects coordinated by the thesis author in his capacity of project manager, the result hereof being the publication of 4 papers in ISI-rated publications, of 21 papers in other specialised publications and the submission of 4 invention patent applications at The State Office for Inventions and Trademarks.

Key words : *advanced oxidation, ozone, photocatalysis, Computational Fluid Dynamics*

PART I. BIBLIOGRAPHIC SURVEY

1. Advanced oxidation processes used for water disinfection, decontamination and treatment

The advanced oxidation processes (AOP) are deemed to be those oxidation processes that involve the synergic action of the highly reactive species of free radicals (the most frequent ones being the ^{o}OH radicals), whose action may lead to the almost complete degradation (till mineralisation, in case of the organic substances) of the chemical compounds that are refractory to the usual processes of oxidative degradation [1,2].

1.1. The oxidation with O_3 in an aqueous solution

Ozone, under a gaseous form, with the view of its utilisation for laboratory or technological purposes, can be produced from oxygen or from dry air, by DBD (Dielectric Barrier Discharge)-type electrical discharges, within discarging systems that generally have a coaxial geometry (Fig.1.1), the forming reactions being based on collisional mechanisms of oxygen molecules splitting, followed by recombination processes [3].

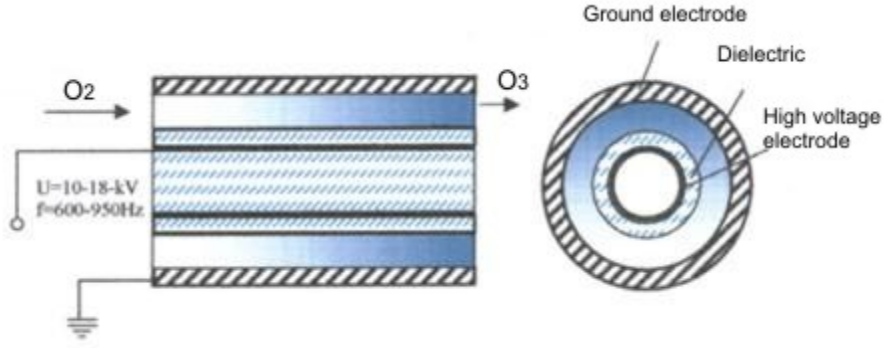


Fig.1.1. The structure of a discharge coaxial DBD system for ozone production

In the aqueous environment, the global ozone decomposition reaction entails the production of free radicals, two molecules of ^{o}OH resulting from the reaction of three molecules of ozone [4]. The ozone treatment systems in an aqueous environment can be simple contact and gas/liquid reaction systems or catalytic systems, which involve the participation of a catalyser, both in a dissolved condition (the homogenous catalysis) and in a distinct phase, as it is the case of the heterogeneous catalysis, with an aim to enhance the efficiency of obtaining the highly reactive species of ^{o}OH radicals.

1.2. H_2O_2/O_3 advanced oxidation processes

The ozone dissociation in an aqueous environment in the presence of H_2O_2 leads to the appearance of the free radicals $(OH)^o$ and of the O_2^{o-} superoxide ion [5]. The O_2^{o-} superoxide ion continues to further the ozone decomposition process.

1.3. The UV/H_2O_2 advanced oxidation

In this case, the free radicals generation process can be looked upon as a process of H_2O_2 direct photolysis [4,5]:

$$H_2O_2 \xrightarrow{h\vartheta} 2(OH)^o \qquad \text{with } \varepsilon_{254} = 18.6\ M^{-1}\ cm^{-1} \text{ (molecular absorptivity at } \lambda=254 \text{ nm)} \qquad (1.1)$$

1.4. O_3/UV advanced oxidation processes

Both the O_3/UV advanced oxidation systems (the ozone photolysis) and the photocatalysis systems lead to the generation of ^oOH free radicals, according to successive reaction chains [6,7]. The global reaction rate for the ozone photolysis process is proportional with the product between the quantic yield of the photolysis reaction and the energy of the UV radiation absorbed in the time unit and in the volume unit [8,9]. The O_3/UV advanced oxidation systems involve the action of two inter-conditioned physical-chemical processes : 1) the gas/liquid mass transfer (O_3/aqueous solution), which is a physically distinct phase, followed by subsequent chemical processes of decomposition of the solubilised ozone ; 2) the transfer of the ultraviolet radiation photons ($\lambda < 310$ nm) in the solution and the initiation of the specific reaction chains.

1.5. Fenton-type processes

The Fenton reactive, used within the classic Fenton process, is a mixture of ferrous ion (Fe^{2+}) (the catalyser) and hydrogen peroxide (the oxidising agent), being known as a strong oxidiser for the organic contaminants [10,11]. The photo-Fenton process involves the formation of the OH^o radicals by the hydrogen peroxide photolysis (H_2O_2/UV) and the Fenton reaction (H_2O_2/Fe^{2+}) [12]. The electro-Fenton process includes electrochemical reactions for the *in situ* generation of the reactives used for the Fenton reaction [13].

1.6. Conclusions

Even though, by the decomposition in an aqueous environment, ozone may lead to the appearance of free radicals, the efficient systems involve the presence of partners in the chain of the physical and chemical processes, as it is the case of the UV radiation, of the presence of the oxygen peroxide or of the photo-catalytic substances. The ^oOH free radicals formation processes are similar to the couples of advanced oxidation of the O_3/UV and H_2O_2/UV type. The performance of the advanced oxidation systems that involve ozone as a process partner crucially depends on the performances of the gas/liquid mass transfer process, on the geometry and the hydrodynamic parameters of the reaction

system. The presence of photocatalytic processes further brings along the necessity of assessing the performances of the photonic transfer processes in the solution.

2. Decontamination processes at the surface of the semiconductors and nanostructured materials

2.1. Heterogeneous photocatalysis processes

The photocatalytic oxidation processes at the surface of the semiconductors in an aqueous solution are processes where the semiconductor, after the absorption of a photon with an appropriate energy, acts like a photocatalytic substrate, giving birth to species of strongly reactive radicals, likely to oxidise the organic substances [14]. The processes of generating the electron-hole pairs constitute the determining factor for the efficiency of using a certain semiconductive compound in photocatalysis processes [15,16]. For the improvement of the photocatalytic activity for specific processes involving TiO_2 (which is the most frequently used photocatalytic compound at the moment) as a photocatalytic environment one may consider several action lines, linked both to the properties and the structure of the semiconductive material and to the configuration and the operational parameters of the reactors used [17,18,19,20]. The classification of the experimental photocatalytic reactors is made both according to the manner of distributing the photocatalytic mass (the photocatalyser being in suspension or immobilised) and according to the distribution of the field created by the radiation source (immersed source, external source, distributed source). In case of the O_3/UV/TiO_2 advanced oxidation systems, subject to the configuration of the ozone in the solution mass transfer system, there can be two basic configurations: with a free level, under atmosphere pressure, and in an pressurized system [21].

2.2. Applications of the nanostructured systems for direct disinfection processes

This sub-chapter sets out considerations on the direct disinfection processes in aqueous systems that include nanostructured constituents of certain noble metals, especially silver. The generally accepted idea is that the antibacterial activity of silver is induced by the interaction with the thiol groups or with some other groups of sulphur that are present in the cellular membrane of the microorganisms, which leads to the death of the cell [22]. As far as the effect of the Ag nanoparticles is concerned, some researchers have suggested that their presence in the solution leads to their detachment from the cellular membrane [23]. Antibacterial properties have also been noticed on altered substrates, on account of the presence of the Ag nanostructures. In case of the colloidal dispersions, the nanoparticles attachment to the cellular membranes gives rise to disturbances of the

bacteria's breathing and permeation process, even though the phenomenon is not yet fully comprehended.

2.3. Conclusions

The heterogeneous photocatalysis processes have clear advantages in the degradation of certain contaminants from the aqueous environment (such as microorganisms, toxins, micropollutants), amongst which : the non-selective degradation of the pollutants (be they organic or inorganic) till the level of extremely low concentrations (ppb), under normal pressure and temperature conditions [24], the utilisation of oxygen as the main oxidiser, the possibility of simultaneously inducing both oxidation reactions and reduction reactions [25,26,27]. Seeing the various kinds of photoreactors, the physical processes of mass transfer and photonic transfer are important, which are regarded from the viewpoint of the establishment of strict optimisation phases.

The antibacterial properties of the Ag nanostructures are well-known and outlined by countless approaches in the literature. The correlation of the disinfection properties to certain physical, especially optical properties of these nanostructures may enable their direct characterisation from the point of view of the antibacterial efficiency. An important part seems to be played by the characterisation of these types of surfaces and by their interactions with the environment by means of the UV/VIS optical absorption spectroscopy and by the Raman SERS [28] spectroscopy.

3. Ozone/water contact systems modeling

The advanced oxidation systems where one of the process partners is ozone mandatorily involve a phase of gas/liquid mass transfer. The presence of two systems – the O_3 injection system and the actual contact & reaction system – is involved. The water/ozone contact systems enable the realisation of a minimal time of contact between the gaseous phase and the liquid one and, at the same time, the subsequent initiation of the other physical-chemical stages involved in the advanced oxidation process (the photonic transfer, the decomposition by means of the ^{o}OH radicals generation 'chain', the adsorption at the level of the catalytic and/or photocatalytic sites).

3.1. Basic theoretical principles for modeling the contact systems in a bubble column

The basic processes that come up in the ozone/liquid biphase systems may fall into the following categories : a) processes of injecting gas into a liquid ; b) mixing processes ; c) mass transfer processes ; d) processes linked to chemical reactions and microbial inactivation. The gas/liquid mass transfer is the most important stage in the process of dissolving the gas in the aqueous solution. The modeling of the intimate mass transfer processes can be tackled with both from the standpoint of ***the double film theory*** and of the subsequent development of the same, ***the theory of penetration*** [29,30,31].

3.2. Models for transport and reaction in bubble columns

There are several models for describing the behaviour linked to such phenomena as transport, mass transfer and chemical reactions in bubble columns. The usual models of column reaction are applicable especially to the column treatment by filling materials, supposing that there is a template of the one-dimensional 'plug and flow'-type reactor, where the convection processes take place strictly along the flowing axis [32,33]. The mixed-axial model was notably developed for validating certain experimental data with a view of determining some basic parameters for the operation of the bubble columns [34], taking into account, for the aqueous environment, a perfectly mixed system and for the gaseous enviroment a 'plug and flow'-type template. The mass transfer is governed by two basic parameters : the m equilibrium constant (according to Henry's law) and the global K_La mass transfer coefficient, which is a global unit for the system transfer and can be constant or depend on the z axial coordinate. While the ozone decomposition takes place at a constant value of pH, the ozone decomposition rate is proportional with a power-function of the dissolved ozone concentration [35].

3.3. CFD (Computational Fluid Dynamics) methods for modeling the ozone/water contact systems

The classic design of the real multi-phase contact systems is generally based on the sampling of experimental data and of the utilisation of empirical templates. In case of the real scale systems, taking empirical information is relatively difficult. Need is to elaborate scaling rules that provide geometrical, kinetic and dynamic similarities between the laboratory scale template and the real scale one. There is the paradox of 'reverse scaling', which consists in the physical impossibility of obtaining experimental data and scale empirical templates for microsystems and nanosystems (electronics, nano-technologies, cellular biology).

The evolution of the CFD (Computational Fluid Dynamics) techniques and applications is closely linked to the evolution of the computing technique and of the software elements, notably to the development of the computer networks and of the distributed data processing [36], involving the solving of linear and non-linear systems of differential equations with partial derivatives, the discretisation of the volume fields being the subject-matter of such numerical methods as the finite difference method (FDM), the finite volume method (FVM), the finite element method (FEM). CFD templating is mainly based on the implementation of ***the transport equations*** (mass, moment, energy), which for a multi-component fluid environment can be written under the form of the transport equations for the Φ general functions, considering the notation of the 3 cartesian axes under the following form : x_j (j=1...3) [37].

$$\frac{\partial(\rho_m \Phi)}{\partial t} + \frac{\partial(\rho_m u_j \Phi)}{\partial x_j} = \frac{\partial}{\partial x_j}\left[\Gamma_{eff}\frac{\partial \Phi}{\partial x_j}\right] + S_\Phi \qquad (3.1)$$

ρ_m - the mixture density

u_j - the velocity field in the fluid

Γ_{eff} - generalised exchange coefficients

S_Φ - the terms of the net generalised sources

For the turbulent flow, the values of the generalised exchange coefficients in case of the laminar flow get modified, ***in the sense of adding terms generated by the turbulent flow***, the mixture transporting properties being dictated by **the flow mode** rather than by the intrinsic properties of the environment. Technically speaking, the set of derived equations, namely ***the Navier-Stokes equations,*** can be used, which also include the expressions of the surface stresses that appear at the level of the volume elements of the fluid, which is a formalism that can be applied, with some modifications, in case of discontinuous domains.

There is a common succession of unitary operations with a view of defining and solving a specific problem linked to : the defining of the flow type that is of interest (including the defining of the spatial field), the selection of the relevant transport equations, the generation of the discretisation network, the conversion of the equations with partial derivatives into algebraic equations in the discretisation field, the selection and the implementation of the numerical method of solving the algebraic equations resulted therefrom, as well as data post-processing.

3.4. Conclusions

Ozone/water contact systems modeling mainly implies the modeling of the gas/liquid mass transfer processes and of the transport processes in the volume of the liquid. In case of the geometries with a high degree of symmetry, the processes can be modeled with enough accuracy, according to analytical models that include simplifying hypotheses. In the event of systems with complex geometries or of those that suppose additional physical mechanisms (such as adsorption, migration in a field of forces, photonic absorption), methods that enable the drawing of new physical processes in the entire already existing hydrodynamic template, on the one hand, and the numerical solving of the differential equations systems under specific frontier conditions, on the other hand, are necessary. In this respect, the CFD methods constitute the ideal candidate, first of all thanks to the current computational possibilities of numerically solving the differential equations systems.

PART II. THE AUTHOR'S CONTRIBUTIONS

Part II of the thesis is structured on 5 chapters that follow the logical line of the researches carried out. Chapter 4 sets out theoretical and experimental contributions to the study of the ozone/water contact systems, as a basic step for the implementation of the advanced oxidation systems. Chapter 5 presents contributions linked to the numerical modeling of the under pressure O_3/UV advanced oxidation circuits and systems, on the basis of the functional block-type systemic representation of the ozone ozonisation and photolysis stages, by using experimental data taken as a result of the implementation of a pilot station. Chapter 6 settles issues linked to the numerical modelimg of the physical processes within the O_3/UV advanced oxidation reactors. Chapter 7 presents the author's own practical accomplishments, at the pilot and industrial scale, based on the results of the researches set out in the previous chapters.

4. Theoretical and experimental contributions to the study of the ozone/water contacting processes

Departing from a specific experimental O_3/water contact configuration, the elaboration of a model based on the utilisation of the CFD (Computational Fluid Dynamics) method, for the numerical modeling and the simulation of the O_3/water contact systems, as a preliminary phase for the development of the real systems, is depicted. The system is but treated **physically**, the functions corresponding to the reaction kinetics and to the reaction mechanisms representing only input functions for the model.

4.1. The numerical model of the O_3/water contact system. Experimental data

The analytical templates that describe the gas/liquid mass transfer processes in the column generally remain in the scope of the simple contact geometries [32,33,34]. On the other hand, the numerical models that exclusively use the CFD method often work with data taken from the literature [38] or they need sophisticated experimental techniques, linked to the analysis of tracers or to the LDV (Laser Doppler Velocimetry) analysis [39].

The template drawn up and presented in this section combines the advantages of the simple analytical templates with the advantages linked to the CFD method. The structure of the developed model is based on the coupling between the mixed axial analytical template (used to determine the mass transfer global coefficient) and a CFD model for complex contact geometries (Fig. 4.1). The implemented CFD model is based on the utilisation of the Euler-Euler template adjusted to the biphase flow [40,41].

The experimental configuration used in the numerical model elaboration and validation process consists in an ozone treatment system in a reaction column, according to the block scheme set out in Fig. 4.2. The ozone was produced from 94 % pure oxygen by an ozone generator with a coaxial

discharging structure and with an adjustable ozone output within the 0.2-20 g O_3/h range. Seeing the problem symmetry, for the CFD numerical modeling we used a 2D representation of the contact system, a reasonable computational effort being necessary in this case.

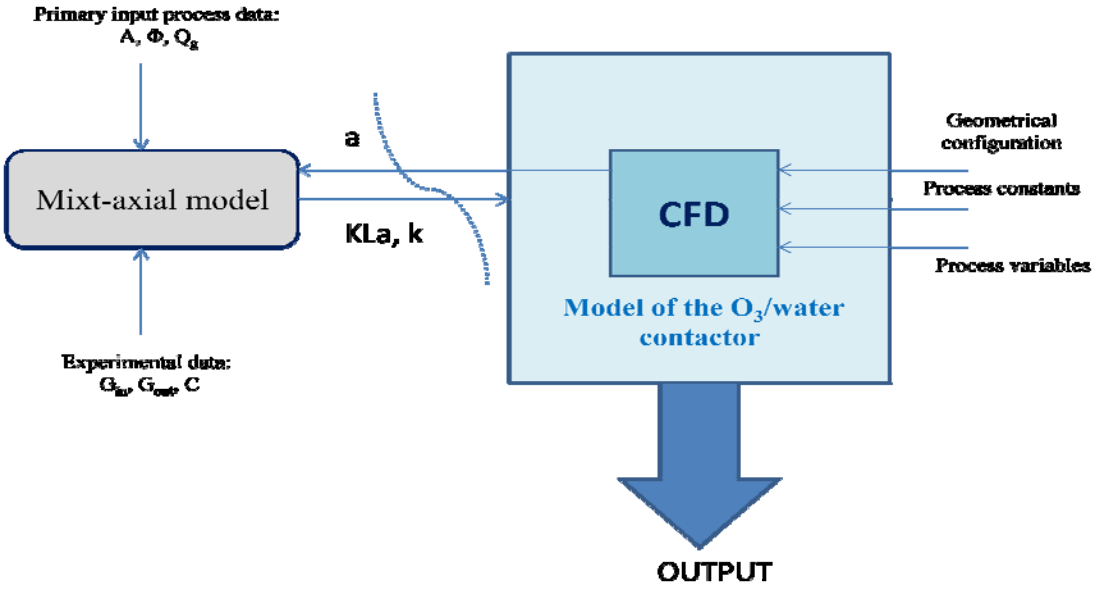


Fig. 4.1. The structure for the model of O_3/water contact system

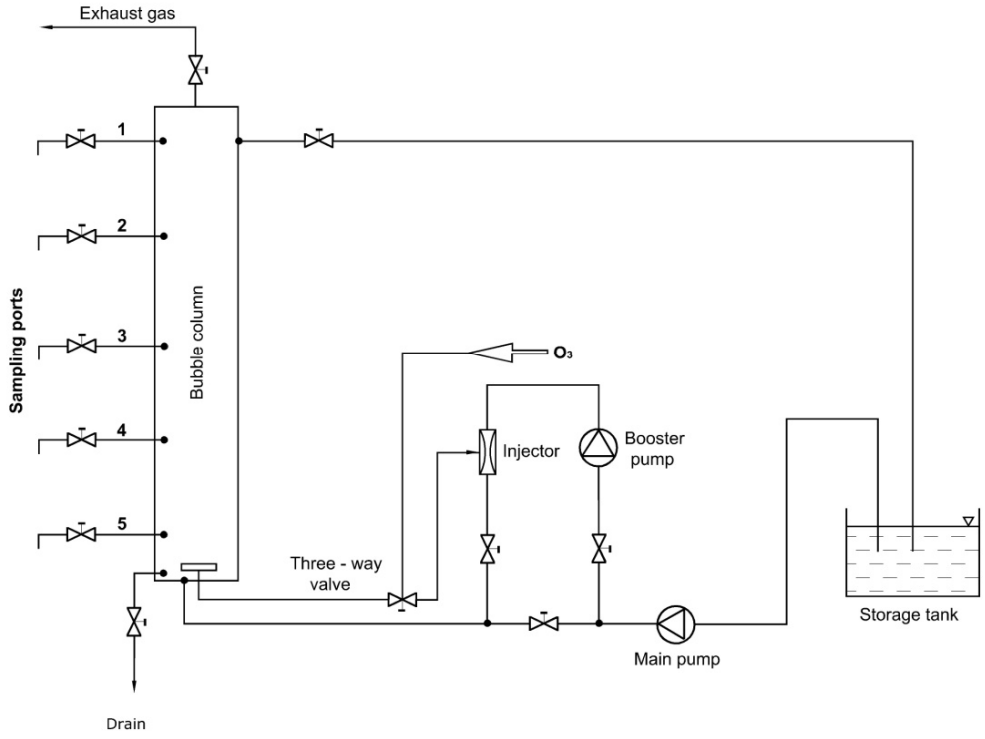


Fig. 4.2. The experimental configuration for the O_3 treatment in the column

In its first part, the experimental protocol aimed at determining the mass transfer global coefficient for the ozonisation column ($K_La[s^{-1}]$) and the k [m/s] mass-related coefficient, by applying the combined template presented above and by using as working fluid pre-processed water by treatment under pressure in an O_3/UV system, with a view of eliminating the initial interferences [42]. The medium value obtained for the K_La mass transfer global coefficient was 0.0037 s^{-1}. Given the implementation of the CFD template for the contact column, we obtained for the mass transfer mean coefficient : $k_{mean} = K_{La}/a_{mean} = 2.14 \times 10^{-5}$ m/s. The values determined by the utilisation of the experimental data and the results of the numerical modeling for the gas/liquid biphase flow were integrated into the extended numerical model, by using the finite element method (FEM). Figure 4.3 presents the variations in time of the experimentaly determined dissolved ozone concentrations (in the median area of the column) and those calculated with the help of the template implemented for various concentrations of ozone upon the entrance in the column [43].

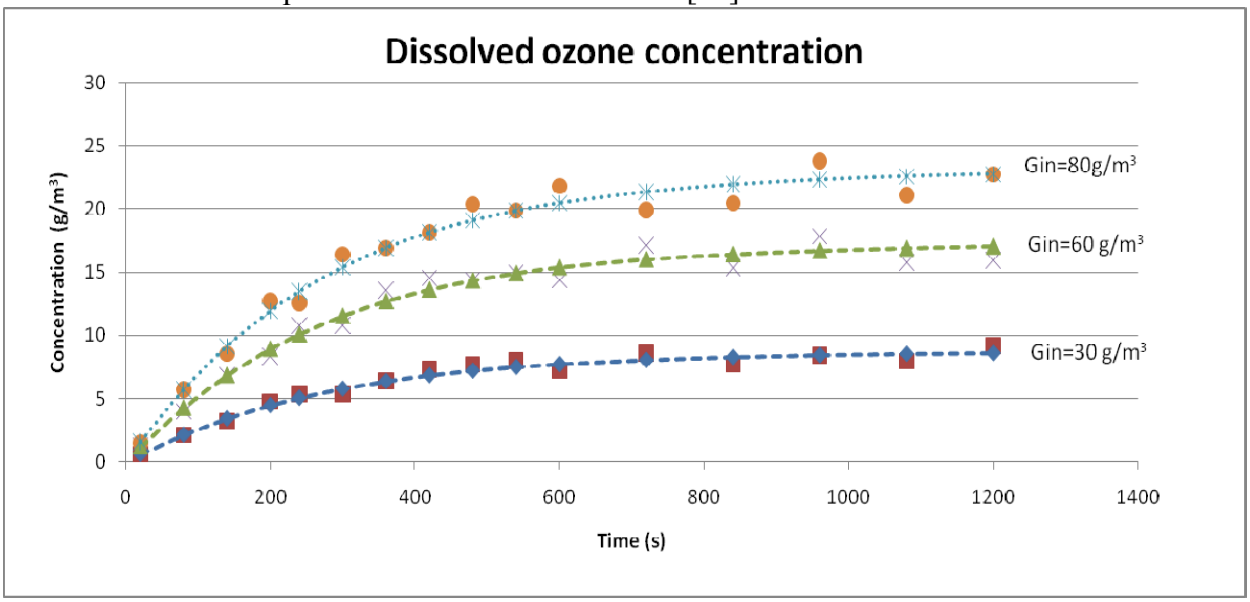


Fig. 4.3. Comparative values for the ozone concentrations upon the exit from the column

The maximal values of the volume fraction of gas are recorded in the proximity of the ozone dispersion device (Fig. 4.4). A good correlation was obtained between the values taken from the template and the experimentally determined ones. The numerical template drawn up was implemented for simulating the evolution of a multi-partitioned ozone/water contact system at real scale (Fig. 4.5).

4.2. Conclusions

The developed numerical template enables the simulation both of the evolution in time and of the behaviour in a stationary mode for the water/ozone contact systems, departing from the geometrical characteristics of the system and from the initial conditions of the process. This template can be applied both to the contact systems in a stationary mode and to those in a co-current flow or

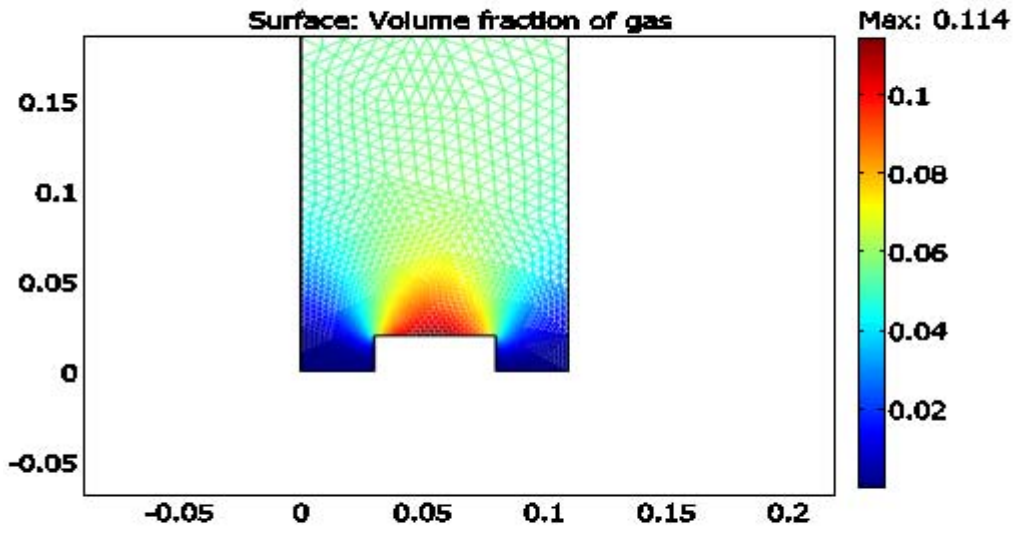


Fig. 4.4. The volume fraction of gas at the bottom of the column

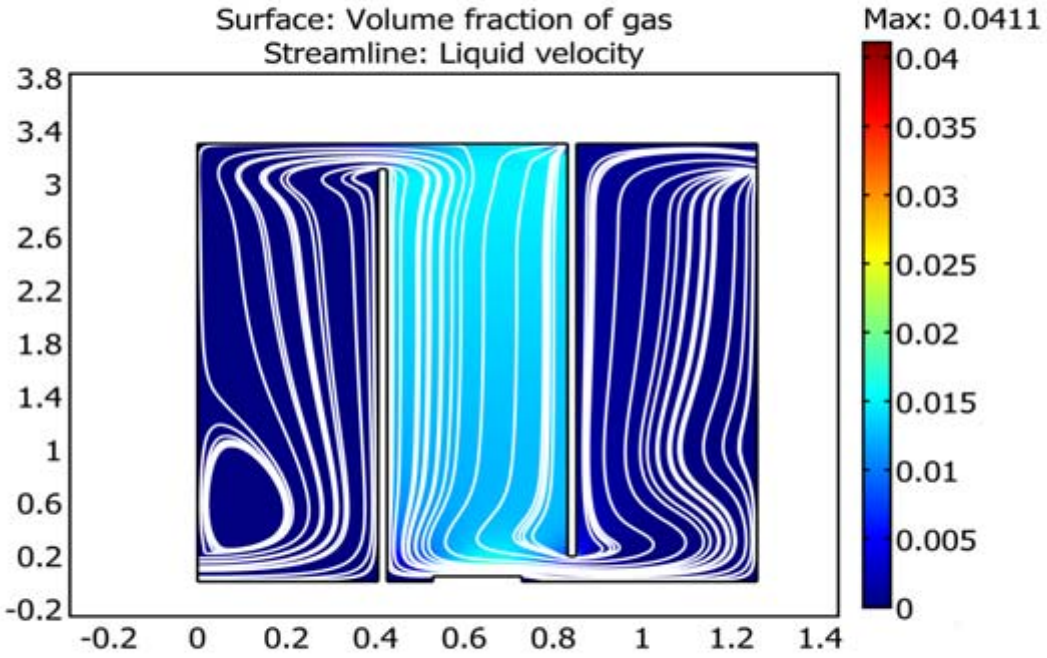


Fig. 4.5.The numerical simulation for the circulation of the ozoned gas and of water in the three compartment system

against the current, to the free level systems or to the under pressure ones and it may constitute the development fundament for more complex models, with the involvement of the ozone decomposition

processes and of the chemical reactions with the natural organic matter (NOM), within multi-phase systems (heterogeneous catalysis systems) or the modeling of the microorganisms inactivation processes in aqueous environments under real operating conditions.

5. The numerical modeling and the experimental study of the circuits and of the O_3/UV pressurized advanced oxidation systems

Subject to the circuits configuration and to the environmental pressure conditions, the O_3/UV advanced oxidation processes may fall into two categories: ozone photolysis systems that operate at atmospheric pressure and systems that operate at pressures higher than the atmospheric one. In terms of efficiency, the process of pressurized photolysis is more attractive, due to the lower rate of ozone desolubilisation from the solution and from the viewpoint of the control capability under industrial conditions. There are studies at the laboratory level linked to the kinetics and the optimal control of the O_3/UV photolysis processes [2,44,45,46], however there are deficiencies related to the experimental study and to the templating of systems at real scale, with an aim to obtain certain calibration parameters needed for the dimensioning of the technological processes and for their automatic control. This chapter presents the experimental study and the numerical modeling of a photolysis system in a configuration that is specific to certain applications linked to the treatment of the waters in a recirculation flow. A study has been carried out on a process of injecting under pressure ozone in a side-stream, followed by O_3/UV pressurized advanced oxidation processes, where the dissolved ozone is the subject of the photolysis process, the presented system constituting the subject-matter of an invention patent application submited to The State Office for Inventions and Trademarks [47].

5.1. The experimental study and method of analysis

According to the block scheme set out in Fig. 5.1, the experimental system has got two basic circuits: a main circuit, where the O_3/UV advanced oxidation reactions take place, and a side-stream circuit, where the process of injecting the ozone by the absorption of an air/ozone mixture at a pre-set concentration by using the INJ injector, mixture and solubilisation by using the MIX static mixer and the (T1) and (T2) reactors, takes place. The system is automatically driven by a PLC module and the data are sent to a SCADA system.

5.2. Experimental results. System modeling

The numerical modeling of the system was performed by using an adaptation of the EPANET (National Risk Management Research Laboratory - USA-EPA) software package [48], adjusted to modeling the stages of treatment in a pressurized system with ozone and UV radiation. Departing

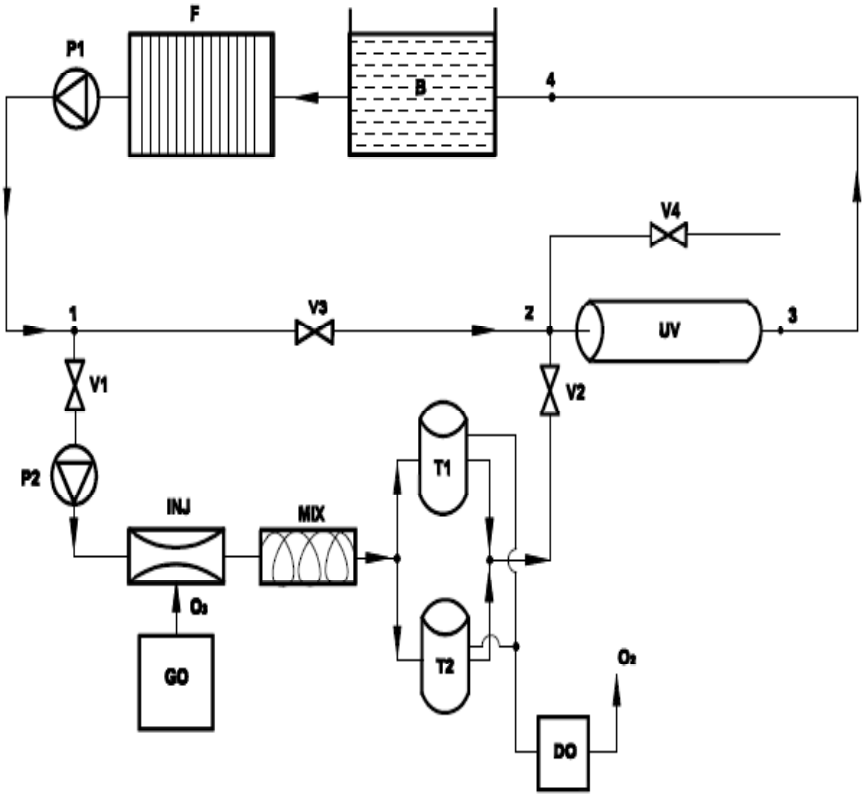


Fig. 5.1. The configuration of the ozone photolysis plant in an pressurized recirculation system

from experimental values of the C_{in}-C_{out} ozone differential concentrations upon the exit from and the entrance in the O_3/UV advanced oxidation reactor (Fig.5.2), according to the templating carried out in EPANET we were able to assess the ozone photolysis reactions rates in the presence of the UV radiation for various values of the relative radiation intensity ($I_R[\%]=(I/I_{max})\cdot 100$), in case of the real scale system (Fig. 5.3) [49].

5.3. Conclusions

For the pressurized circuit of O_3/UV advanced oxidation system, the experimental study carried out on the pilot plant was supplemented by the numerical modeling of the system, carried out according to the EPANET pack, which enabled the performance of accurate predictive analyses related to its operation (the evolution of the ozone concentration, the assessment of the photolysis reactions rate, the parametrical dependance on the concentrations of the injected gaseous phase and of the UV radiation intensity). The depicted model could be used with good results for technologically designing at real scale the O_3/UV advanced oxidation plants and for setting up the basis of the automatic control algorithms for such systems.

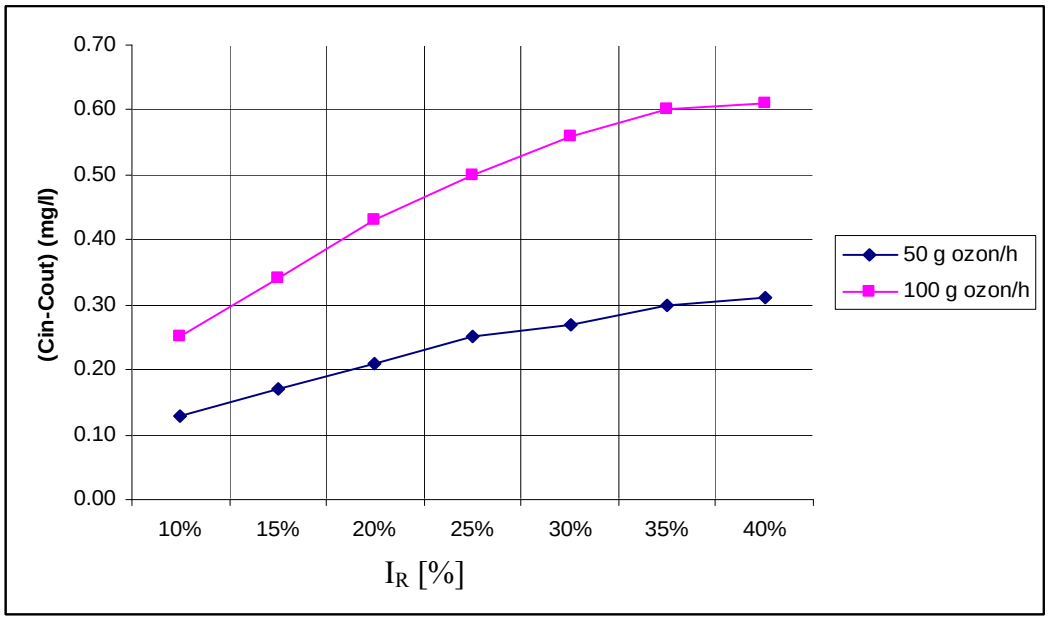


Fig. 5.2. The ozone differential concentration for the UV reactor

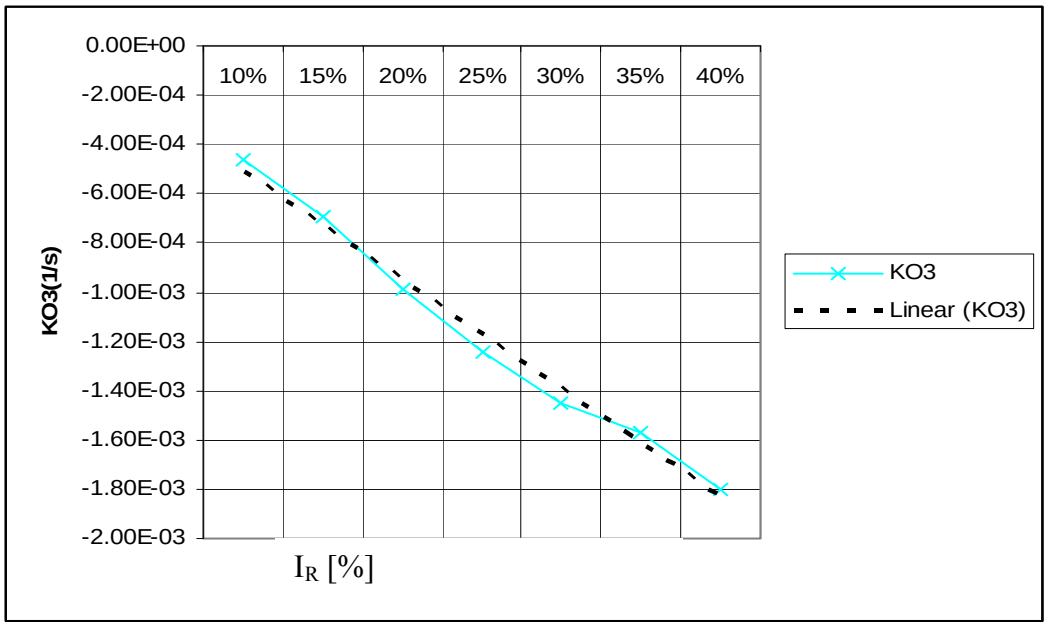


Fig.5.3. Variation of the reaction rate vs UV radiation intensity

6. The numerical modeling and the analysis of the O_3/UV advanced oxidation reactors by using the CFD method

6.1. The CFD model fundaments and hypotheses for the O_3/UV advanced oxidation reactors

The numerical modeling of the photolysis process supposes, first of all, awareness of the spatial distribution of the radiation's energetic intensity. Hypotheses for the CFD model : 1) The fluid flow is governed by the Navier-Stokes equations for incompressible fluids, completed by a k-ε turbulent flow template [37] ; 2) The global reaction kinetics is governed by the two basic equations: the equation of the reaction rate induced by the photolysis process (the photonic absorption) and the mass transport equation (the non-conservative convection-diffusion equation). 3) The template for the energetical distribution of the UV radiation in the reactor is the LSSP template [2,50].

Geometry of the O_3/UV advanced oxidation reactor

One has selected two particular geometries, with practical correspondences from the point of view of the geometrical characteristics, of the flowing parameters and of the functional parameters of the UV radiation source : ***the longitudinal geometry*** – with one radiation source – and ***the crosswise geometry*** – with two UV radiation sources.

6.2. Results analysis and interpretation

The longitudinal-type reactor

The interpretation of the numerical templating results was made upon analysing the variation of the ozone photolysis reaction rate, the ozone concentrations in the volume of the reactor and upon the exit therefrom, taking into account the intrinsic dependance between the velocity field in the system (determined according to the Navier-Stokes equations), the ozone concentration and the intensity of the UV radiation in each point of the reactor (Fig. 6.1- 6.3). A parametrical analysis depending on the value of the lamp irradiance (I_0(mW/cm^2)) is set out in Fig. 6.4**.**

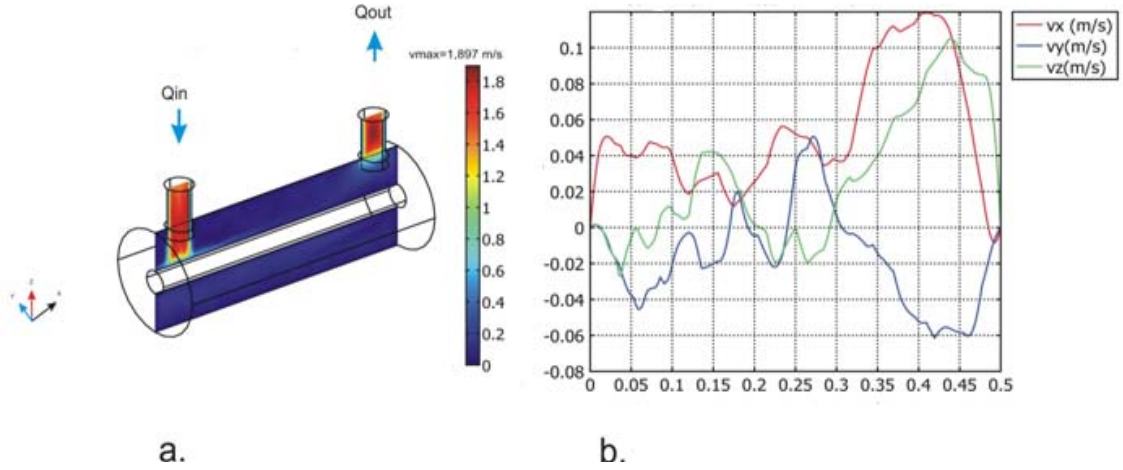


Fig. 6.1.a. The distribution of the velocity field in a longitudinal section; b. The variation of the fluid velocities components

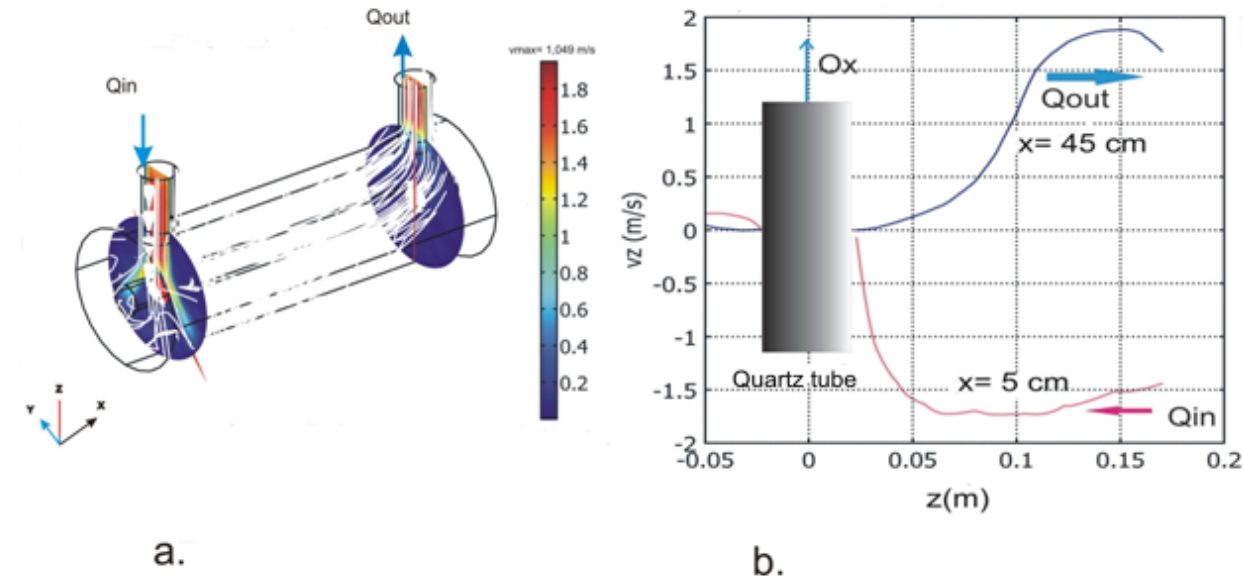


Fig. 6.2.a. The distribution of the v_z component of velocity in two sections; b. The variation of the v_z component (y = 0)

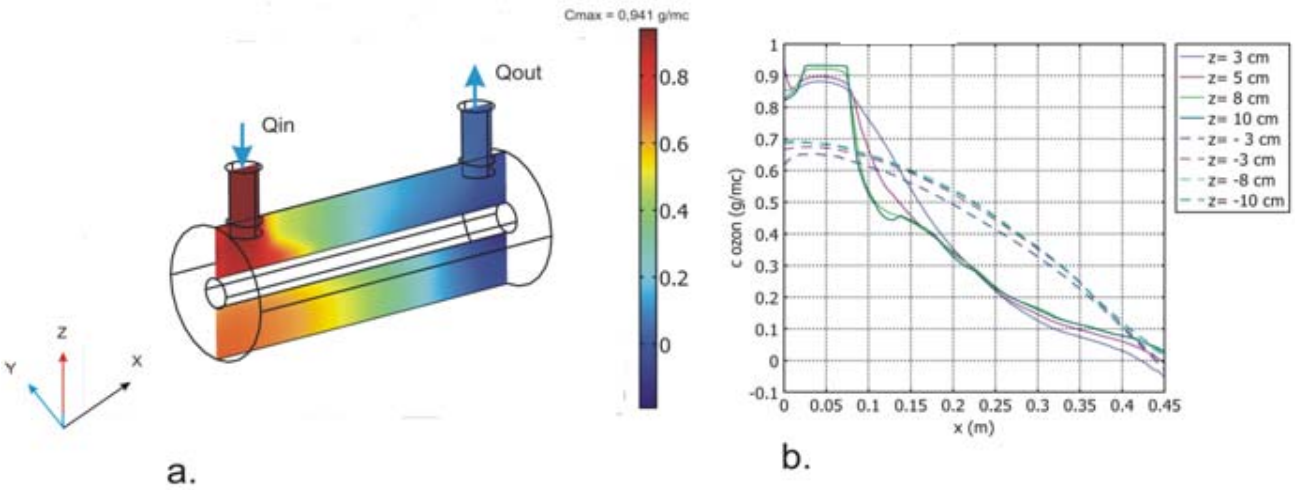
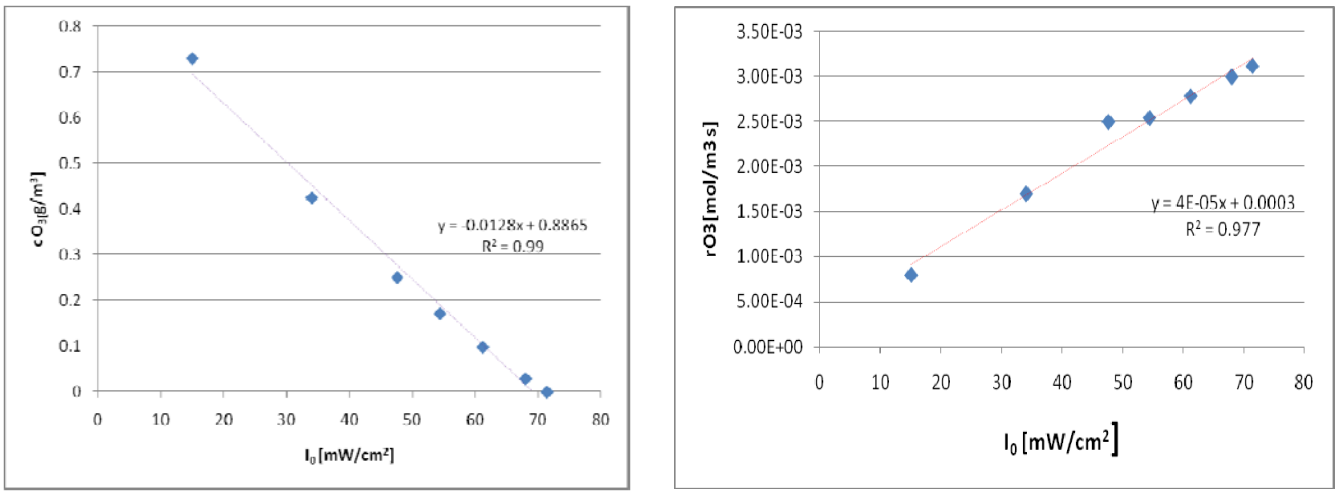


Fig. 6.3.a. The distribution of the O_3 concentrations in a longitudinal section ; b. The variation of the O_3 concentration in a longitudinal profile

The crosswise-type reactor

The crosswise module for the UV photolysis of ozone enables the approach of some flow rates upon the entrance in the system higher than the longitudinal-type module, while obtaining fluid velocities higher than 5 m/s in the median area, between the two quartz tubes. The results obtained are presented in Fig. 6.5-6.7.



a. b.

Fig. 6.4.a. The parametrical variation of the average O_3 concentration, subject to the UV lamp irradiance
b. The parametrical variation of the reaction rate

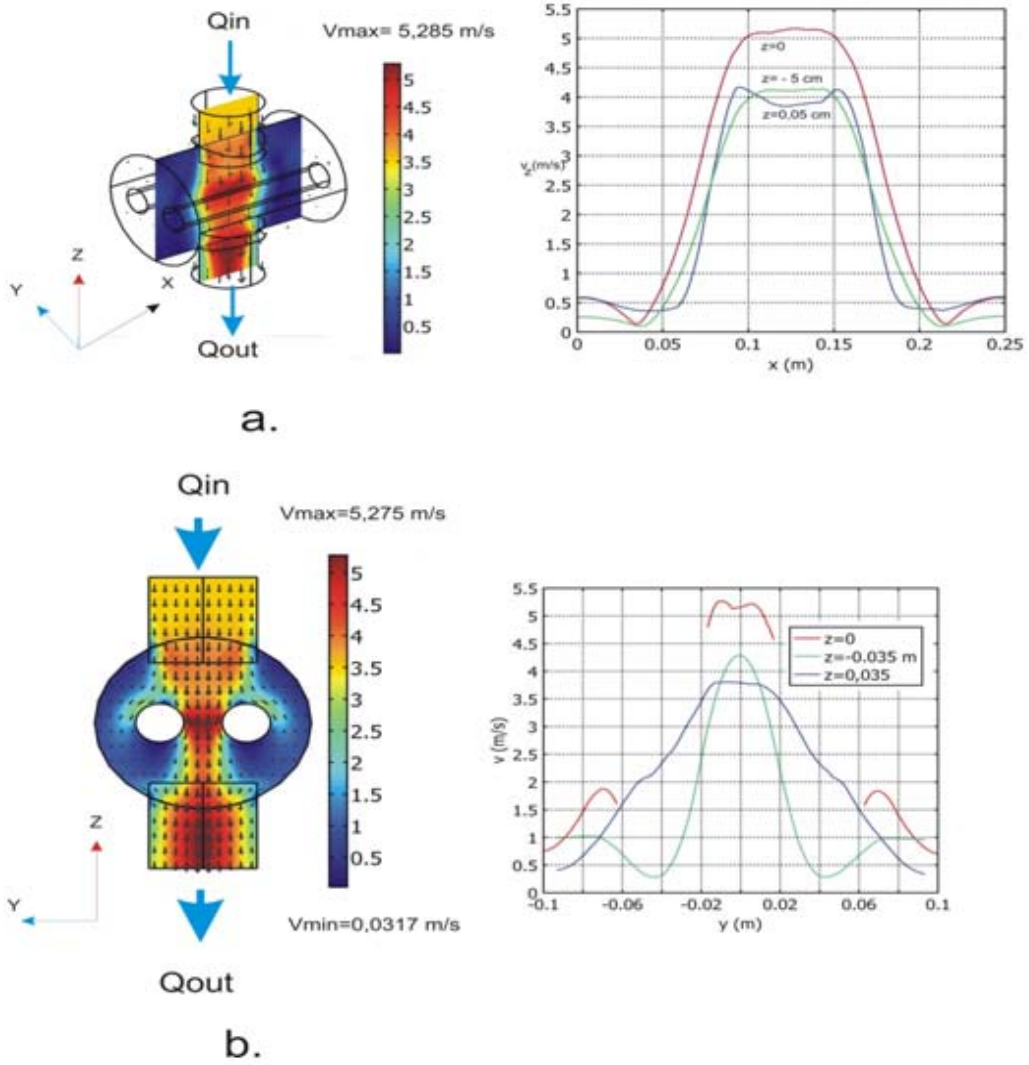


Fig. 6.5.a. The distribution of the velocity field in a crosswise section; b. The variation of the velocity value in the central section

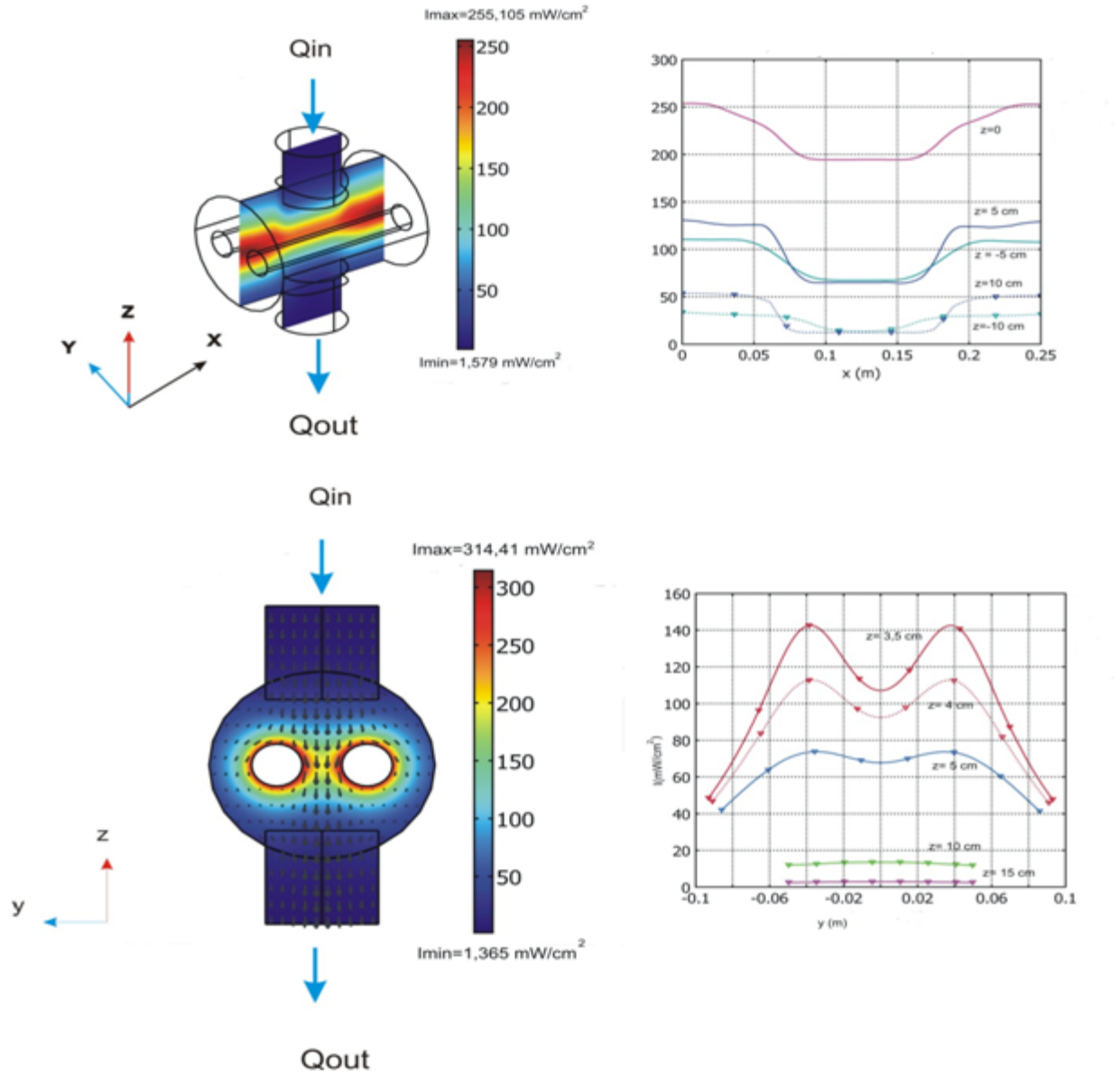
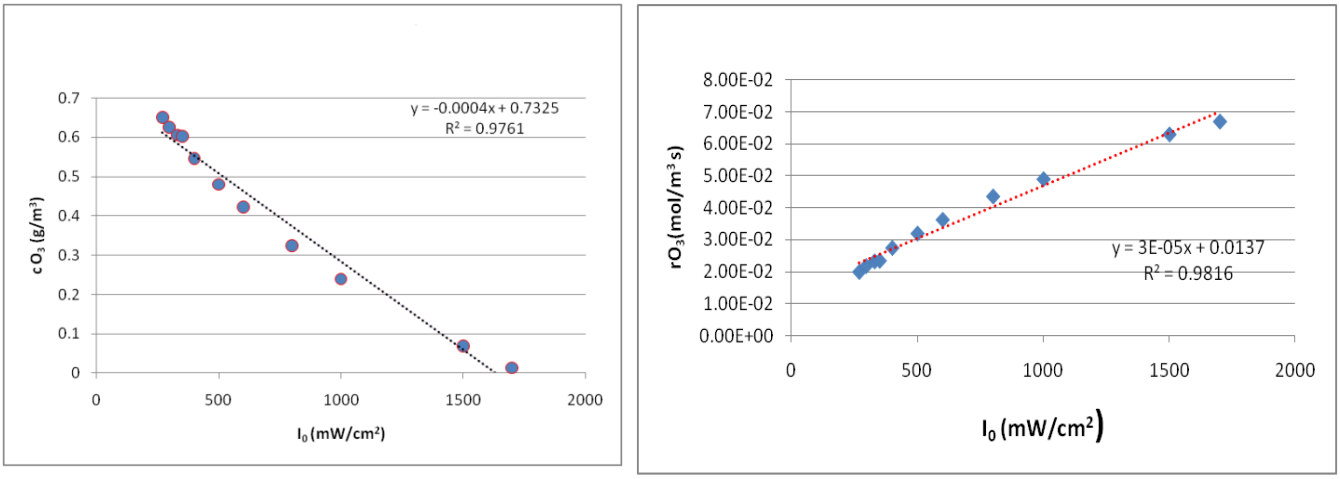


Fig. 6.6.a. The distribution and the variation of the radiation intensity in a longitudinal section
b. The distribution and the variation of the radiation intensity in the central radial section

The variation on the longitudinal plane of the UV radiation intensity shows a minimal value in the central area, especially due to a more intense absorption, correlated to the high velocity of the fluid flow (a high concentration of O_3). The maximal values in the longitudinal plane coincide with the stagnant areas. The radial distribution of the intensity shows two maximal values, which become increasingly pronounced if the distance till the quartz tubes reduces gradually (Fig. 6.6.b). The parametrical analysis subject to the UVA radiance of lamp shows, like in case of the longitudinal template, a quasilinear dependance of the average concentrations upon the exit from the reactor, a similar dependance being also recorded for the average reaction rate in the volume (Fig. 6.7.a and b).



a. **b.**

Fig. 6.7.a. The parametrical variation of the O_3 concentration upon the exit from the reactor, subject to I_0
b. The parametrical variation of a average reaction rate in the volume, subject to I_0

6.3. Conclusions

By using the Navier-Stokes equation systems and the convection-diffusion equations in the geometrical domain of the reactor, combined with a template of distribution of the UV radiation intensity in its volume, a numerical model was drawn up for the prediction both of the photolysis reaction rate and of the ozone concentrations from and upon the exit from the reactor [51]. The utilisation of this numerical model enables the analysis of different geometries of reactors, with the possibility of extending the model by new additional physical-chemical processes, such as the photocatalysis, catalytic ozonisation, sonolysis or electrochemical separation ones.

7. Contributions to the design, the realisation and the implementation of the water decontamination systems by advanced oxidation processes

7.1. The automated station for potabilising water by ozone

The station is meant to treat the water coming from underground sources, with a view of oxidising the organic substances, of removing the Fe and the Mn, of oxidising certain categories of micropollutants and of performing disinfection. The basic step is the advanced oxidation with ozone, in a two-compartment contact column, with a free level, followed by a filtering step on a bed of active carbon and quartz sand.

The main treatment parameters in the ozonisation columns, obtained as a result of the CFD templating, are set out in Fig. 7.1-7.3.[52].

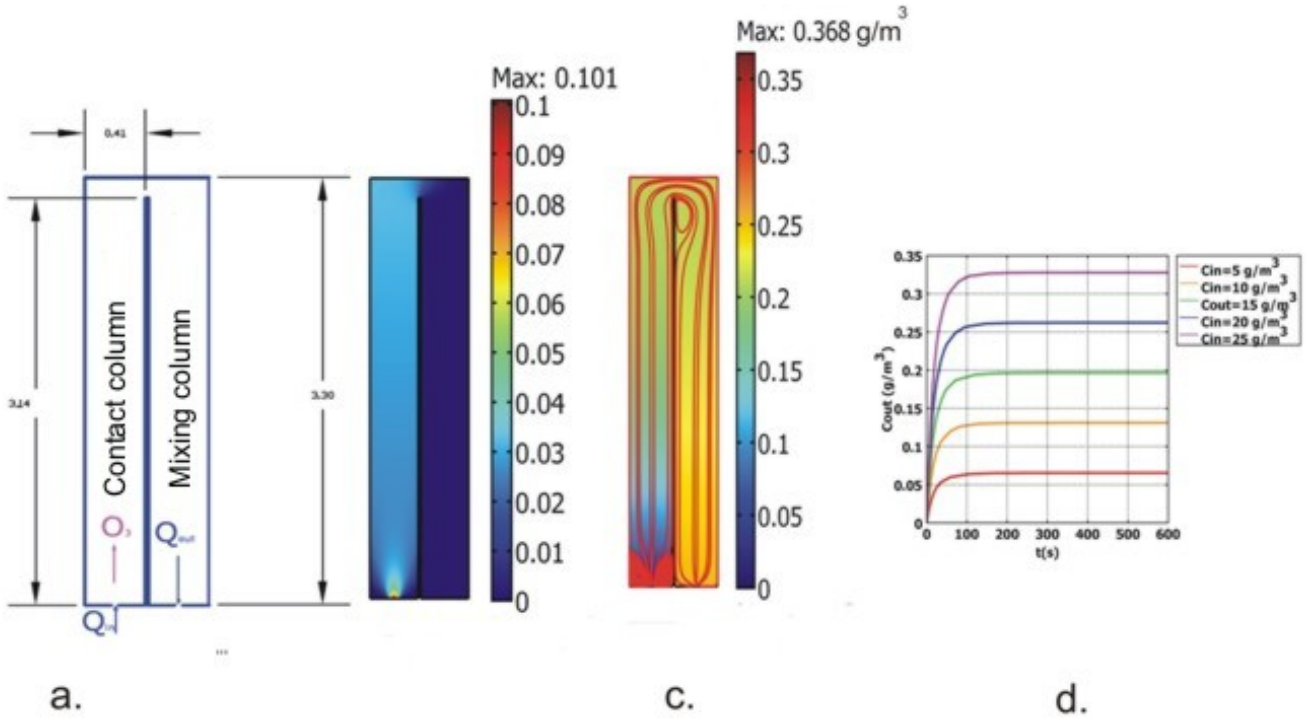


Fig. 7.1. The operating parameters for the free level treatment columns (p = 0)

a) The dimensional structure of the treatment columns ; b) The volume fraction of gas ; c) The concentrations and the streamlines distribution ; d) The variation in time of the ozone concentrations upon the exit from the treatment columns, subject to the ozone concentration in the admission gas

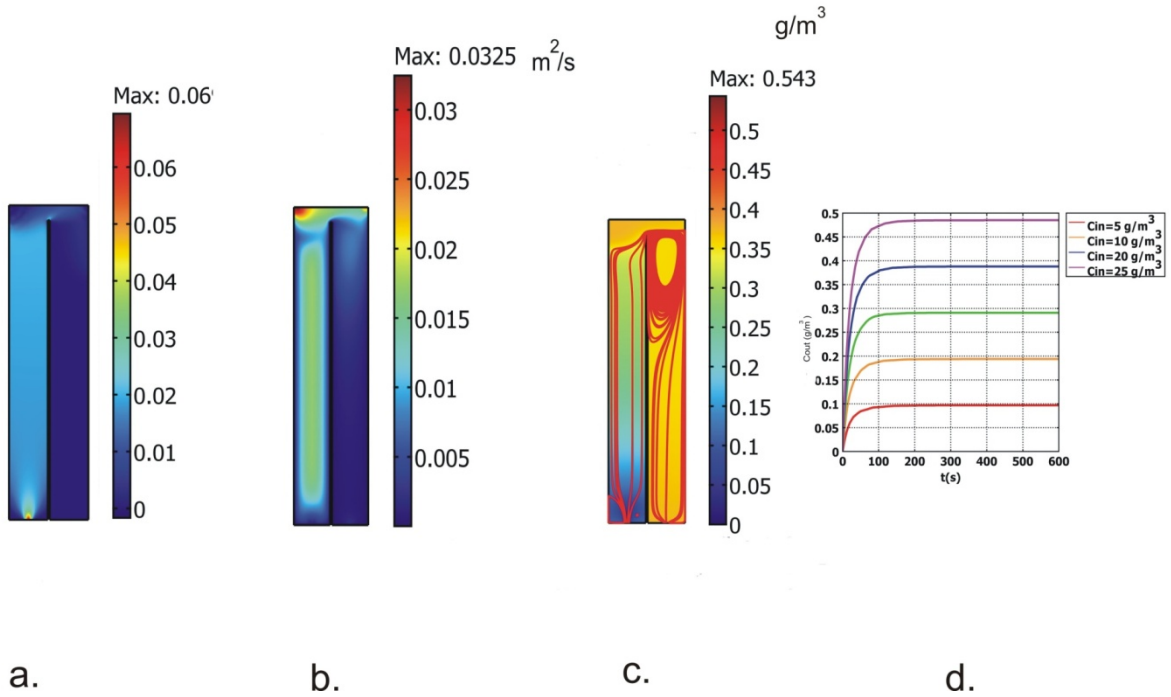


Fig. 7.2. The operating parameters for the pressurized treatment columns (p = 1 atm (g)).

a) The volume fraction of gas ; b) The distribution of the turbulent diffusion coefficient ; c) The concentrations and the streamlines distribution ; d) The variation in time of the ozone concentrations upon the exit from the treatment columns, subject to the ozone concentration in the admission gas

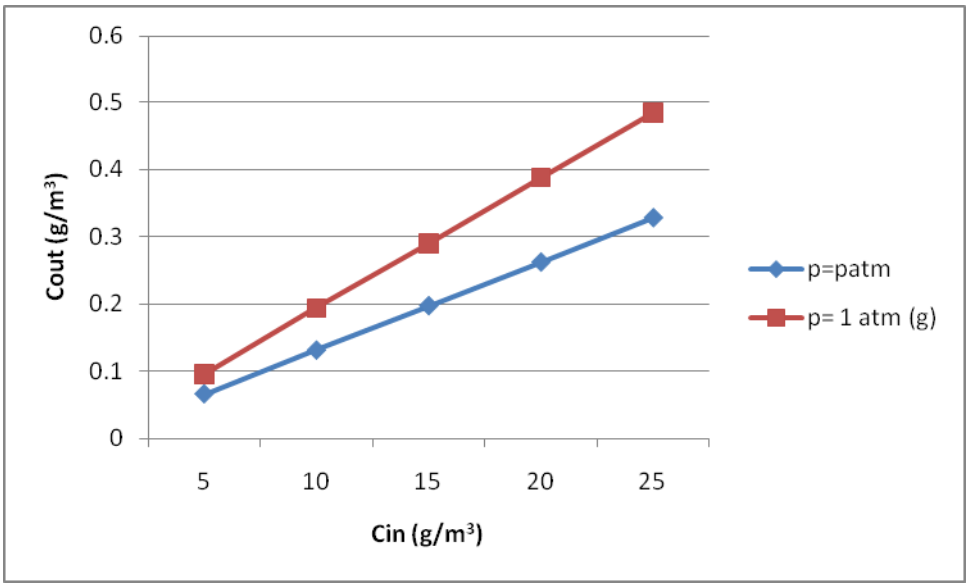


Fig. 7.3. The variation of the ozone concentration upon the exit from the treatment columns, subject to the concentration of the admission gas and to the operating conditions

The treatment station operates with no human operators, being equipped with a GSM modem; its main functions can be controlled remotely, by INTERNET, with the help of a SCADA system. The project financing was provided by **S.C. Hidroelectrica S.A. – the Porțile de Fier Subsidiary (2007-2010)**

7.2. The O_3/UV advanced oxidation system with applications in the treatment of the swimming pools recirculated water

Project goal : The elaboration of a new environmentally friendly technology for treating the swimming pools waters by under pressure O_3/UV advanced oxidation processes, with an aim to enhance the disinfection efficiency, the recirculation degree and to avoid the formation of harmful secondary products. Schematically speaking, the plant made is presented in Fig. 7.5.

Functional characteristics

- the maximal flow rate of treated water : 600 m^3/h
- the output of the ozone generator : 100 g O_3/h
- the UV energetic dose in the photolysis reactor : 60 mJ/cm^2
- the water flow taken over in the ozonisation pipeline : max. 100 m^3/h

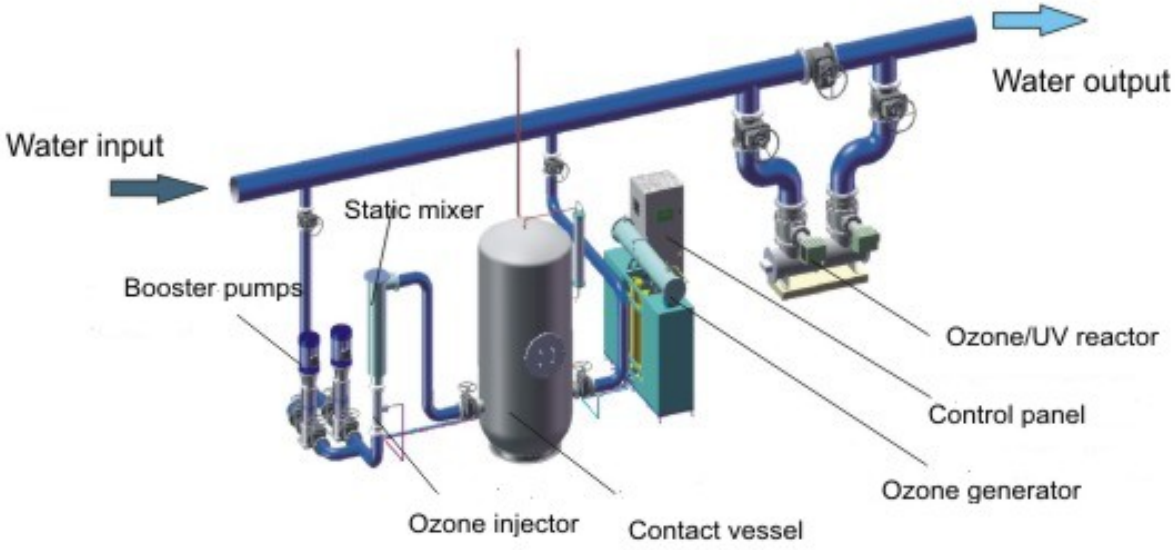


Fig. 7.4. The isometric scheme of the O_3/UV advanced oxidation treatment plant for the swimming pools recirculated waters

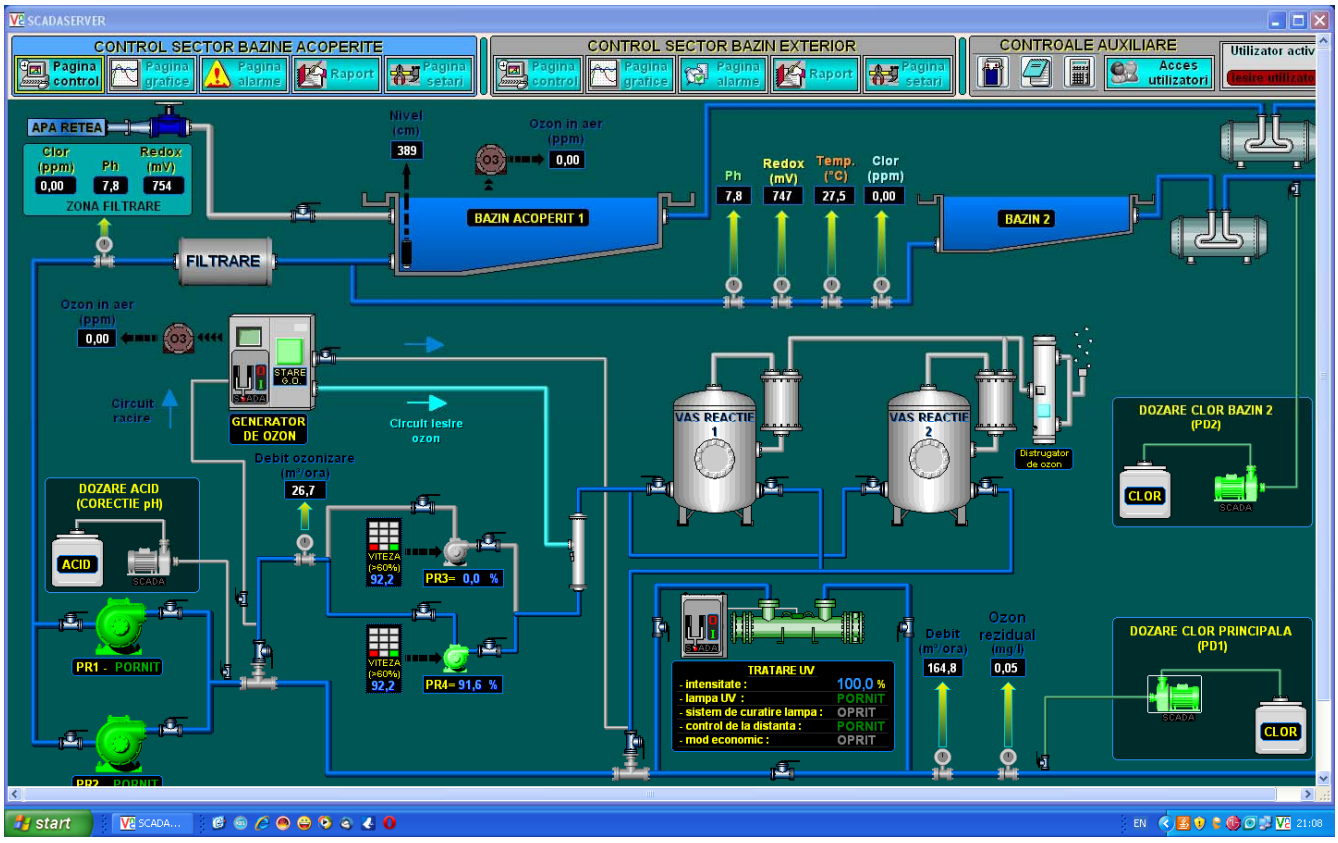


Fig.7.5. The SCADA control screen

Even after a continuous recirculation time lapse of up to 90 days, the findings of the tests carried out were that the microbiological load of the water complied with the norms imposed by the standards (Fig. 7.6) [49].

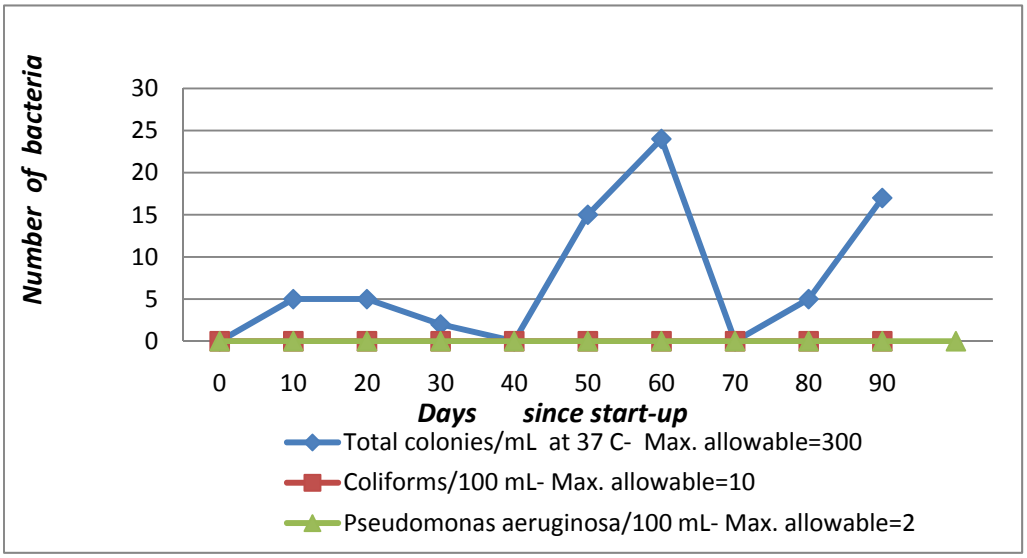


Fig. 7.6. The variation in time of the treated water microbiological load

The invention patent application :

'An Environmentally Friendly Automated Method of Treating the Public Swimming Pools Waters with an Aim to Enhance the Users' Safety' **-** The State Office for Inventions and Trademarks patent application no. A/00510 dtd. 07.07.2008 [47].

Project financing :

PNCDI II – INNOVATION Programme, (2007-2009), **ECOLIMP – *'Environmentally Friendly Advanced Technologies for Treating Olympic Pools Waters'***

7.3. The plant for obtaining ultra pure water from primary sources by using O_3/UV advanced oxidation

1. Project goal :

The elaboration and the implementation of an **innovative** solution for obtaining ultra pure water from primary sources, including two basic modules: **the pre-treatment (purification) module,** which includes such technological steps as pressure increase, mechanical filtration, O_3/UV advanced oxidation, multimedia filtration followed by filtration on a bed of active carbon, and **the ultra-purification module,** which comprises a step of filtration on active carbon, a reverse osmosis step and a continuous electro-deionisation step (CEDI) [54] (Fig. 7.7).

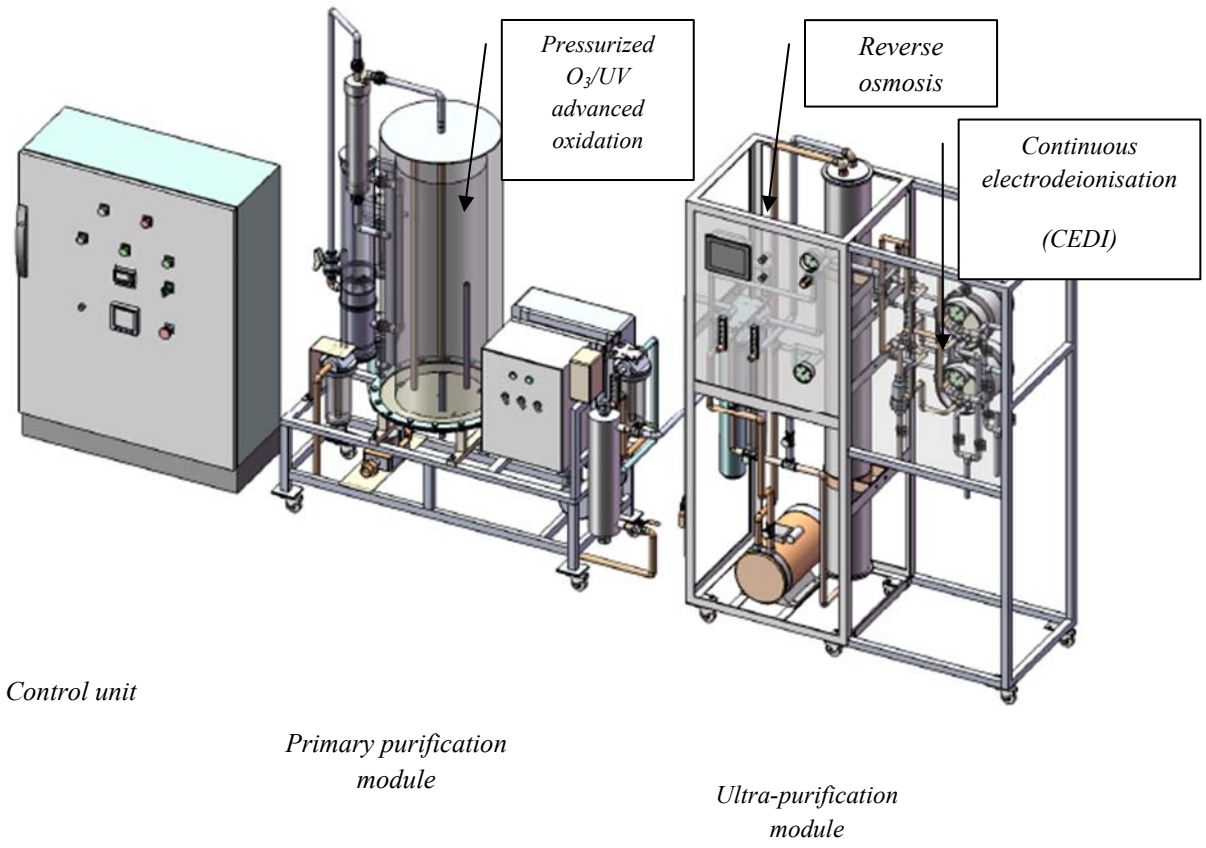


Fig. 7.7. The isometric scheme of the plant used to obtain ultra pure water from primary sources

FUNCTIONAL CHARACTERISTICS

- the quality of the ultra pure water meets the conditions of the following standards : ASTM D1193, EU and USP (ρ>18 MΩ.cm, TOC<10 ppb) ;
- the primary water source (the well water, the decanted water) ;
- automated operation ;
- flexibility : it may provide the water according to the quality steps : from plain water to ultra pure water, depending on the modules configuration, at different flow rates.
- **Scopes :** medicine, analysis laboratories, the pharmaceutic industry, the cosmetic industry, the special materials industry, the food industry, the textile industry and the energetic industry

Invention patent applications :

- **'An Advanced Oxidation Module for Purifying the Water Contaminated with Hard Degradable Chemical Compounds and Biological Products'** - The State Office for Inventions and Trademarks no. A/00913/2009 [42]
- **'A High Voltage Electric Contact Device for the Corona Discharge Tubular Electrodes' -** The State Office for Inventions and Trademarks no. A/00912/2009 [53].

Project financing :

PNCDI II – INNOVATION Programme (2008-2010) - **TEHNOPUR – 'A Plant for Obtaining Ultrapure Water from Primary Sources'**

7.4. Conclusions

The main results of the researches put into practice within the process of designing and developing the applications depicted above are linked to the theoretical, experimental study and to the numerical modeling of the water/ozone contact steps and of the O_3/UV advanced oxidation systems. The numerical models for the ozone/water contact systems drawn up and experimentally validated during the research phase were used for designing the ozone advanced oxidation stages, both in a free level configuration and under pressure. The numerical models for the ozone photolysis systems and for the O_3/UV pressurized oxidation circuits have constituted the design fundament for creating the pilot and industrial scale systems for treating the recirculated water and the advanced oxidation step included in the ultrapure water production plant.

Seeing the development of these applications at the industrial scale, we may say that the modeling methods used, the numerical models developed as a result of the theoretical and experimental studies have a certain immediate applicability for designing and creating functional systems both at the laboratory level, at the level of pilot stations, and at the industrial level.

8. GENERAL CONCLUSIONS, PERSONAL AND ORIGINAL CONTRIBUTIONS, FUTURE RESEARCH DIRECTIONS

The thesis aimed at studying the O_3/UV advanced oxidation processes both from the standpoint of the theoretical issues, of the experimental approach, and especially from the perspective of numerically modeling processes and systems for setting up the scientific and technical fundaments needed for designing the advanced oxidation modules and for integrating the same into treatment plants and systems. The physical aspects studied involved tackling with the water/ozone contact processes in various physical configurations, with the processes of oxidation by ozonisation, with the O_3/UV advanced oxidation processes in photolysis systems, as well as with their integration into complex plants and systems.

According to the facts presented within the thesis, the personal original contributions include the following :

1. drawing up a new numerical model for the O_3/water contact systems, based on the data obtained as a result of the experimental studies carried out on a set of testing operations specially **developed** and **created** for this kind of applications

2. developing and creating a pilot plant for studying the O_3/UV pressurized advanced oxidation processes

3. drawing up and implementing a numerical model for the topography of the circuits and of the O_3/UV presssurized advanced oxidation systems

4. drawing up a numerical model for the O_3/UV advanced oxidation reactors by using the CFD (Computational Fluid Dynamics) method

5. the applicative research, the design, the execution and the implementation of applications for the advanced oxidation processes, by means of researches financed both from the budget of the Ministry of Education and Research, by projects whose beneficiaries included AMCSIT (The Scientific Research, Innovation and Technological Transfer Managerial Agency), and by direct beneficiaries (Hidroelectrica S.A.).

The contributions in the field, presented within this thesis, have got extended applicability, enabling the approach and the development of new directions in the field of the applicative research regarding the advanced oxidation processes, including heterogeneous photocatalysis processes both on dispersed environments and on immobilised ones, catalytic ozonisation processes, electro- and sonolysis processes.

The establishment and the approach of **new future research directions** are based on the results of the researches carried out, set out in this thesis, which are focused on three main directions :

A. The study, the research and the development of new processes and configurations of advanced oxidation by ***catalytic ozonisation*** for ***water decontamination*** processes

B. The study, the research and the development of ***catalytic ozonisation*** processes in the presence of the ***aerosols*** and of the ***dispersed environments***, with a view of treating gases and disinfecting the air

C. Studies and researches regarding the application of the ***heterogeneous photocatalysis*** and ***electrophotocatalysis*** processes for ***water treatment*** systems. The theoretical study, the physical and numerical modeling of the heterogeneous photocatalysis processes in the presence of the nanostructured photocatalytic substrates based on TiO_2-Ag, TiO_2-C, both under a dispersed form and under an immobilised one, focusing on the utilisation of the activated photocatalytic substrates for using the solar energy, are envisaged.

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