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Faculty of Biotechnical Systems Engineering
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Environmental Engineering

PHD THESIS SUMMARY

Photocatalytic systems applied for the removal of detergents from wastewater

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FOREWORD

The main objective of the PhD thesis is to describe, configure, construct and evaluate photocatalytic reactors based on the utilization of TiO_2 nanoparticles. Subsidiarily, it also aims to evaluate the performance of TiO_2 nanoparticles in the oxidation of specific organic compounds.

The PhD thesis is structured in 5 chapters, developed in 225 pages, contains 53 figures and graphs, 34 tables, and a bibliography of 362 references.

CHAPTER 1 - IMPORTANCE OF THE TOPIC. THE OBJECTIVES OF THE PhD THESIS sets out the main objectives pursued and substantiates the scientific premises underlying the research in the thesis. In this chapter, the main research premises are defined by bringing solid scientific arguments that reinforce the need for research and further investigation of the topic addressed. In this chapter a general definition of wastewater is given as well as a list of the reasons why photocatalysis is an important wastewater treatment process in the field.

CHAPTER 2 entitled LITERATURE REVIEW ON THE APPLICATION OF NANOTECHNOLOGY IN WASTEWATER TREATMENT is a synthesis of the literature in the field of domestic and industrial water treatment and current treatment techniques. The chapter forms the basis for further research and is divided into 6 sub-chapters addressing current problems, techniques, materials and devices in the field. In Chapter 2.1 Water treatment, conventional and advanced water treatment techniques are presented, following the generally accepted classification of these techniques: primary treatment, secondary treatment, tertiary treatment and advanced treatment techniques. In chapter 2.2 - Wastewater and surfactants, the most current studies on surfactants used in industrial and domestic applications are summarized, showing the extent of the use of these types of compounds and their impact on the environment. In the first two subchapters we find information on their presence in industry and in the residential space. In the next three subchapters we follow the characterization and effects of surfactants on the environment, following three main types of surfactants: cationic, anionic and non-ionic and amphoteric. In Chapter 2.3 - Water treatment techniques we find conventional and non-conventional techniques for the treatment of the compounds presented in Chapter 2.2. It is structured according to the main types of water treatment techniques: adsorption, biodegradation, sedimentation aeration and catalytic oxidation. In addition to the definition and characterization of the treatment processes, the chapter emphasizes their efficiency in terms of surfactant removal. Catalytic oxidation is treated extensively and is also the treatment method underlying the laboratory experiments in the thesis. In Chapter 2.4 - The use of TiO_2 in the application of advanced water treatment techniques the literature research work is focused on the characteristics, properties and photocatalytic mechanism of TiO_2 this chapter comes as a complement to the previous chapter and goes into detail regarding the use of the photocatalyst in the title. Chapter 2.4 - Photocatalytic reactors using

the TiO_2 catalyst in aqueous solutions is the result of literature research on photocatalytic reactors used in water treatment. This subchapter defines and summarizes the main photocatalytic reactors proposed in the literature. Considering the aim of the thesis and the research field, the chapter summarizes the following types of reactors: photocatalytic membrane reactor, fixed bed reactor, corrugated plate reactor, rotating disk reactor, Carberry photoreactor, fiber optic reactor.

In CHAPTER 3. EXPERIMENTAL RESEARCH METHODOLOGY the experimental research methodology is established. In addition, the same chapter describes the methods of measurement and calibration of laboratory apparatus, which is crucial for the understanding and reproducibility of the results presented in Chapter 4.

CHAPTER 4. EXPERIMENTAL RESEARCH is dedicated exclusively to the experimental research carried out for the PhD thesis. The chapter is simply structured into three sub-chapters, each of which focuses on the characterization and evaluation of the three types of proposed photo reactors. Each of the three reactors is presented and rigorously characterized from a technical point of view, also the results obtained by their use are presented and interpreted, after each subchapter conclusions are presented on the efficiency, positive and negative technical aspects of the reactors.

In CHAPTER 5. ORIGINAL CONTRIBUTIONS. FINAL CONCLUSIONS. PERSPECTIVES the conclusions, original contributions of the PhD thesis and research perspectives are presented. The thesis concludes with a list of publications and conferences attended during the PhD, appendices and bibliography.

The experimental data obtained in the PhD thesis made possible the publication of 3 articles in national and international journals, which appear in the ISI Web of Knowledge database.

CHAPTER 1. IMPORTANCE OF THE TOPIC. OBJECTIVES OF THE DOCTORAL THESIS

1.1. Importance of the theme

The subject of the thesis is focused on the effects of catalysts. This choice is mainly based on the advantage of a considerably larger specific surface area. The importance of the thesis and the research included in it are closely related to the listed objectives and aim at developing and improving current processes and methods for advanced water treatment, specifically, by the photocatalysis process using nanomaterials. Photocatalysis presents several advantages as follows:

Efficient removal of contaminants: photocatalytic reactors are highly successful in breaking down various organic pollutants, such as drugs, pesticides, dyes and industrial chemicals, which are usually resistant to traditional treatment procedures.

Mineralization of pollutants: Photocatalysis differs from other treatment techniques by completely converting contaminants into harmless end products, such as carbon dioxide and water, rather than simply converting them into other compounds.

Harnessing solar energy: photocatalytic processes have the ability to utilize solar energy, which is a renewable and abundant source of energy. This makes these processes more sustainable and reduces dependence on non-renewable energy sources.

Reduced use of chemicals: These reactors limit the need for chemical additives, thus reducing chemical waste and the corresponding environmental consequences.

Reduced operational costs: Har harnessing solar energy as an energy source can significantly reduce the operational costs associated with wastewater treatment compared to conventional energy-intensive approaches.

Long-term economic benefits: efficient pollutant removal and reduced use of chemicals result in reduced long-term maintenance and operational costs.

Treating hard-to-remove pollutants: photocatalytic reactors are effective in removing new pollutants, including pharmaceuticals, personal care products and endocrine disruptors that are difficult to remove by conventional methods.

Progress in innovation and technology: research in photocatalytic reactors contributes to the development of new materials for photocatalysts that have improved activity, stability and selectivity. This leads to more efficient treatment procedures.

Advanced reactor design: analysis of these reactors results in advances in reactor design, maximizing light scattering, increasing photocatalyst exposure and improving the overall efficiency of the treatment process.

Reduced greenhouse gas emissions: photocatalytic reactors can help reduce greenhouse gas emissions in wastewater treatment operations by har harnessing solar energy and minimizing dependence on fossil fuels.

Climate adaptation: These reactors have the ability to adjust and operate efficiently under different climatic circumstances, making them a flexible and adaptable solution for different geographic regions.

In conclusion, the study of photocatalytic reactors for wastewater treatment is crucial for scaling up water treatment technologies, promoting environmental sustainability, combating emerging contaminants and creating cost-effective and efficient water treatment solutions. These studies have the potential to establish a more environmentally friendly and sustainable future.

1.2. Objectives of the PhD thesis

The objective of the thesis is to develop a water treatment method based on the photocatalysis process using nanotechnology. Due to the large number of industrial pollutant categories and diverse physico-chemical characteristics, the photocatalysis process can be successfully applied to organic pollutants with restricted success. Furthermore, due to the complexity of organic compounds, I had to restrict the pollutant range only to detergent-type surfactants.

Therefore, through this thesis, I set out to achieve the following research objectives:

1. The first objective of the thesis is the configuration of photocatalytic reactors based on the most recent research in this field. For this purpose, three types of reactors have been produced, each with different characteristics.
2. A second objective of the thesis is the optimization of these three reactors by modifying their different characteristics such as: the amount of photocatalysts used, the mode of exposure to UV light or the recirculation of the solution.
3. A third objective of the thesis is to test and monitor the efficiency and throughput of the three reactors by conducting practical experiments using the three photocatalytic reactors.
4. A last objective of the thesis is to propose an innovative technical solution for real-time detection of the mineralization yield of the reactor.

CHAPTER 2. LITERATURE REVIEW ON THE APPLICATION OF NANOTECHNOLOGY IN WATER TREATMENT

2.1. Wastewater and surfactants

Water pollution is a significant global problem now facing society. Water pollution not only affects the environment and human health, but also has economic and social cost implications.

There are a multitude of strategies used commercially and non-commercially to combat the problem which is progressively intensifying as a result of technological advances [2].

The leaching of pollutants into groundwater has the potential to pollute and degrade its quality. Water pollution caused by toxic substances from industrial and residential processes can have immediate negative effects on human health. This can occur when pollution is the result of bacteria and chemical compounds in human waste, making the water unfit for drinking or swimming. Alternatively, these negative effects may manifest themselves after a prolonged period of time due to the accumulation of these substances in the environment and subsequent pollution of the food chain [2-4].

Figure 1 Domestic water polluted with surfactants

Types of detergents

Detergents are compounds based on soaps or other surfactants that are specifically designed for use in water-based washing and disinfection procedures. Detergents are used in various physical states, including liquid, powder, paste, tablets, etc. They find extensive applications in household laundry, household and industrial cleaning products, cosmetics and industrial settings [9].

Surfactants are an important category of detergent constituents and are found in all types of detergents. Surfactants, in general, refer to compounds characterized by the presence of both a polar and a non-polar end in their molecular structure. Surfactants are molecules that possess a dual nature, exhibiting both hydrophobic and hydrophilic properties. Hydrophobic component, usually a long alkyl chain, which is linked to hydrophilic or solubility enhancing functional groups.

Surfactants can be classified into four distinct categories based on the nature of the charge present in the chain-bearing segment of the molecule after dissociation in aqueous solution. Thus we distinguish the following categories:

1. **Anionic surfactants:** Most detergents are composed of high concentrations of anionic surfactants compared to nonionic surfactants. The literature extensively covers the description of anionic surfactants and their associated manufacturing techniques [10]. The main surfactants in this category are: soap, alkylbenzenesulfonates (LAS and TPS), secondary alkanesulfonates (SAS), alpha--Olefinsulfonates (AOS), alpha--Olefinsulfonates (AOS), alpha--Sulfo Esters of fatty acids (MES), alkyl sulfates (AS), alkyl ether sulfates (AES), alkylphenol ethoxylates (APE), N-methyl glucamides (NMG);
2. **Nonionic surfactants:** Ethoxylated Alcohol (EA), Fatty Acid Alkanolamides (FAA), Alkylamine Oxides and Alkyl Polyglycoside (AGP);
3. **Cationic surfactants:** These have exhibit excellent adsorptive power in terms of their ability to interact with a wide range of surfaces. Natural fibers such as cotton, wool and flax have a high surface adsorption for these substances [11]. Their specifics and type will be dealt with in more detail in the following lines;
4. **Amphoteric surfactants:** Compounds belonging to the alkylbetaine or alkylsulfobetaine category exhibit the presence of both anionic and cationic groups within the same molecular structure, even when dissolved in an aqueous medium. Although these surfactants possess remarkable detergent qualities, they are hardly used in laundry detergents because of primarily economic considerations. They are mainly used in the formulation of hand dishwashing products [12].

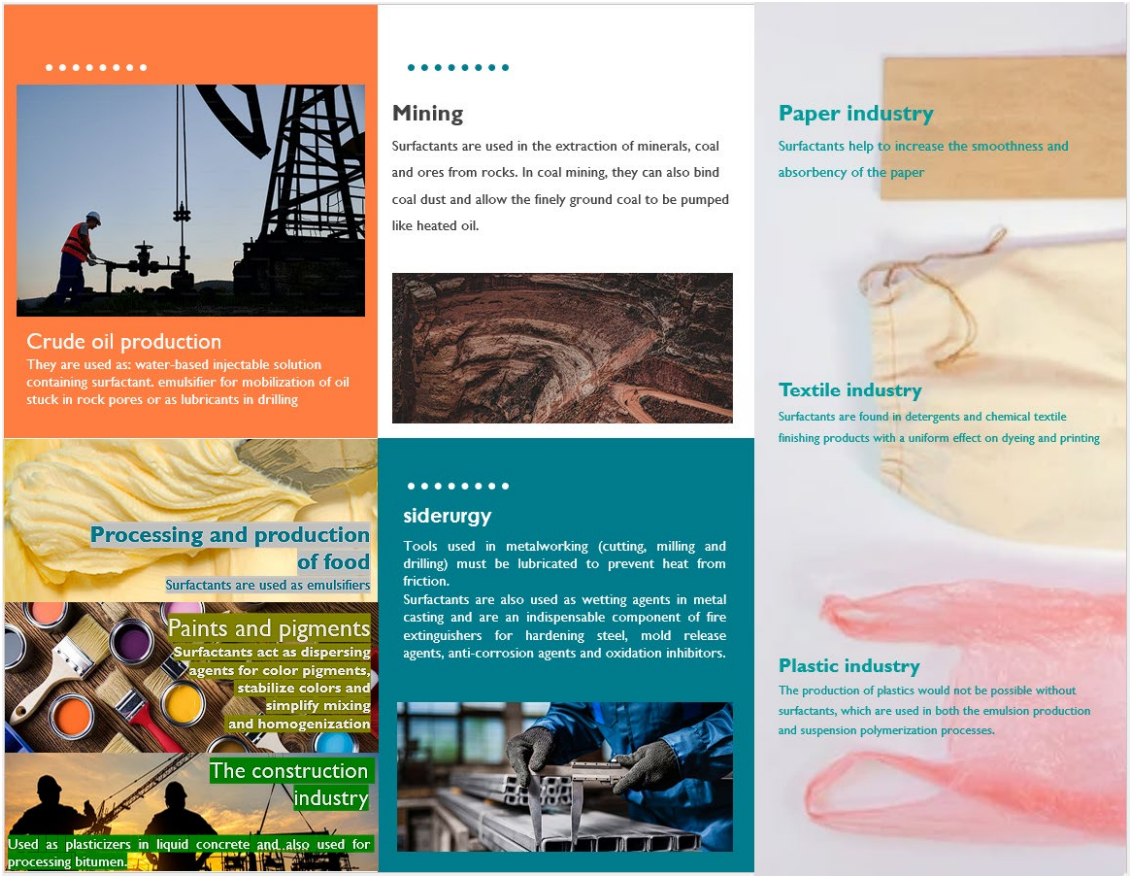

Figure 1b The use of surfactants in industry [1]

Surfactants have a diverse range of applications in many industrial sectors, where they perform crucial functions that facilitate a wide variety of manufacturing and production processes, ultimately increasing their efficiency. Due to their distinctive characteristics, they can be used as lubricants, coolants or carriers for other substances involved in various processes, in addition to their typical emulsifying, dispersing, wetting and mixing functions Figure 1b.

2.2. Water treatment techniques

Ahmed [62] states that there is a continuous pursuit of developmental steps in the field of wastewater treatment aimed at developing new techniques to meet the need for clean water. However, the treatment of wastewater containing pollutants has proven to be a challenging task using existing approaches [63]. Numerous methodologies have been documented in the water treatment literature. The processes often encompass chemical, physical and biological mechanisms that are considered sufficiently effective for water treatment in several dimensions. The choice of

pollutant removal method is influenced by a number of criteria, including pollutant concentration, wastewater composition, process cost and the presence of other pollutants in the wastewater [64]. Each treatment approach has specific characteristics that may offer advantages in some aspects but may also have limitations in other areas. Treatment approaches that include substantial installation and operational expenses, prolonged processing times, limited throughput, and generation of hazardous by-products post-treatment are usually considered less viable for industrial applications [65]. It is therefore imperative to identify an alternative treatment technique capable of degrading or completely removing the pollutants [66].

Chemical methods

Multiple chemical oxidation processes have been documented in various catalytic applications [67, 68]. The advanced oxidation method is well recognized as a significant approach in wastewater treatment. AOPs, which stands for Advanced Oxidation Processes, refers to a collection of techniques used in water treatment. These techniques share common principles in their ability to generate oxidizing species, including hydroxyl radicals (- OH). Oxidation processes can comprise different mechanisms, including electrochemical oxidation, photo-electrochemical oxidation, UV-assisted Fenton oxidation and ozonation. Catalysts and pH are crucial factors in the oxidation process, as pointed out by Ahmad [69].

Physical methods

The foundation of physical pollution removal methods lies in the implementation of mass transfer strategies [70]. The increased utilization of this approach can be attributed to its inherent characteristics such as simplicity, adaptability, remarkable effectiveness and ability to recycle pollutants [71, 65]. Another benefit of this strategy is the reduced demand for chemicals, Physical treatment appears to exhibit a higher degree of reliability compared to other treatment modalities due to its independence from living creatures [70]. In recent years, researchers have increasingly used adsorption as a physical approach due to its notable efficacy and cost-effectiveness [71].

Biological Methods

Biosorption is an adsorption method that has the ability to remove pollutants such as metal ions and organic dyes found in aqueous solutions. As their name suggests, biosorbents are derived from biological sources or obtained by biological processes. Biosorbents have an inherent ability to attract or bind pollutants due to the presence of specific functional groups on their surface [72]. The process involves a liquid phase comprising species that are either suspended or dissolved, which must be adsorbed onto the surfaces of a solid phase known as the biosorbent [73]. The above-mentioned procedure effectively removes various organic and inorganic substances by passively binding them to biosorbents based on the polarity of their functional groups [74].

For the removal of toxic dyes and heavy metals, extensive studies have been reported on biochar as a biosorbent [75]. These are considered suitable for water treatment applications such as removal of various inorganic, ammonium-N and organic pollutants from wastewater. Biochar has been used for the sorption of phosphate ions, at the same time it has also been used for the isolation of phosphorus and dissolved nitrogen from municipal wastewater [76, 77].

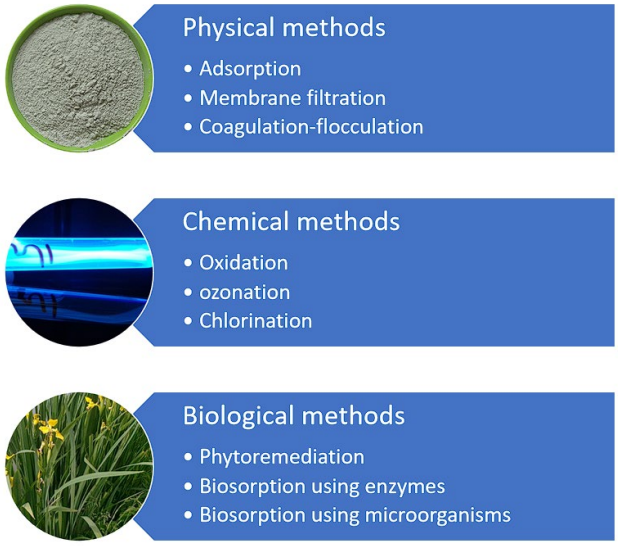

Figure 2b: Conventional techniques used for water treatment

2.2.1. Adsorption

Adsorption is a surface phenomenon that presents a common mechanism for the removal of both organic and inorganic pollutants. In the presence of a solid material, which possesses a surface structure characterized by high porosity, by intermolecular forces of attraction between liquid and solid lead to the concentration or deposition of certain solute molecules from the solution on the solid surface. The substance that is held on the surface of a solid by the adsorption method is referred to as adsorbate, while the solid material on which it is held is known as adsorbent. The phenomenon in which adsorbate accumulates on the surface of an adsorbent is called adsorption. The formation of an adsorbed phase with a composition distinct from the fluid phase serves as a fundamental principle of adsorption technology for separation purposes.

In solution volume, the constituent atoms tend to form chemical bonds, be they ionic, covalent or metallic, with other atoms present within the substance. However, atoms located at the surface of the adsorbent are not completely surrounded by other adsorbent atoms, thus allowing them to exert an attractive force on the adsorbates. The specific binding characteristics depend on

the particular species involved. The adsorption process is usually categorized as either physical sorption, which is associated with weak Van Der Waals forces, or chemisorption, which is associated with covalent bonds. In addition, this phenomenon is likely to occur due to electrostatic attraction.

2.2.2. Biodegradation

Most studies on the biodegradation of quaternary ammonium compounds (CACs) have been carried out using activated sludge or enriched cultures, but there is evidence that marine micro-organisms can degrade ATMAC and BAC in 5-10 days. Previous research based on enrichment and isolation of BAC-resistant bacteria has identified species capable of degrading and even mineralizing BAC to carbon dioxide. These include strains of Pseudomonas, Xanthomonas, Aeromonas, Stenetrophomonas and Achromobacter [134 - 139] Various bacterial cultures have also elucidated biotransformation pathways for a number of CCAs. In addition to the tetradecyl trimethylammonium trimethylammonium bromide monooxygenase, a type 1 oxygenase, three loci encoding oxygenases that metabolize naturally occurring CCAs, have been identified. However, further research is needed to determine whether such degradation occurs in aquatic systems due to the presence of complex microbial communities.

2.2.3. Sedimentation

A considerable amount of QAC is lost by sedimentation in surface waters due to their strong affinity for both organic and inorganic particles. With total QAC concentrations ranging from 1 g/kg to 74 g/g, QACs have been found in surface sediment samples from rivers in Austria, sewage effluent-impacted estuaries in New York, and sewage-impacted lakes in Minnesota. [29, 31, 159, 160, 160]. BAC and DADMAC concentrations are typically much higher than ATMAC concentrations, with C12-BAC (3.6 g/g), C14-BAC (7.2 g/g) In surface sediment samples taken from effluent-polluted estuaries in New York, the average total QAC concentration was found to be about 25 times higher than the average concentration of polycyclic aromatic hydrocarbons at the same site. (30) quantified in sediment layers from Minnesota lakes and urban estuaries near Tokyo, Hong Kong and New York City that have been dated. Since the 1950s, QACs have been found and peak concentrations are consistent with deposition from the 1960s through the 1980s. It is a pattern shared by all these sediments, representing a temporal archive of pollutant inputs to aquatic environments. Sediment concentrations subsequently decrease, most likely as a result of improved domestic and industrial water treatment implementations, for most QACs and sites, with the exception of some short-chain DADMACs and long-chain ATMACs. Current and future increased use as a result of the COVID-19 pandemic may lead to increased sediment levels. Although CCAs have been detected at high concentrations in sediments around the globe, there

are few conclusive data on their bioavailability once assimilated. Only Li et al. showed that the total amounts of BACs and ATMACs decreased by 39-55% between two sediment samples taken 12 years apart from the same site and dated. This shows that ATMACs and BACs degrade in situ, especially those with short chains.

2.2.4. Aeration

Aeration plays a crucial role in almost all water treatment procedures, especially in aerobic biological treatment. The aeration process is responsible for the majority of the energy costs in plants, constituting a significant part ranging from 45% to 75% of the daily energy expenditure [161]. Aeration systems facilitate the passage of oxygen in a liquid medium by two primary mechanisms: diffusion of the gas over a gas-liquid interface or dissolution of the gas in the liquid solution through a semi-permeable membrane. Environmental technologies typically depend on gas transfer, which involves the creation of a gas-liquid interface using methods such as shearing the liquid surface using mixers or turbines or by introducing air through bubbles or porous materials. Surface aerators are devices that generate a high velocity flow, resulting in the shearing of the wastewater surface. This shearing action results in the formation of a fine mist of droplets, which rapidly descends on the surface of the wastewater, covering an area with a radius of several meters. Diffusers refer to nozzles or porous surfaces of various geometries that are positioned at the bottom of a tank, allowing the release of bubbles that rise to the surface of the tank. Typically, bubbles are classified as coarse bubbles when their diameter exceeds 50 mm, while those with sizes less than 5 mm are classified as fine. Significant differences in their gas-liquid velocity gradients and can be classified as low flow regime interfaces.

The use of fine pore diffusers has gained widespread popularity as the predominant aeration technology for water treatment in OECD (Organization for Economic Co-operation and Development) member countries. The standard aeration efficiency (SAE), measured in kgO2 - kWh21 , indicates that they are more efficient in terms of energy consumption per unit. Quantification of the influence of pollution on aeration performance is usually done by using a factor, noted as the ratio of the mass transfer coefficients between process water and clean water. Gas-liquid interfaces in the lower flow regime, such as those generated by fine pore diffusers, typically exhibit a lower factor compared to interfaces in the higher flow regime, such as those generated by coarse bubble diffusers or surface aerators, under equivalent conditions [162]. Discrepancies in many aspects of ventilation systems were first noted in the 1930s, but their significance was largely overlooked until the energy crisis of the 1970s led to increased recognition of energy-efficient solutions. In the run-up to the 1980s, many installations were developed using a factor of 0.8, which was widely regarded as a universally applicable coefficient for all categories of ventilation systems. Previous studies have shown that different aeration techniques exhibit distinct factors. In the case of fine pore diffusers, the a-factor initially decreases during operation due to fouling or deposition, as indicated by Rosso and Stenstrom [161]. In addition, it should be

noted that for fine bubble systems, this factor is influenced by many process variables, such as the average cell retention time or air flow rate [161].

2.2.5. Catalytic oxidation

The mechanism

Photocatalysts absorb abundant electromagnetic radiation and convert it into energy to drive chemical reactions. Among the many varieties of reactions facilitated by photocatalysts, wastewater treatment is an important application. Photocatalysis is a cost-effective, environmentally friendly and persistent method for purifying water, an important resource whose demand is increasing while its supply is decreasing. Atomically dispersed metals and metal oxides are currently the most promising photocatalytic materials. In conventional materials, the utilization functionality of the photocatalytic active material is rather low because only a small fraction of the surface molecules can function as active materials. This effectiveness improves as particle size decreases.

Subnanometer catalysts, such as single-atom catalysts, atom dispersed catalysts and heterogeneous catalysts, have distinct advantages over their bulk and nanometer counterparts. Several methods are now available for the preparation of stable single-atom catalysts, as most of the hurdles associated with their preparation have been removed.

Numerous atomically dispersed photocatalytic materials have been developed and many new insights have been gained, thus revealing the vast potential of utilizing solar radiation for wastewater treatment. In this chapter, the advantages of subnanometer photocatalysts in terms of increased activity, enhanced selectivity, economical use of the material, and a better understanding of the structure-activity relationship are examined.

Photocatalysts

To increase surface area, the particle size of the catalysts was reduced. Therefore, the progression from bulk materials from nanomaterials to cluster materials to single atom catalysts (CSA) was logical. Each catalytic atom, which are often unusual and expensive noble metals, had to be considered. Very importantly, this progressive reduction in particle size results in significant changes in its physicochemical properties, in particular the proportion of bonds that are unsaturated and the metal-support metal relationships. Note that subnanometer catalysts are not only restricted to CSA.

Subnanometer catalysts comprise single-site heterogeneous catalysts (SSHCs) and atomically dispersed metal catalysts (ADMCs). SSHCs consist of groups of isolated molecules, molecules,

atoms and ions, as long as all sites possess similar properties [190]. ADMCs consist of metals ranging from small groups to monomers, with an emphasis on uniform dispersion [191].

Single atom catalysts

CSAs are novel materials that have garnered significant interest in the field of heterogeneous catalysis in recent years. In single-atom catalysts, they consist of isolated single atoms that are scattered on the surface of a support material, whereas in conventional catalysts, metal nanoparticles are dispersed throughout most of the support material. Numerous support materials have been evaluated and used as single-atom isolated compatible sites [192].

Similar to homogeneous catalysts, CSAs have uniform structural configurations and active sites, as well as similar electronic and spatial relationships, with the support materials resulting in increased catalytic activity and selectivity [193]. Single atoms placed on suitable supports can enhance the activation capacity and adsorption of the photocatalyst through metal-substrate interactions that can modify the electronic structure of CSAs, thereby enhancing their catalytic activity and stability [185, 194]. As the size of individual metal atoms in CSAs decreases, the metal-substrate interaction increases.

2.3. Using TiO_2 in the application of advanced wastewater treatment techniques

2.3.1. Photocatalyst mechanism - TiO_2

The field of photocatalytic reactors has witnessed significant and varied research activity over the last three decades. Numerous studies have been carried out on an extensive number of fixed-film photocatalyst suspended particle configurations. The primary factors to be considered in the context of photocatalytic reactors, however, remain consistent: efficient transport of pollutants to the photocatalyst surface and optimal positioning and exposure of the photocatalyst to light. This paper examines the primary configurations of the type of immobilized photocatalytic photocatalytic reactor types investigated alongside the TiO_2 catalyst that have been documented so far.

Photocatalytic reactors have a high degree of adaptability, making them suitable for the treatment of different types of water and gaseous pollution. Moreover, these methods have also been used in drinking water treatment. The successful implementation of photocatalytic reactors in waste and drinking water treatment plants was also presented. Another potential use of photocatalytic reactors is related to greenhouse emissions. Different systems have been

documented to mitigate carbon dioxide by converting this greenhouse gas into combustible products [207].

Semiconductor photocatalysis has been used in a wide range of environmental applications, including air, drinking water and wastewater treatment. This adaptable approach has also been used to eradicate microorganisms, including bacteria [208] and viruses [209].

Excitation and charge generation

The process of photoexcitation results in the generation of an electronic vacancy, i.e. a vacancy (h+), at the valence band edge. This occurs when an electron (e-) is excited at the edge of the conduction band. The overall reaction can be represented as: Photocatalyst + hυ → Photocatalyst (e- + h+). The electron-gol pairs (e⎯ h+) created during photoexcitation are commonly referred to as exciton pairs. These pairs possess energy due to the correlated motion of electrons and holes, but do not contribute to the electron current flow. Exciton pairs can manifest as either weakly or strongly bonded electron-hole pairs characterized by the presence of attractive Coulomb interactions. The Wannier-Mott exciton, often referred to as the free exciton, is a type of exciton characterized by its free bonding. These excitons are commonly observed in semiconductor nanocrystals, i.e. quantum dots, where the exciton wave function is delocalized. The mobility of Wannier-Mott excitons is constrained by particle or crystal sizes due to their significant radius and susceptibility to dissociation. Frenkel excitons, which are tightly bound excitons with small radii, are commonly observed in organic dye groups [215].

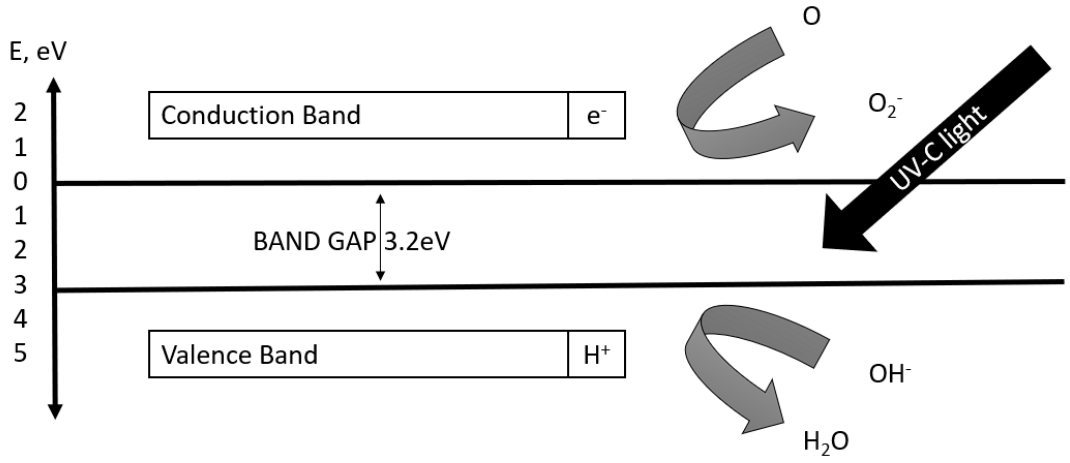

Figure 4: Processes that occur in TiO_2 photoexcitation

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CHAPTER 3. METHODOLOGY OF EXPERIMENTAL RESEARCH

Experimental research was conducted to investigate the effectiveness of different types of photocatalytic reactors for the removal of specific surfactants from wastewater. In the experiments, the catalyst used for photocatalysis was TiO_2 at nanometer size.

Three photocatalytic reactors each with distinct properties and characteristics were used. All 3 reactors were designed in the laboratory of which 2 were specifically created for this thesis.

- Non-submersible fixed bed photocatalytic reactor
- Submersible fixed bed photocatalytic reactor
- Submersible photocatalytic reactor with detection

The first reactor was used to determine its effectiveness in the treatment of water polluted with Benzethonium Chloride (BZT). The second experiment was carried out on Surfactants C12, C14 and C16 as the last reactor.

The relevant academic literature has provided the necessary knowledge underlying the use of nanomaterials in empirical investigations.

In the course of these experimental investigations, the impact of changing the amounts of nanomaterials and the influence of the type of photocatalytic reactor was examined. The objective was to evaluate the effects of these variations, together with the duration of treatment, on the removal efficiency of pollutants from wastewater. The findings resulting from the empirical investigation were organized in a tabular format and represented visually by graphical representation.

Methodology, work plan and scientific tests were developed and executed in the Laboratory of Environmental Quality Analysis, coordinated by Prof. dr. eng. Cristina-Ileana Covaliu-Mierlă within the Doctoral School of Biotechnical Systems Engineering of the National University of Science and Technology Politehnica Bucharest.

The measurements for the experiments in chapter 4.1 and chapter 4.2 were made using the spectrophotometer produced by Analytik Jena, model Specter 200 together with its software: WINASPECT.

The spectrophotometer software does not include in its packages calibration curves for the surfactants used in the experiments, for this reason the calibration curves were made in the laboratory using standard solution concentrations.

CHAPTER 4. EXPERIMENTAL RESEARCH

4.1. Non-submersible fixed bed photocatalytic reactor

4.1.1. Features and system configuration

The system was designed from the outset as a simple reactor with low operating costs and high efficiency. The reactor has no moving parts, so maintenance cost is low.

The photocatalytic reactor consists of a low-voltage UV-C lamp, a water tank, an acrylic glass support that serves as a substrate for the TiO_2 bed and a coupling/decoupling system.

Configuration

The choice of reactor configuration is simple, with the lamp positioned at a distance of 100 mm from the maximum filling point of the wastewater tank. The lamp is suspended within the basin. The acrylic sheet support or bed entirely covers the base of the basin and is placed directly in the basin without any other method of attachment as shown in Figure 17.

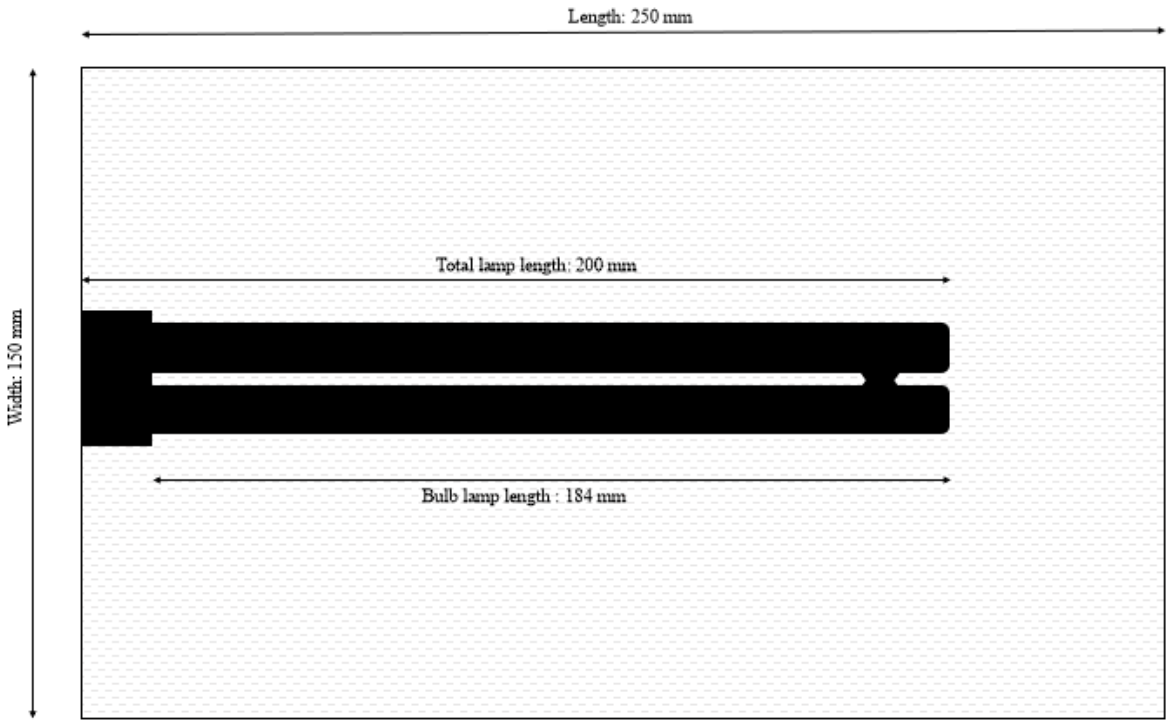

Figure 17 Sketch of a fixed bed non-submersible photocatalytic reactor - top view

4.1.2. Results

To calculate the yield, we used the following calculation method in which the absorbance of light was measured using the UV-VIS spectrophotometer. The absorbance was measured on an in situ calibration curve (Figure 11), calculated with an accuracy of r2 = 0.9863 for all 6 variables (solutions of standard concentrations in situ).

$$\eta = \frac{Ce}{Ci} \times 100$$

I mention that experiments were carried out to determine the optimum depth for the filling level of the basin. As a result of the experiments the depth of 20 mm to the reactor bed was chosen.

In the experiments we used 6 concentrations, starting from 12.5 mg/L up to 75 mg/L. The concentrations were chosen taking into account the limitations of the UV measurement method, whereby concentrations below 5 mg/L are difficult to measure, as light absorption is very low at similar concentrations. On the other hand, according to specialized studies, normal concentrations in nature are between 0.06 mg/L and 5 mg/L, and a possible increase in in situ concentrations may lead to inhibition of microorganisms or to a decrease in yield through membrane filtration from classical ones, which is another reason to choose the tested concentrations. Moreover, for low concentrations, the current technology used in wastewater treatment plants can be considered sufficient to maintain a balance between cost and efficiency.

Wastewater treatment efficiency - Concentration 12.5 mg/L

Table 7 Photocatalysis results Non-submersible reactor at concentration of 12.50 mg/L

Crt. no.	Duration of exposure (H)	Ci (mg/L) Initial concentration	Ct (mg/L) Achieved concentration	Yield (%)
1	1	12.5	12.50	0.00
2	2	12.5	11.78	5.80
3	3	12.5	8.79	29.70
4	4	12.5	6.57	47.41
5	5	12.5	0.27	97.84
6	6	12.5	0.27	97.84

By analyzing the results in Figure 19, we observe that by using the above method, we can identify a constant time rate of increase in yield. The results were obtained in a much shorter time than under natural conditions, managing to obtain yields of: 97.84% in only 5 hours of exposure.

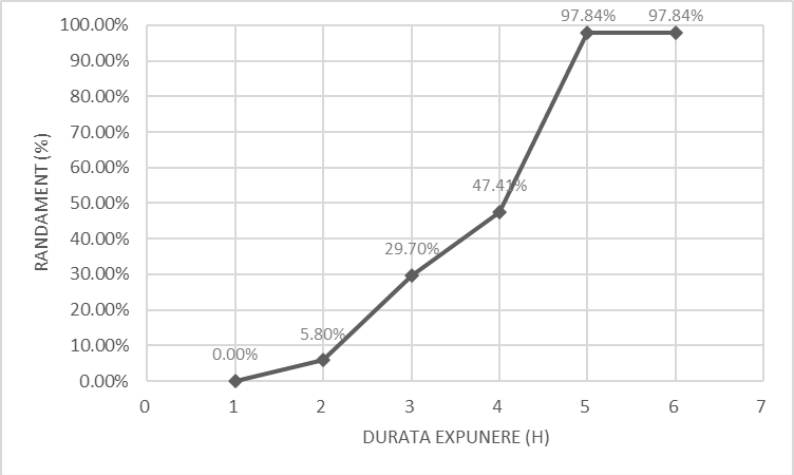

Figure 19 Photocatalysis results Non-submersible reactor concentration 12.50 mg/L

Water treatment efficiency - Concentration 25 mg/L

Table 8 Photocatalysis results Non-submersible reactor concentration 25 mg/L

Crt. no.	Duration of exposure (H)	Ci (mg/L) Initial concentration	Ct (mg/L) Achieved concentration	Yield (%)
1	1	25	25.00	0.00
2	2	25	23.60	5.62
3	3	25	17.58	29.69
4	4	25	12.51	49.98
5	5	25	5.55	77.82
6	6	25	0.21	99.15
7	7	25	0.21	99.15

For the 25 mg/l concentration, the maximum yield was obtained in 6 hours of exposure (Figure 20) The maximum yield was 99.15%. Even though the yield was higher than the 12.5 mg/l concentration, it was obtained in 6 hours compared to 5 hours for the previous concentration. At an exposure time of 5 hours, the calculated yield is 77.84%.

Figure 20 Photocatalysis results Non-submersible reactor at 25 mg/L concentration

Water treatment efficiency - Concentration 35.5 mg/L

Table 9 Photocatalysis results Non-submersible reactor at concentration of 37.50 mg/L

Crt. no.	Duration of exposure (H)	Ci (mg/L) Initial concentration	Ct (mg/L) Achieved concentration	Yield (%)
1	3	37.5	37.50	0.00
2	4	37.5	36.81	1.83
3	5	37.5	27.86	25.72
4	6	37.5	4.67	87.54
5	7	37.5	4.67	87.54

For the concentration of 37.5 mg/l, the maximum yield was obtained in 6 hours of exposure (Figure 21) The maximum yield obtained was 87.54%. The yield is lower than those obtained for the concentrations of 12.5 mg/l and 25 mg/l. Moreover, the yield obtained with a 5 hours exposure as in the case of 12.5 mg/l concentration is much lower, only 27.72%.

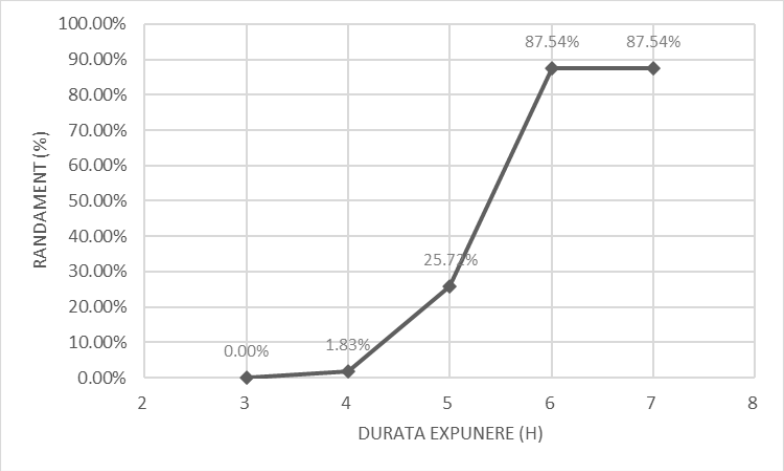

Figure 21 Photocatalysis results Non-submersible reactor concentration 37.5 mg/L

Water treatment efficiency - Concentration 50 mg/L

Table 10 Photocatalysis results Non-submersible reactor at 50 mg/L concentration

Crt. no.	Duration of exposure (H)	Ci (mg/L) Initial concentration	Ct (mg/L) Achieved concentration	Yield (%)
1	1	50	50.00	0.00
2	2	50	37.59	24.83
3	3	50	32.69	34.62
4	4	50	23.59	52.82
5	5	50	18.37	63.27
6	6	50	5.14	89.72
7	7	50	5.14	89.72

For the 50 mg/l concentration, the maximum yield was obtained in 9 hours of exposure (Figure 22), a time 50% longer than for previous concentrations. The maximum yield was 89.72%. The yield is lower than those obtained for the concentrations of 12.5 mg/l and 25 mg/l and 37.5 mg/l. The yield obtained at an exposure of 5 hours as in the case of the 12.5 mg/l concentration is significantly lower and similar to that obtained at 5 hours in the case of the 37.5 mg/l concentration, i.e. 63.27%.

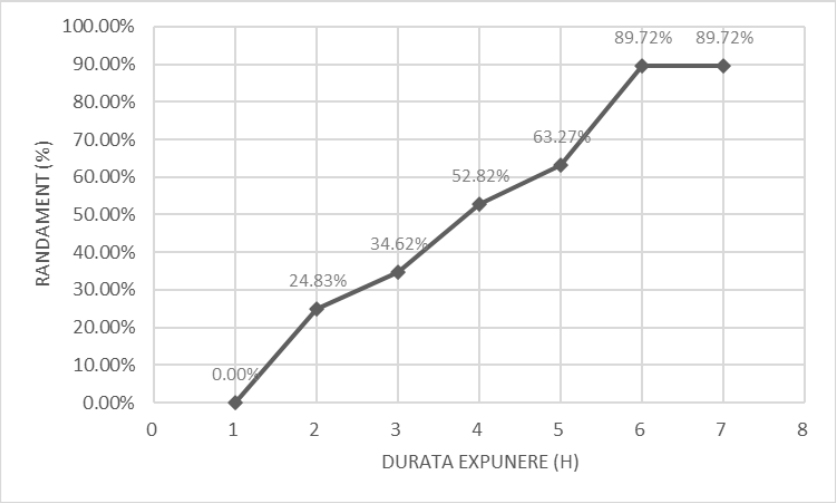

Figure 22 Photocatalysis results Non-submersible reactor concentration 50 mg/L

Water treatment efficiency - Concentration 62.5 mg/L

Table 11 Photocatalysis results Non-submersible reactor at concentration of 62.50 mg/L

Crt. no.	Duration of exposure (H)	Ci (mg/L) Initial concentration	Ct (mg/L) Achieved concentration	Yield (%)
1	2	62.5	62.50	0.00
2	3	62.5	46.89	24.97
3	4	62.5	40.94	34.49
4	5	62.5	34.68	44.52
5	6	62.5	22.97	63.25
6	7	62.5	6.21	90.07
7	8	62.5	6.21	90.07

For the 62.5 mg/L concentration, the maximum yield was obtained in 10 hours of exposure (Figure 23), a time similar to that obtained for the 50 mg/L concentration. Furthermore, the yield curve is similar to that obtained for the 50 mg/L concentration. The maximum yield was 90.07%. The yield is lower than that obtained for the concentrations of 12.5 mg/l and 25 mg/l and 37.5 mg/l. The yield obtained at 5 hours exposure as in the case of 12.5 mg/l concentration is significantly lower and similar to that obtained at 5 hours exposure as in the case of 50 mg/l concentration, i.e. 44.52%.

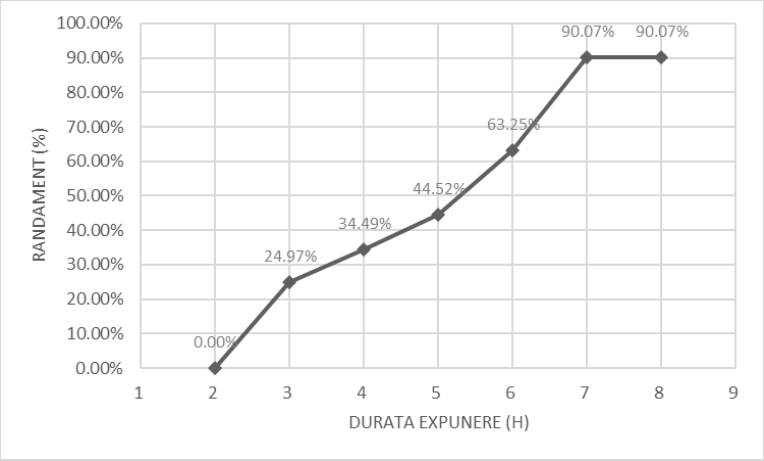

Figure 23 Photocatalysis results Non-submersible reactor concentration 62.5 mg/L

Water treatment efficiency - Concentration 75 mg/L

Table 12 Photocatalysis results Non-submersible reactor concentration 75 mg/L

Crt. no.	Duration of exposure (H)	Ci (mg/L) Initial concentration	Ct (mg/L) Achieved concentration	Yield (%)
1	5	75	75.00	0.00
2	6	75	66.03	11.96
3	7	75	56.38	24.83
4	8	75	45.02	39.97
5	9	75	35.39	52.82
6	10	75	15.02	79.98
7	11	75	15.02	79.98

The highest concentration of the experiment is 75 mg/l, the maximum yield was obtained in 11 hours of exposure (Figure 24), a long time which despite being still clearly higher than that obtained by photolysis, does not find its economic basis, considering that the energy consumed is directly proportional to the exposure time and secondly, such an increased concentration has not been reported by any study so far. The efficiency is inferior to those obtained for lower concentrations and shows the limit of the system.

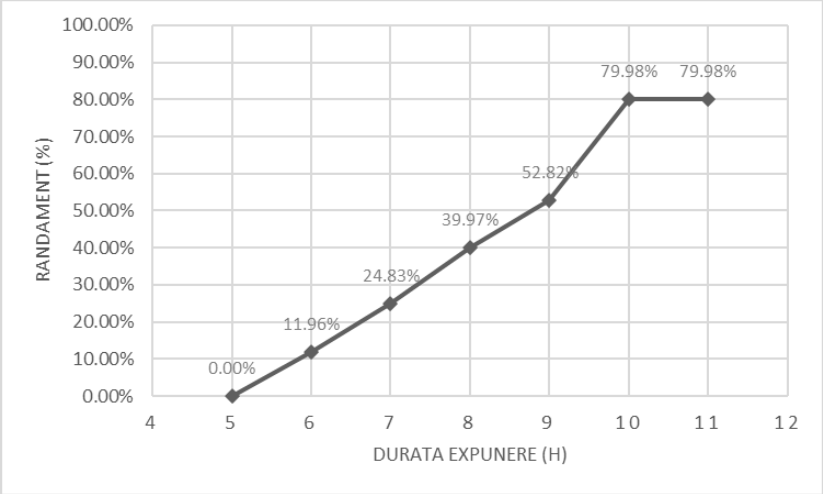

Figure 24 Photocatalysis results Non-submersible reactor concentration 75 mg/L

4.1.3. Conclusions

Using the TiO_2 catalyst and the described photocatalytic reactor configuration we achieved near maximum yields in up to 92% less than the natural half-life. Consequently, we expect better exposure over time results by introducing new economical features in our system configuration, such as aeration and stirring of the solution during exposure or pH modification.

From the research presented above, as well as from preliminary tests that have been carried out in the laboratory, we expect a reduction in exposure time to less than 4 hours at lower concentrations.

4.2. Fixed bed submersible photocatalytic reactor

4.2.1. Features and system configuration

In the submersible fixed-bed reactor configuration the main aim was to obtain the highest possible yield with the use of a reduced amount of catalyst relative to the wastewater. If in the first case the capacity of the reactor is 0.75 L, in this reactor the filling capacity is up to 21 L, 10 times higher. By comparison, the surface area of the exposure bed in relation to the amount of water is almost double 0.05 m^2/L in the case of the non-submersible reactor versus ~0.0248 m^2/L.

The submersible photocatalytic reactor consists of 6 UV-C lamps with a power of 50 Wh, 6 quartz tiles to protect the lamps from submersion, a water tank, four acrylic glass supports to act as substrate for the TiO_2 bed and a coupling/uncoupling system.

UV lamp

In the choice of the lamp, the spectrum of the light it emits and its power were taken into account. In the literature, the reactors have lamps with a wattage between 75 W and 150 W. The lamps emit UV light in the C-spectrum, between 200 nm and 250 nm. Its physico-technical characteristics can be consulted in the table below.

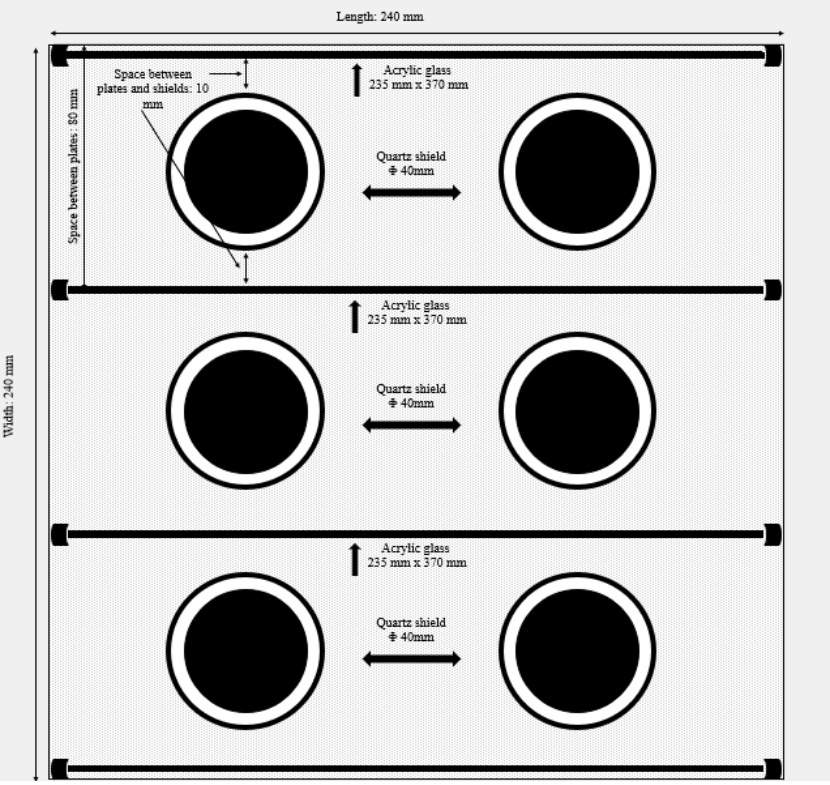

Figure 27 Sketch Submersible fixed bed photocatalytic reactor - top view

4.2.2. Results

In the experiments we used 2 concentrations in the case of the C12-C16 surfactant solution and a single concentration for the C12-C14 pollutant. The use of solutions consisting of pairs of pollutants can tell us more about the partitioning of detergents in wastewater, where we will almost never find a single type of surfactant.

Compared to the previous experiment, the used concentrations of pollutants are closer to the natural ones being much lower, respectively 5 mg/L and 10 mg/L in the case of the C12-C16 solution and 5 mg/L in the case of the C12-C14 solution.

Water treatment efficiency C12-C16 - C12 concentration - 5 mg/L

Table 15 Rezultate fotocataliza Reactor submersibil cu pat fix concentraţie 5 mg/L - C12 în soluţie C12-C16

Crt. no.	Duration of exposure (H)	Ci (mg/L) Initial concentration	Ct (mg/L) Achieved concentration	Yield (%)
1	1	5.40	5.1	5.56
2	2	5.40	4.9	9.26
3	3	5.40	4.9	9.26
4	4	5.40	4.8	11.11
5	5	5.40	4.7	12.96
6	6	5.40	4.6	14.81
7	7	5.40	4.5	16.67
8	8	5.40	4.5	16.67
9	9	5.40	4.2	22.22
10	10	5.40	4	25.93
11	11	5.40	3.8	29.63
12	12	5.40	3.6	33.33

The experiment was run for 12 hours in order to establish a maximum reactor efficiency. In the graph below (Figure 29) we observe an increasing trend towards the maximum yield, however, given the operating costs that such a reactor involves and the concomitant natural degradation time of these detergents the utility of continuing the experiment is low between the 2 parameters being an inversely proportional relationship (increasing degradation time in the treatment plants increases the cost of treatment, with an increasingly lower marginal utility).

We can observe that the removal of surfactant C12 is cumbersome and during the experiment it reached a maximum yield of 33.33%, a low yield insufficient for commercial applications.

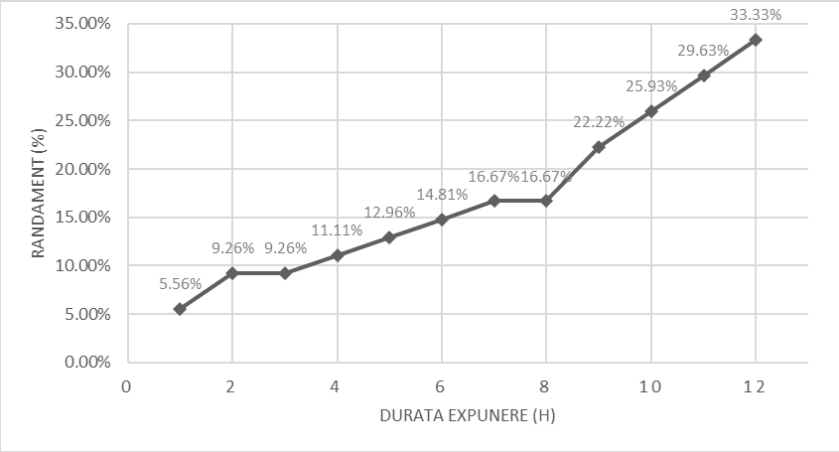

Figure 29 Photocatalysis results Submersible fixed-bed reactor concentration 5 mg/L - C12 in C12-C16 solution

Water treatment efficiency C12-C16 - C16 concentration - 5 mg/L

Table 16 Photocatalysis results Fixed-bed submersible reactor concentration 5 mg/L - C16 in C12-C16 solution

Crt. no.	Duration of exposure (H)	Ci (mg/L) Initial concentration	Ct (mg/L) Achieved concentration	Yield (%)
1	1	5	4.93	1.40
2	2	5	4.45	11.00
3	3	5	4	20.00
4	4	5	3.75	25.00
5	5	5	3.25	35.00
6	6	5	3	40.00%
7	7	5	2.75	45.00%
8	8	5	2.75	45.00%
9	9	5	2.6	48.00%
10	10	5	2.18	56.40%
11	11	5	1.75	65.00%
12	12	5	1.55	69.00%

In the case of surfactant C16, the results are better with a 2-fold better yield, however not reaching the level obtained in the experiments with the non-submersible reactor in the previous chapter. Possible explanations for this result may be the surface area of the exposure bed in relation to the amount of wastewater and the combined effect of the 2 surfactants on the oxidation process.

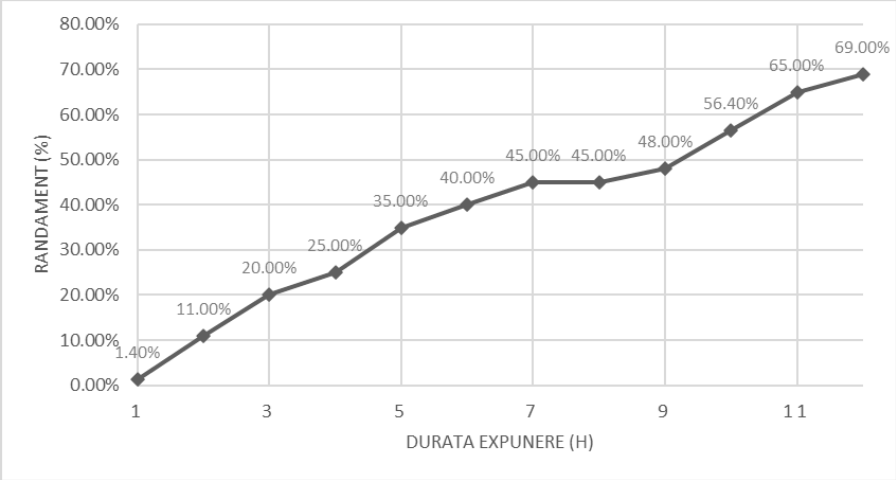

Figure 30 Photocatalysis results Fixed-bed submersible reactor concentration 5 mg/L - C14 in C12-C16 solution

Water treatment efficiency C12-C16 - C12 concentration - 10 mg/L

Table 17 Photocatalysis results Submersible fixed-bed reactor concentration 10 mg/L - C12 in C12-C16 solution

Crt. no.	Duration of exposure (H)	Ci (mg/L) Initial concentration	Ct (mg/L) Achieved concentration	Yield (%)
1	1	10	9.80	2.00
2	2	10	9.70	3.00
3	3	10	9.70	3.00
4	4	10	9.70	3.00
5	5	10	9.60	4.00
6	6	10	9.40	6.00
7	7	10	9.30	7.00
8	8	10	9.30	7.00

The yield obtained at a concentration of 10 mg/l of the solution in the first experiment is superior, being 26% better in the case of the C12 surfactant. However, as can be seen in the graph below (figure 31) it reaches a maximum yield after 8 hours, remaining at 7%.

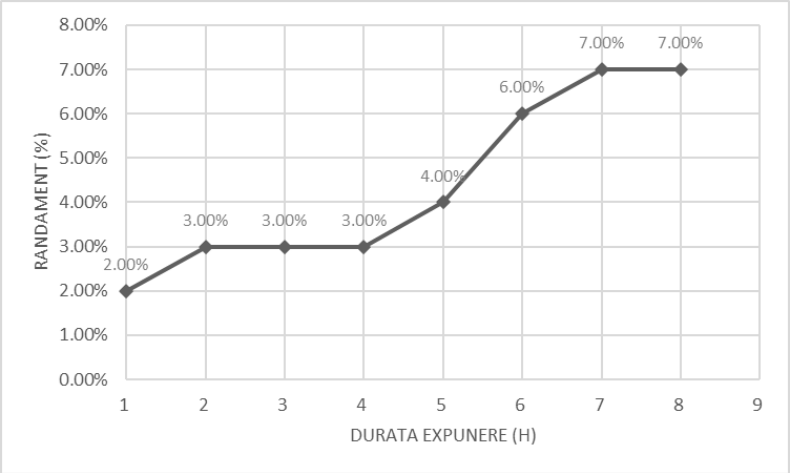

Figure 31 Photocatalysis results Submersible fixed-bed reactor concentration 10 mg/L - C12 in C12-C16 solution

C12-C16 water treatment efficiency - C16 concentration - 10 mg/L

Table 18 Photocatalysis results Submersible reactor with fixed bed concentration 10 mg/L - C16 in C12-C16 solution

Crt. no.	Duration of exposure (H)	Ci (mg/L) Initial concentration	Ct (mg/L) Achieved concentration	Yield (%)
1	1	10	9.9	1.00
2	2	10	9.9	1.00
3	3	10	8.55	14.50
4	4	10	8.4	16.00
5	5	10	7.5	25.00
6	6	10	6.6	34.00
7	7	10	6.45	35.50
8	8	10	6.3	37.00

The surfactant C16 at a concentration of 10 ppm has a much higher yield than its pair in the C12-C16 solution, but the yield is also very low, with the same possible explanations as for the C12 results.

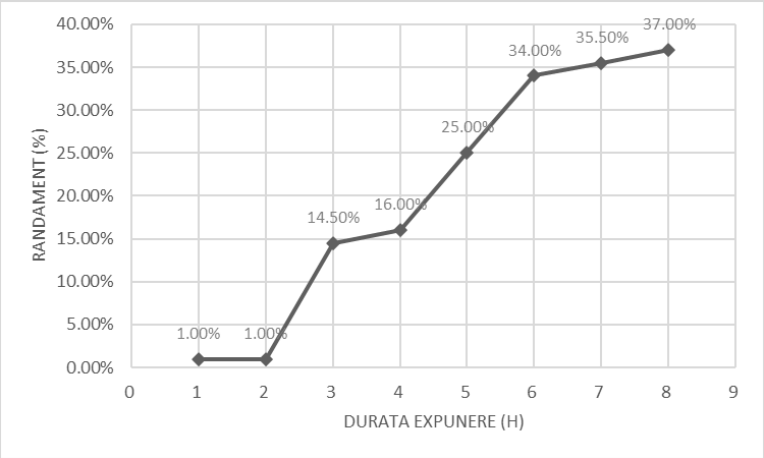

Figure 32 Photocatalysis results Submersible reactor with fixed bed concentration 10 mg/L - C16 in C12-C16 solution

Water treatment efficiency C12-C14 - C12 concentration - 5 mg/L

Table 19 Photocatalysis results Submersible reactor with fixed bed concentration 5 mg/L - C12 in C12-C14 solution

Crt. no.	Duration of exposure (H)	Ci (mg/L) Initial concentration	Ct (mg/L) Achieved concentration	Yield (%)
1	1	5	4.8	4.00
2	2	5	4.8	4.00
3	3	5	4.8	4.00
4	4	5	4.74	5.20
5	5	5	4.4	12.00
6	6	5	4.2	16.00
7	7	5	4.19	16.20
8	8	5	4.1	18.00
9	9	5	4.1	18.00
10	10	5	4.1	18.00
11	11	5	3.7	26.00
12	12	5	3.8	24.00

By analyzing the catalytic oxidation behavior of C12-C14 surfactants in pairs, we can compare the results obtained in the case of hyamine (C16). Thus we can draw some conclusions regarding the oxidation mode of these compounds in the photocatalytic reactor presented in this

chapter. The use of the C12-C14 pair of surfactants is based on an attempt to formulate a relationship between the pairwise oxidation behavior of these types of pollutants and the type of reactor used.

In this perspective we observe that compared to the C12-C16 pair the reactor efficiency is even lower. Moreover, as we will see below, also in the C14 case, the efficiency is lower than in the C16 case.

What's more, after 11 hours of exposure, the degraded molecules start to recompose, with the final efficiency even lower.

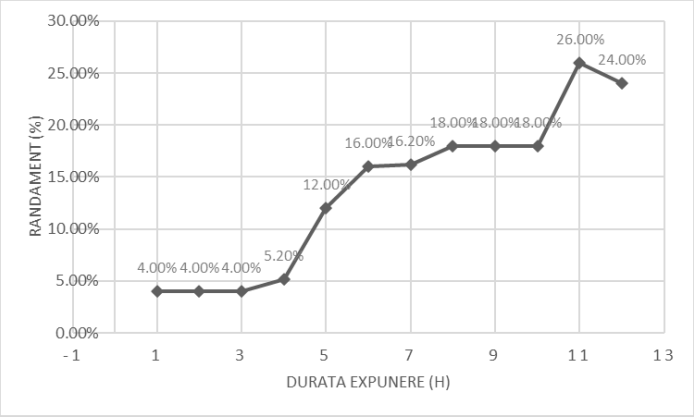

Figure 33 Photocatalysis results Submersible reactor with fixed bed concentration 5 mg/L - C12 in C12-C14 solution

Water treatment efficiency C12-C14 - C14 concentration - 5 mg/L

Table 20 Photocatalysis results Submersible reactor with fixed bed concentration 5 mg/L - C14 in C12-C14 solution

Crt. no.	Duration of exposure (H)	Ci (mg/L) Initial concentration	Ct (mg/L) Achieved concentration	Yield (%)
1	1	5	4.25	15.00
2	2	5	4.20	16.00
3	3	5	4.20	16.00
4	4	5	4.05	19.00
5	5	5	3.90	22.00
6	6	5	3.90	22.00

7	7	5	3.70	26.00
8	8	5	3.64	27.20
9	9	5	3.45	31.00
10	10	5	2.85	43.00
11	11	5	2.55	49.00
12	12	5	2.25	55.00

As anticipated, the efficiency of the oxidation process of C14 inside the reactor shown is lower (55%) compared to the efficiency obtained for C16 (69%). One explanation may be based on the structure of the three molecules. Thus, the longer the carbon chain, the higher the chances of hydroxyl radicals to degrade the surfactant molecule. This hypothesis is also supported by the much lower efficiency in oxidizing C12.

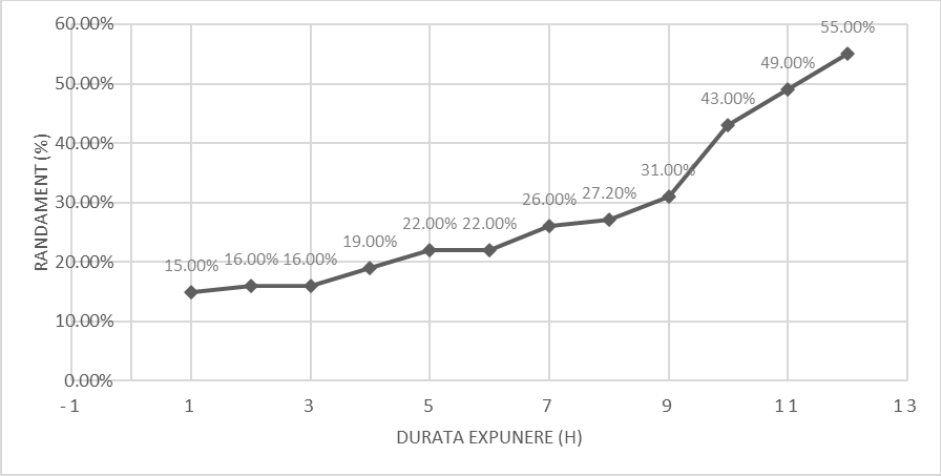

Figure 34 Fixed bed submersible reactor 5 mg/L concentration - C14 in C12-C14 solution

4.2.3. Conclusions

Thanks to the chosen configuration, the reactor occupies much less space than a non-submersible reactor and has the advantage of being able to be built vertically, which is important when considering its construction at industrial level.

The results obtained are not yet at the level required for the implementation of such a technical solution in industrial and domestic water treatment. However, the experiments in Chapter 4.2 can help us to better understand the mechanisms of photocatalysis, the capabilities of the TiO_2

catalyst and the influence of reactor design on the efficiency of chemical damage by photocatalysis.

4.3. Submersible photocatalytic photocatalytic detection reactor

Figure 35 Reactor built during research

4.3.1. Features and system configuration

In the configuration of the submersible sensing reactor the main goal was to obtain the highest possible efficiency by using a nanosized powder catalyst. As a secondary objective, in view of the previous experiments, new functionalities were added: a total volatile organic carbon and carbon dioxide detection system, a temperature measurement system, an automatic data storage system and the automation of the experiments.

The reactor has a single 110 Wh UV-C lamp, 1 quartz sheath to protect the lamps from submergence, two water tanks, and a digital system for programming, storing and measuring reactor parameters.

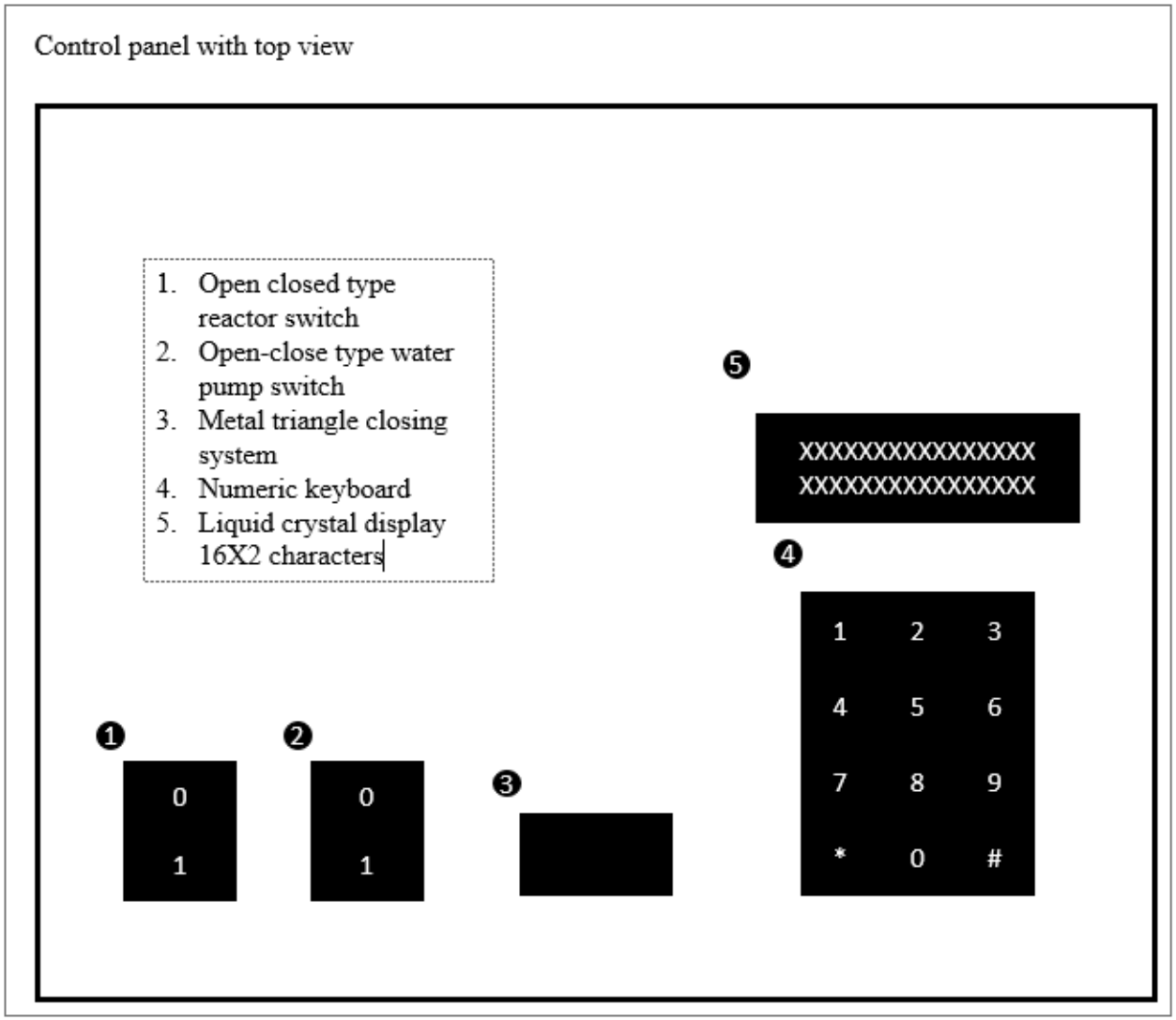

Figure 36 Submersible reactor control panel with submersible

PhD student:
Alexandru Vişan

Scientific coordinator
Prof. habil. dr. eng. Cristina-Ileana Covaliu-Mierlă

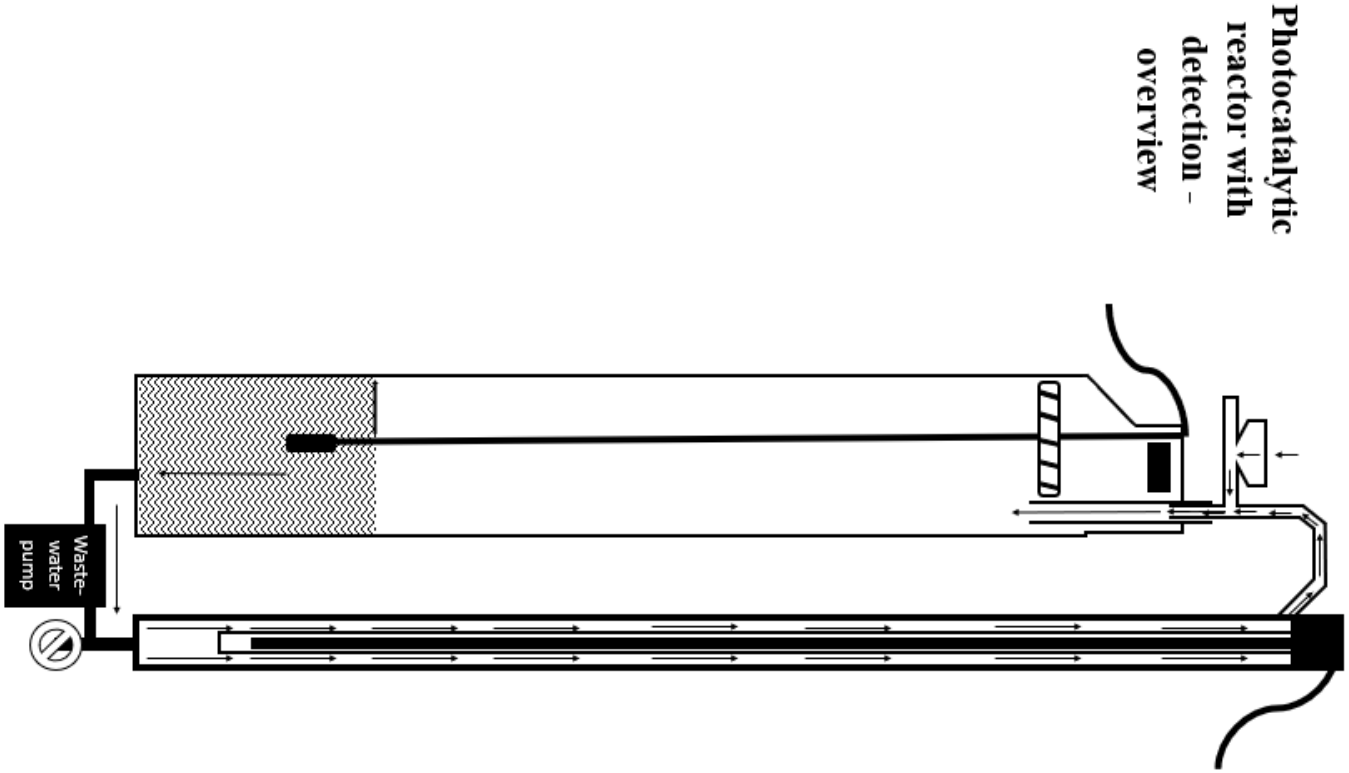

Figure 44 Submersible sensing reactor design - overview

PhD student: Scientific coordinator
Alexandru Vişan Prof. habil. dr. eng. Cristina-Ileana Covaliu-Mierlă

4.3.2. Results

In order to determine the efficiency of the photocatalyst described in this chapter, we proposed the following experiment: using the three pollutants (C12-C14-C16) in a single wastewater solution with two different concentrations of 5 mg/L and 10 mg/L. The wastewater solutions were made in the laboratory starting from standard solutions with concentrations of 1 g/L.

As in the previous experiment, by combining the three surfactants, the experiment shows us the degree of oxidation over time when they are put together, a situation often encountered in water treatment plants.

The experiments were carried out over a 12-hour period for each concentration, with hourly concentration measurements to determine the treatment efficiency.

The reactor built for this chapter can be used with a fixed bed as well as with suspended particles, for this experiment we used suspended particles by adding directly to the wastewater 0.5 g/L TiO_2 powder.

Water treatment efficiency C12-C14-C16 - C12 concentration - 5 mg/L

Table 27 Rezultate fotocataliza Reactor submersibil cu detecţie concentraţie 5 mg/L - C12 în soluţie C12-C14-C16

Crt. no.	Duration of exposure (H)	Ci (mg/L) Initial concentration	Ct (mg/L) Achieved concentration	Yield (%)
1	1	5	4.60	8.00
2	2	5	4.60	8.00
3	3	5	4.60	8.00
4	4	5	3.80	24.00
5	5	5	3.80	24.00
6	6	5	3.41	31.80
7	7	5	3.38	32.40
8	8	5	3.21	35.80
9	9	5	3.20	36.00
10	10	5	3.20	36.00
11	11	5	2.40	52.00
12	12	5	2.34	53.20

The oxidative degradation of surfactant C12 in C12-C14-C16 wastewater at an initial concentration of 5 ppm over the course of the experiments is increasing, reaching a maximum yield of 53.20% at t12. In the first 3 h of exposure, the yield is low, only 8%. Moreover, in comparison with the results obtained in the previous chapter for the same type of pollutant at the same concentration, the yield curve is similar, which helps us to distinguish a certain oxidative behavior of the pollutant. Taking into account the yield obtained and its duration, we can say that the results obtained are not sufficiently performing for a commercial scale solution.

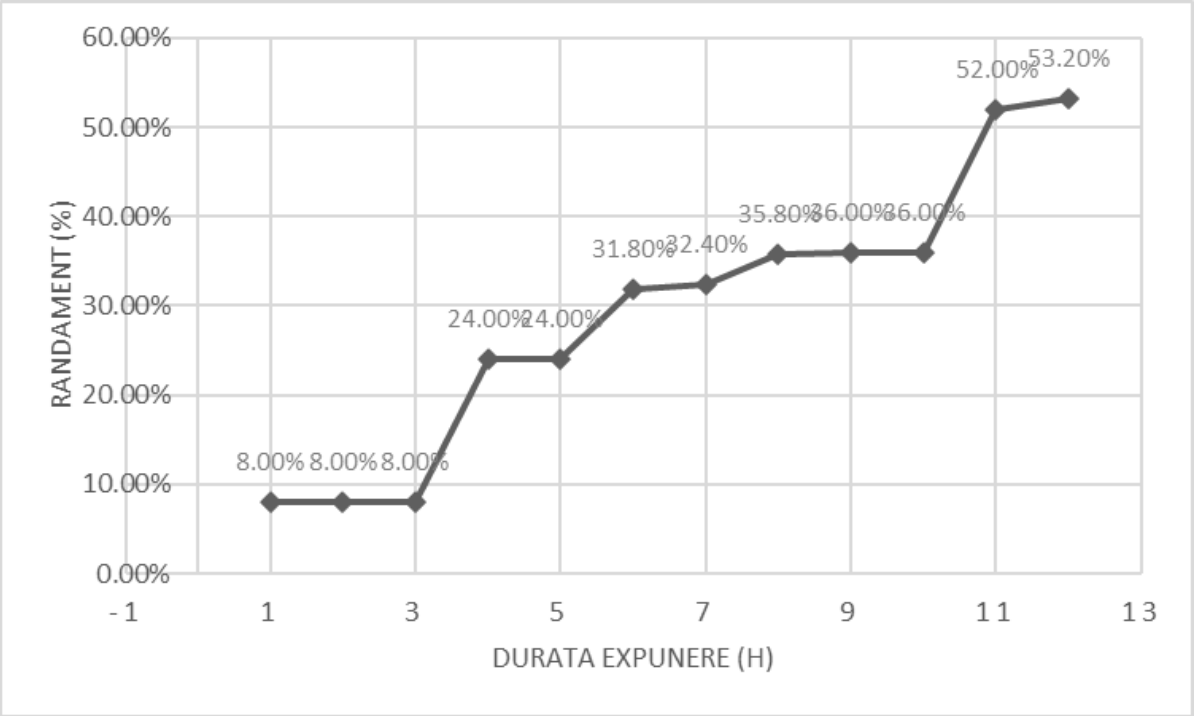

Figure 45 Photocatalysis results Submersible reactor with detection concentration 5 mg/L - C12 in C12-C14-C16 solution

PhD student: Scientific coordinator

Alexandru Vişan Prof. habil. dr. eng. Cristina-Ileana Covaliu-Mierlă

Water treatment efficiency C12-C14-C16 - C14 concentration - 5 mg/L

Table 28 Photocatalysis results Submersible reactor with detection concentration 5 mg/L - C14 in C12-C14-C16 solution

Crt. no.	Duration of exposure (H)	Ci (mg/L) Initial concentration	Ct (mg/L) Achieved concentration	Yield (%)
1	1	5	4.83	3.40
2	2	5	4.74	5.20
3	3	5	4.74	5.20
4	4	5	4.48	10.40
5	5	5	4.22	15.60
6	6	5	4.22	15.60
7	7	5	3.88	22.40
8	8	5	3.78	24.40
9	9	5	3.45	31.00
10	10	5	2.41	51.80
11	11	5	1.90	62.00
12	12	5	1.38	72.40

The results obtained for C14 at a concentration of 5 mg/L are 32% better than the fixed-bed reactor, even though three surfactants are present in the wastewater solution this time instead of two. Another important point to mention is that during the first 8 hours, oxidation is steady but at a slow rate, reaching a yield of only 24.4%, and then the rate of pollutant degradation increases rapidly, reaching 72.4% in only 4 hours.

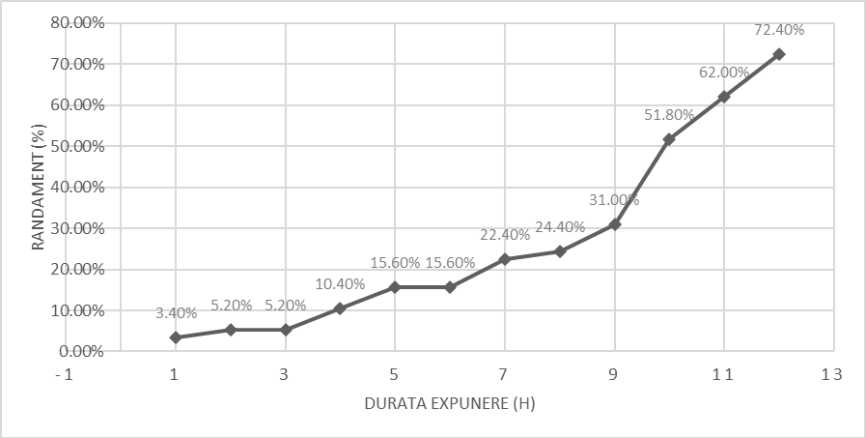

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Figure 46 Photocatalysis results Submersible reactor with detection concentration 5 mg/L - C14 in C12-C14-C16 solution

Water treatment efficiency C12-C14-C16 - C16 concentration - 5 mg/L

Table 29 Photocatalysis results Submersible reactor with detection concentration 5 mg/L - C16 in C12-C14-C16 solution

Crt. no.	Duration of exposure (H)	Ci (mg/L) Initial concentration	Ct (mg/L) Achieved concentration	Yield (%)
1	1	5	4.90	2.00
2	2	5	4.18	16.40
3	3	5	3.50	30.00
4	4	5	3.13	37.40
5	5	5	2.39	52.20
6	6	5	2.00	60.00
7	7	5	1.64	67.20
8	8	5	1.64	67.20
9	9	5	1.41	71.80
10	10	5	0.78	84.40
11	11	5	0.14	97.20
12	12	5	0.12	97.60

The removal efficiency of the pollutant C16 from the proposed solution is superior to the other 2 pollutants and reaches close to the maximum efficiency in the 12 hours of the experiment. Over time, the photocatalytic oxidation rate of the detergent photocatalyst is constant throughout the experiment except for the time interval 7 h -8 h where the calculated inter-sample yield is equal.

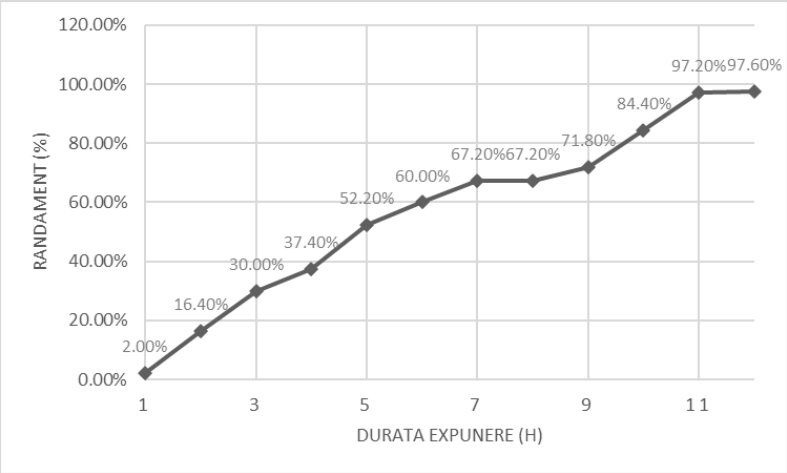

Figure 47 Photocatalysis results Submersible reactor with detection concentration 5 mg/L - C16 in C12-C14-C16 solution

Water treatment efficiency C12-C14-C16 - C12 concentration - 10 mg/L

Table 30 Photocatalysis results Submersible reactor with detection concentration 10 mg/L - C12 in C12-C14-C16 solution

Crt. no.	Duration of exposure (H)	Ci (mg/L) Initial concentration	Ct (mg/L) Achieved concentration	Yield (%)
1	1	10	9.64	3.60
2	2	10	9.43	5.70
3	3	10	9.43	5.70
4	4	10	8.8	12.00
5	5	10	8.65	13.50
6	6	10	8.3	17.00
7	7	10	8.2	18.00
8	8	10	8.2	18.00
9	9	10	7.6	24.00
10	10	10	6.4	36.00
11	11	10	5.8	42.00
12	12	10	5.3	47.00

Surfactant C12 at a concentration of 10 ppm obtained a yield comparable to that obtained at a concentration of 5 ppm, being only 12% lower. In addition, for experiment 2, the graph shows us that the oxidation process is a constant compared to that in experiment 1. Another thing worth mentioning is the major difference between the result obtained using the submersible fixed-bed photoreactor for the C12-C16 pair at 10 ppm concentration of only 7% and the result obtained for the suspended particle reactor. The difference being 671%.

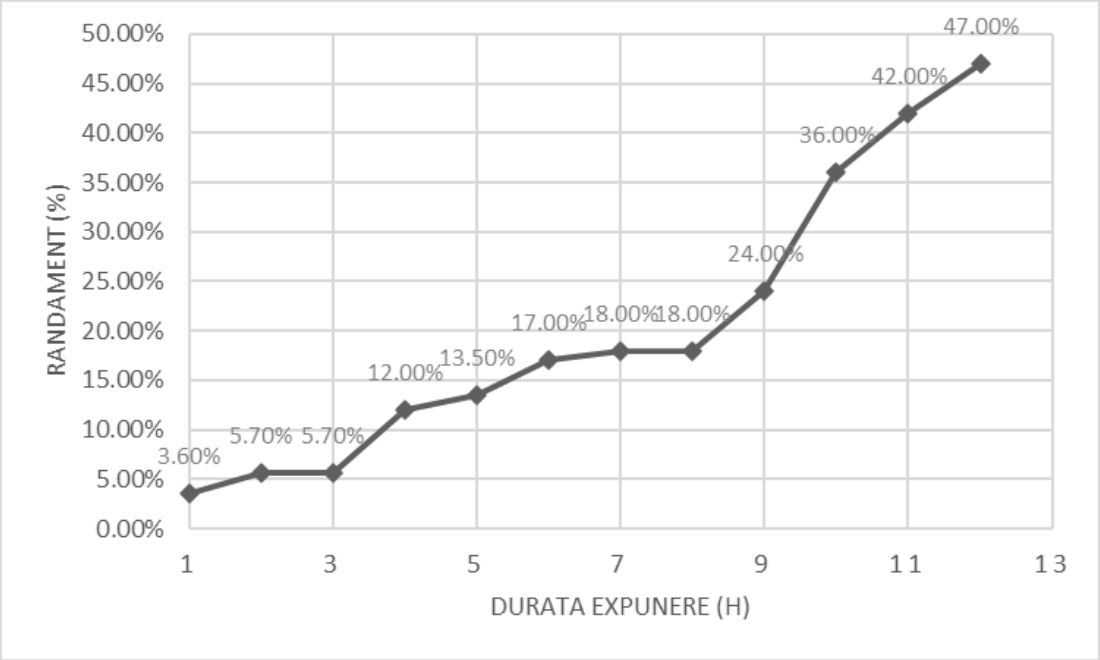

Figure 48 Photocatalysis results Submersible reactor with detection concentration 10 mg/L - C12 in C12-C14-C16 solution

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Water treatment efficiency C12-C14-C16 - C14 concentration - 10 mg/L

Table 31 Photocatalysis results Submersible reactor with detection concentration 10 mg/L - C14 in C12-C14-C16 solution

Crt. no.	Duration of exposure (H)	Ci (mg/L) Initial concentration	Ct (mg/L) Achieved concentration	Yield (%)
1	1	10	8.9	11.00
2	2	10	8.16	18.40
3	3	10	8.16	18.40
4	4	10	7.78	22.20
5	5	10	7.42	25.80
6	6	10	7.04	29.60
7	7	10	6.68	33.20
8	8	10	6.66	33.40
9	9	10	5.58	44.20
10	10	10	4.84	51.60
11	11	10	4.1	59.00
12	12	10	3.14	68.60

The concentrations obtained for surfactant C14 at a concentration of 10 mg/L following photocatalytic oxidation using the submersible particle-suspended photoreactor are lower than those obtained using the fixed-bed photoreactor in the previous chapter, managing to obtain a better efficiency of 68.6% even though, in the experiments in the previous chapter, the initial concentration is 5 mg/L. In comparison with the results obtained by the same reactor, but at a lower concentration, the efficiency is similar, lower by only 5%.

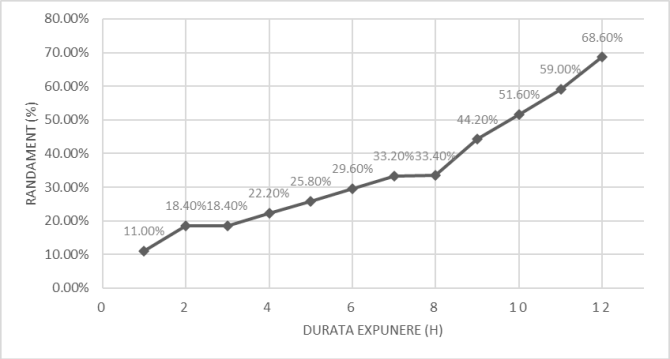

Figure 49 Photocatalysis results Submersible reactor with detection concentration 10 mg/L - C14 in C12-C14-C16 solution

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Water treatment efficiency C12-C14-C16 - C16 concentration - 10 mg/L

Table 32 Photocatalysis results Submersible reactor with detection concentration 10 mg/L - C16 in C12-C14-C16 solution

Crt. no.	Duration of exposure (H)	Ci (mg/L) Initial concentration	Ct (mg/L) Achieved concentration	Yield (%)
1	1	10	9.75	2.50
2	2	10	9.65	3.50
3	3	10	9.20	8.00
4	4	10	8.34	16.60
5	5	10	7.91	20.90
6	6	10	7.5	25.00
7	7	10	6.38	36.20
8	8	10	6.00	40.00
9	9	10	3.75	62.50
10	10	10	1.50	85.00
11	11	10	1.13	88.70
12	12	10	0.75	92.50

The efficiency of the photocatalytic oxidation process of the submersible suspended particle submersible reactor for surfactant C16 for experiment two at an initial concentration of 10 mg/L, follows the general trend and reaches the value of 92.6%. Compared to the result obtained in the first experiment, it is 5% lower.

Compared to the results obtained in chapter 4.2 using the submersible fixed-bed reactor, these are superior, obtaining a concentration of 92.5% compared to only 37%. However, in comparison with the non-submersible fixed-bed reactor in the hyamine assay, the results are comparable and can help us to better understand oxidative chemical mechanisms.

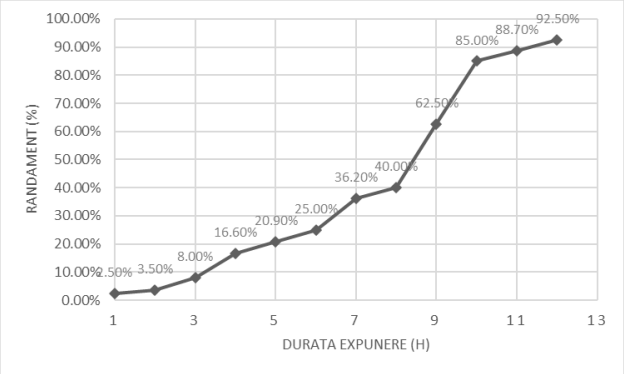

Figure 50 Photocatalysis results Submersible reactor with detection concentration 10 mg/L - C16 in C12-C14-C16 solution

Measurement of Total Volatile Organic Carbon

In both experiments, the parameters were saved by the reactor software and calibrated after each exposure session. In the collected data, due to the principle of sensor operation the data obtained during a session are linear for this reason, it is sufficient to calibrate the values at the beginning of the session and the end of the sessions. Calibration of the sensors was done using the results measured using the method outlined in chapter 4 by UV spectrophotometry.

Table 33 Detected values of vTOC C12-C14-C16 at a concentration of 5 mg/L

Detected values of vTOC C12-C14-C16 5 mg/L			
Duration of exposure (H)	**Ci (mg/L) Initial concentration**	**Delta vToc registered**	**Total yield (%)**
1	5	0	2.00
2	5	142	16.40
3	5	98	30.00
4	5	227	37.40
5	5	274	52.20
6	5	327	60.00
7	5	379	67.20
8	5	405	67.20
9	5	376	71.80
10	5	445	84.40
11	5	612	97.20
12	5	639	97.60

Table 34 Detected values of vTOC C12-C14-C16 at a concentration of 10 mg/L

Detected values of vTOC C12-C14-C16 10 mg/L			
Duration of exposure (H)	**Ci (mg/L) Initial concentration**	**Delta vToc registered**	**Total yield (%)**
1	5	0	2.50
2	5	146	3.50
3	5	106	8.00
4	5	357	16.60
5	5	461	20.90
6	5	610	25.00
7	5	604	36.20
8	5	869	40.00
9	5	756	62.50
10	5	867	85.00
11	5	1098	88.70
12	5	1263	92.50

In the tables above, the parameters obtained in the tests are presented, below we can see that in the case of the first experiment (C12-C14-C16 Ci=5 mg/L), the calibrated vTOC curve respects the trend of the yield measured by classical methods.

The parameters measured by the vTOC sensor in experiment 2 (C12-C14-C16 Ci=5 mg/L) also follow the general trend (Table 35) but the measurements are not as accurate.

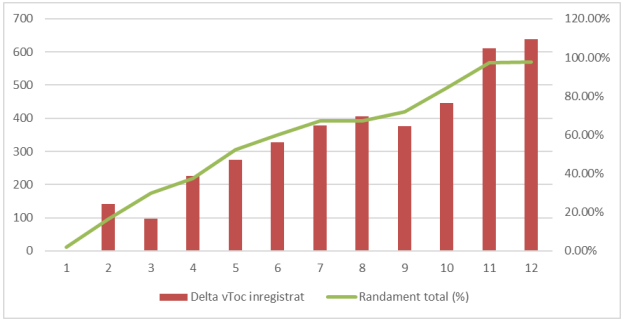

Figure 52 Values detected by the vTOC C12-C14-C16 sensor at a concentration of 5 mg/L

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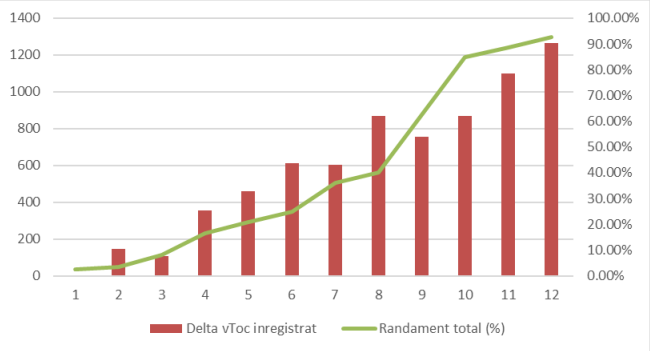

Figure 53 Values detected by the vTOC C12-C14-C16 sensor at a concentration of 10 mg/L

4.3.4. Conclusions

The reactor presented in this chapter has both functional and catalytic oxidation yield advantages. The functionality of the reactor benefits the researcher by facilitating experiments. At the same time, experiments enjoy greater accuracy of exposure times.

In terms of yields obtained, through the above experiments, the reactor was able to improve the photocatalytic processes of the catalyst obtaining notable results in the case of surfactant C16. Moreover, in the case of the other surfactants the obtained results are superior compared to the submersible fixed bed type reactor.

Another advantage of this type of reactor is its versatility in the amount of TiO_2 used in the experiments. In the 2 experiments, the amount of TiO_2 was the same - 10 mg/L. Another advantage is the possibility to use other oxidants such as peroxide in advanced photocatalysis experiments.

CHAPTER 5. ORIGINAL CONTRIBUTIONS. FINAL CONCLUSIONS. PERSPECTIVES

5.1. Original Contributions

Through reactor research and construction, we have made the following original contributions:

1. Literature review on the use of traditional and non-conventional techniques for water treatment and the use of nanotechnology for the removal of organic pollutants from wastewater;

2. Evaluation of TiO_2 catalyst in photocatalytic processes for the removal of BZT, C12, C14 and C16 sulfactants;
3. Configuration and construction of the non-submersible fixed-bed photocatalytic reactor;
4. Fixed bed submersible photocatalytic reactor configuration;
5. Configuration and construction of the submersible photocatalytic photocatalytic reactor with detection;
6. Introduction and configuration of sensors for measuring volatile substances in the photocatalytic reactor;
7. Evaluation of the performance of the configured reactors on the above noted pollutants.

5.2. Final conclusions

The main functional distinction between the three reactors is the mode of exposure of the photocatalyst to electromagnetic energy. Thus the first two reactors presented are of the fixed bed type, where the catalyst is deposited on acrylic glass and the last reactor, even though it can also be used with a fixed bed, was tested by disposing the catalyst in suspension. One of the main limitations of photocatalytic reactors is the efficient distribution of light to the catalysts that are in direct contact with aqueous pollutants. Another important thing to keep in mind is the catalyst separation process, suspension photocatalyst systems require an additional step. Thus, in addition to the functionality of the reactors, the two methods have a direct impact on the results, especially by directly comparing the yields between the two submersible reactors. Reactor three, shows a higher yield compared to reactor two, with the slurry catalyst giving up to 30% better results compared to the fixed bed one.

In the experiments we obtained near maximum yields using the TiO_2 catalyst non-submersible reactor (Chap. 4.1) , with an exposure time up to 92% shorter than the natural half-life. Therefore, by introducing new economical features in the system configuration such as aerating and stirring the solution during exposure or changing the pH, we expect better exposure time results.

At lower concentrations, we expect a reduction in exposure time to less than 4 hours from the research presented above and preliminary laboratory tests. Compared to non-submersible reactors, the results are superior and give us a starting point in choosing the type of photocatalytic reactor in future research.

As for the submersible reactor presented in Chap. 4.2, the results obtained in the tests are inferior to those obtained with the non-submersible reactor. Nevertheless it gives us a starting point for the construction of new types of photocatalytic reactors.

At present, the results are not at the level required for the application of such a technical solution in domestic and industrial water treatment. However, we can gain a better understanding of the mechanisms of photocatalysis, the capabilities of the TiO_2 catalyst, and the impact of reactor design on the efficiency of chemical damage by photocatalysis using the experiments presented in Chapter 4.2. One of the advantages of submersible reactors (Chapters 4.2 and 4.3) is that they occupy less space than the non-submersible one due to the chosen configuration. They also have the advantage of being built on a vertical axis, which is essential for its industrial construction.

Regarding the yields obtained in chapter 4.3, the results of the experiments demonstrated that the reactor was able to improve the photocatalytic processes of the catalyst, which led to good results in the case of surfactant C16. In addition, in comparison with the submersible fixed-bed reactor, the preliminary results obtained for other surfactants are better.

The reactor described in Chapter 4.3 offers advantages in both functionality and catalytic oxidation yield. The functionality of the reactor helps the researcher to carry out the experiments in a controlled environment. Furthermore, by using this reactor, real-time detects can be obtained and exposure times are carefully monitored.

Another advantage of this type of reactor is that it is versatile in terms of the amount of TiO_2 used in the experiments. An additional advantage is the possibility to use other oxidants, such as peroxide, in advanced photocatalysis experiments.

5.3. Perspectives

The result provides a solid foundation for future research aimed at refining the theory and efficiency of nanotechnology-based photocatalytic wastewater systems.

Further development of the detection system by measuring volatile compounds using affordable sensors and equipment that can lead to affordable equipment for monitoring and detection of organic compounds in wastewater.

Another direction that can be pursued is to analyze the performance of the configured photoreactors in other organic compounds. Moreover, new methods for advanced photocatalysis can be evaluated and investigated using the particle suspension photoreactor.

Due to the versatility of the presented reactors, in future researches, different water pollutants can be tested, by comparison with the presented results it is possible to theorize new

mechanisms in the photocatalysis process. Moreover, the differences between the results obtained by the reactor in Chapter 4.2 and the reactor in Chapter 4.3, under the conditions of future tests, by continuously observing this difference can reveal the importance of the mixing process and gradual exposure of the catalyst to electromagnetic radiation. Another theoretical perspective may be the impact of the partial pressure at the solution surface on the water treatment efficiency.

PUBLICATIONS LIST

1. Cristina Ileana Covaliu, Gigel Paraschiv, Oana Stoian and Alexandru Vișan, Nanomaterials applied for heavy metals removal from wastewater, IOP Conf. Series: Materials Science and Engineering 572 (2019) 012074, 1-7;
2. Alexandru VISAN, Leon COVALIU, Cristina Ileana COVALIU-MIERLĂ, REMOVAL FROM WASTEWATER OF BENZETHONIUM CHLORIDE (BZT) BY PHOTOCATALYSIS, U.P.B. Sci. Bull., Series B, Vol. 86, Iss. 2, 2024.
3. Alexandru VISAN, Leon COVALIU, Cristina Ileana COVALIU-MIERLĂ, Review - Ecological treatment of wastewater containing a cationic surfactant pollutant, Land Reclamation, Earth Observation & Surveing, Eniviromental Engineering ISSN 2285-6064, acceptat spre publicare la 20 octombrie 2023

PRESENTATIONS AT INTERNATIONAL CONFERENCES

4. Oral presentation - Vișan A., Butnariu C. I., Voicu Ș., Iovu H., Deák Gy., Paraschiv G., WASTEWATER TREATMENT USING NANOTECHNOLOGY, International Symposium ISB-INMA TEH Agricultural and Mechanical Engineering, 2023;
5. Oral presentation - Vișan Al., Covaliu L.D., Matei E, THE PHOTOCATALYTIC DEGRADATION OF BENZETHONIUM CHLORIDE (BZT) USING TIO2 NANOPARTICLES, International Symposium ISB-INMA TEH Agricultural and Mechanical Engineering, 2022;
6. Oral presentation - Vișan A., Butnariu C. I., Voicu Șt., Iovu H., Deák Gy., Paraschiv G., WASTEWATER TREATMENT USING NANOTECHNOLOGY, International Symposium ISB-INMA TEH Agricultural and Mechanical Engineering, 2018;
7. Oral presentation - C. I. Covaliu, G. Paraschiv, O. Stoian, A. Vișan, Nanomaterials applied for heavy metals removal from wastewater, International Conference on Innovative Research – ICIR EUROINVENT, 2019;
8. Poster - Vișan A., Butnariu C. I., Voicu Șt., Iovu H., Deák Gy., Paraschiv G., WASTEWATER TREATMENT USING NANOTECHNOLOGY , EmergeMAT, 2018

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