National University of Science and Technology POLITEHNICA BUCHAREST

Faculty of Biotechnical Systems Engineering

Doctoral School of Biotechnical Systems Engineering

Field of Environmental Engineering

DOCTORAL THESIS

UNCONVENTIONAL TECHNIQUES FOR ELIMINATION OF DETERGENTS FROM WASTEWATER

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CONTENT

WORD BEFORE

The doctoral thesis with the theme "Unconventional techniques for removing detergents from wastewater" includes studies and research whose main objective was the use of nanomaterials with an adsorbent role and a semiconductor nanomaterial, TiO_2, in order to develop unconventional techniques for removing surfactants of the type of quaternary ammonium salts from wastewater, as well as the development of a combined, integrated, photocatalytic chemical (TiO_2/UV) and biological (with the help of bacteria) purification technique for them.

The doctoral thesis is structured in nine chapters.

In chapter 1 of the doctoral thesis entitled "Objectives of the doctoral thesis. The importance of the topic" presents the objectives proposed and achieved based on experimental research and the importance of the topic chosen to be developed in this doctoral thesis.

Chapter 2 entitled "General considerations regarding the presence of surfactants in the environment - the current state of knowledge" contains data from the specialized literature regarding the identification of the main sources of pollution with cationic surfactants, mainly from the class of quaternary ammonium salts, the level of their concentrations in the samples environmental as well as their use either as disinfectants, preservatives, antistatic agents, softening agents and dispersing agents.

Chapter 3 entitled "The current state of the conventional water treatment techniques that contain surfactants from the class of quaternary ammonium salts" contains data from the literature on techniques for removing cationic surfactants through techniques that are based on physical methods using adsorbent materials, biological using microorganisms found in activated sludge.

Chapter 4 entitled "Perspectives on new non-conventional water purification techniques" contains information from the specialized literature related to cationic surfactant removal techniques that are based on adsorption methods on non-conventional materials, techniques that are based on advanced chemical oxidation processes, as well as photocatalytic and chemical hybrid methods.

Chapter 5 "Experimental research on methods for the analysis and control of surfactants in the environment" describes a method adapted and developed in the laboratory for the determination of benzalkonium chlorides in environmental samples and wastewater used in experimental research.

Chapter 6 entitled "Methodology of experimental research" includes in detail the equipment, reagents and materials that were necessary to carry out the experimental research presented in the doctoral thesis.

Chapter 7 entitled "Experimental research on the application of nanomaterials with an adsorbent role for the purpose of purifying waters containing cationic surfactants such as quaternary ammonium salts" describes in detail all the research, experiments and studies undertaken for the development of techniques for the purification of wastewater containing surfactants cations using magnetite and zeolite ZSM-5 adsorbent nanomaterials and active carbon adsorbent material in powder form made throughout the doctoral internship.

Chapter 8 entitled "Hybrid techniques for removing surfactants from wastewater using TiO_2 semiconductor nanomaterial through the process of photocatalysis combined with biodegradation using bacterial strains" describes experimental research carried out to develop technologies for removing surfactants from wastewater using TiO_2 semiconductor nanomaterial in the form of powder and film, a hybrid technology has also been developed consisting of two purification stages: the photocatalytic stage and the biological stage, which can be used for the advanced purification stage of a sewage treatment plant (tertiary stage).

Chapter 9 contains the final conclusions, original contributions and future perspectives.

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

1.1. The objectives of the doctoral thesis

The problem of water pollution with detergents is a serious issue, in an accentuated way since the beginning of the 2020s with the onset of the Coronavirus (COVID-19) infection, given on the one hand their increasing consumption, and on the other hand, determination of fairly high concentrations in wastewater and surface water.

The active substances in the composition of detergents that have a negative influence on the environment are surfactants. Surfactants are the most widely used organic substances in personal and household products as well as in industrial products, being considered emerging pollutants. Since the removal of surfactants from wastewater by conventional methods, which use activated sludge as a purification method, cannot be achieved, because they have bactericidal and disinfectant properties, the research direction chosen for the doctoral thesis is the development of unconventional techniques that use materials or nanomaterials with adsorptive or photocatalytic role.

To support this research direction, the following objectives were achieved:

1. The study of materials or nanomaterials with an adsorbent role in order to develop techniques for purifying wastewater with surfactants

2. The study of the existing photocatalysts for their selection and testing in order to develop a technique for purification by photodegradation of wastewater with surfactants

3. The study of the bacteria that are found in the activated sludge of the sewage treatment plant in order to select a certain species for the development of biodegradation techniques of wastewater with surfactants.

The main objective of the doctoral thesis is the use of nanomaterials with an adsorbent role and a semiconducting nanomaterial, TiO_2, in order to develop unconventional techniques for the removal of surfactants such as quaternary ammonium salts from wastewater, as well as the development of a combined purification technique, integrated, photocatalytic chemical (TiO_2/UV) and biological (with the help of bacteria) of them.

1.2. Importance of theme

It is a necessity to take measures to combat water polluted with surfactants because there is a continuous development of cleaning and disinfection products.

At the same time, the development of easily biologically degradable products is being pursued in sewage treatment plants and in their discharges (usually surface waters).

New techniques for wastewater treatment or improvement of current techniques are researched, to achieve a faster and more complete decomposition of surfactants, the development of methods for the determination and monitoring of surfactants from the effluent of treatment plants, from surface and underground waters, and from distribution networks.

It is necessary to implement some legislative measures in order to establish maximum concentrations allowed for discharge in treatment plants or outfalls.

The ever-increasing use of disinfectants and cleaning products has led to the continuous increase in surfactant concentrations in wastewater, which makes conventional wastewater treatment technologies no longer effective and high concentrations of surfactants are discharged in surface waters.

Cationic surfactants have been shown to have a toxic effect on the environment due to the attachment of their positive charge to predominantly negatively charged particles in sewage sludge, soil and sediments. Also, cationic surfactants have negative influences on the environment by increasing the eutrophication of lakes or by disrupting the wastewater treatment process by decreasing the microbial community and subsequently disrupting the biochemical reactions of the activated sludge. In order to solve this pressing problem of removing surfactants from wastewater, unconventional wastewater treatment techniques are sought, such as techniques based on adsorption methods using nanomaterials, techniques based on advanced oxidation methods using photocatalysts, and combined techniques that they are based on combined methods of photocatalysis with the help of semiconductor nanomaterials, with the help of UV radiation and biodegradation with the help of bacterial strains. Surfactant polluted water treatment using adsorbent materials, especially nanomaterials, provides better performance compared to conventional techniques.

CHAPTER 2. GENERAL CONSIDERATIONS REGARDING THE PRESENCE OF SURFACTANTS IN THE ENVIRONMENT - CURRENT STATE OF KNOWLEDGE

Detergents are commercial products that have in their chemical composition mainly surfactants. More specifically, a detergent is a solid or liquid cleaning formula containing a number of compounds, at least one of which is a surfactant [1].

Surfactants are substances with cleaning properties, with the ability to lower the surface tension of the liquid in which they are dissolved, acting as surface agents. The cleaning action, typical of surfactants, is a consequence of the particular structure of their molecule, which consists of a non-polar or weakly polar group and a strongly polar, ionizable or non-ionizable group.

According to the nature of the polar grouping, two important categories of surfactants are distinguished: nonionic surfactants and ionic surfactants (which in turn are divided into anionic, cationic and amphoteric).

2.1. The main sources of surfactant pollution

Sources of surfactant pollution can act permanently, temporarily or accidentally and are mainly:

- textile industry;
- leather and dyes industry;
- household and utility activities;
- insecticides and fungicides;
- chemical industry.

2.2. Applications of surfactants of the class of quaternary ammonium salts

With the emergence and spread of COVID-19, disinfection products have been used more and more. If until the onset of the COVID-19 pandemic, the usual disinfectants based on ethyl alcohol, chlorine or hydrogen peroxide were used, during the pandemic, disinfectants based on quaternary ammonium salts began to be used [2]. The United States Environmental Protection Agency (EPA) has published a list of disinfectants that can be used to destroy the SARS-COV-2 coronavirus. Most of the compounds specified in this list are quaternary ammonium salts such as dialkyldimethylammonium salts, alkyltrimethylammonium salts, and benzalkonium salts [3].

Quaternary ammonium salts are most commonly used as disinfectants. A recent study demonstrates that quaternary ammonium salts (benzalkonium chloride) completely and rapidly inactivate the SARS-CoV-2 virus within 15 seconds [4].

Quaternary ammonium salts are also used as preservatives for the protection of historic materials (wood and brick) against microbial growth. Thus tests were carried out for *Staphylococcus equorum, Bacillus cereus, Sporosarcina aquimarina*, the bacteria *Rhodococcus fascians* and the molds *Cladosporium cladosporoides* I and *Acremonium strictum* and all were shown to have a high sensitivity to them. So, they can be successfully used for the preservation of historical materials [6].

Quaternary ammonium salts are also used in the pharmaceutical industry where they are included in the composition of pharmaceutical preparations acting as a preservative.

Quaternary ammonium salts are used as surfactants in personal care products such as shampoos and hair conditioners, shower gels, hand soap, hand sanitizer gel, wet wipes, as well as in household cleaning products, dish detergents, in laundry detergents, in fabric softeners, in floor cleaners. They are also used in industrial cleaning products, for cleaning surfaces and even for degreasing industrial parts and appliances.

They can also be used as antistatic agents, softening [8] dispersing agents [9] and anticorrosives [10-11].

Quaternary ammonium salts together with natural zeolites form organozeolites which are used for the adsorption and removal of numerous non-polar organic substances, such as drugs, mycotoxins, etc. Thus, a natural zeolite - clinoptilolite was modified with three concentrations of benzalkonium chloride and was used for the adsorption of two mycotoxins, namely ochratoxin A and zearalenone under in vitro conditions [14]. And for the adsorption of the mycotoxin zearalenone, modified zeolites with different amounts of benzalkonium chloride and cetylpyridine chloride were prepared [15].

Activated carbon when placed in water is negatively charged, meaning only cations in the water can be removed. The introduction of quaternary ammonium salts in water, mainly benzalkonium chloride, causes the charge to change from negative to positive in the newly obtained activated carbon material modified with cationic surfactant. The new material obtained has been used for the removal from wastewater of fluorides [22], perchlorates [23], hexavalent chromium compounds [24] and even non-polar substances such as volatile organic compounds [25].

2.3. Structure and properties of surfactants from the class of quaternary ammonium salts used in the study of purification by non-conventional techniques

Benzethonium chloride (diisobutylphenoxyethoxyethyl dimethylbenzylammonium chloride), is a cationic surfactant, in the class of quaternary ammonium salts, known as Hyamine 1622. Benzethonium chloride is used as an antimicrobial and antibacterial ingredient in many industrial and medical consumer products, including drops for eyes and noses, soaps, mouthwash, and cosmetics [26]. In the composition of medical products, benzethonium chloride is usually found at a concentration below 1% [27]. Benzethonium chloride can be found in the food industry where it is used as a surface disinfectant [28].

Benzalkonium bromide, chemical name benzyldodecyldimethylammonium bromide. Benzalkonium bromide is a cationic surfactant used as a biocide in cosmetic products (hair conditioners and dye preparations), detergents, pesticides and as an inactive ingredient in pharmaceutical products. It was introduced to the market in 1953 and was widely used in chemical disinfectants due to its low price. Benzalkonium bromide demonstrated its bactericidal properties when it was used to remove Bacillus cereus biofilm from stainless steel surfaces. Bacillus cereus is a common pathogen in dairy products, which is a Gram-positive bacterium that could produce enterotoxin [34].

Benzalkonium chlorides (alkyl dimethylbenzyl ammonium chlorides) were introduced to the market in 1935 by Gerhard Domagk under the trade name of zephiran chlorides, as disinfectant and antiseptic products, and since 1947 they have been registered with the Environmental Protection Agency of the United States of America America [38].

Benzalkonium chlorides are applied as bactericides and disinfectants in sanitary products and antistatic agents in the formulation of laundry conditioners. C18-alkyl benzyldimethyl ammonium is mostly applied as the main ingredient of hair conditioners [39].

Benzalkonium chloride is an antimicrobial agent included in some nasal solutions to prevent bacterial growth [40].

Benzalkonium chloride demonstrated its bactericidal properties in a study carried out on six important pathogens in the food industry, namely: three Gram-positive bacteria (*Staphylococcus aureus, Listeria monocytogenes and Bacillus cereus*) and three Gram-negative bacteria (*Salmonella typhimurium, Escherichia coli and Pseudomonas aeruginosa*). The bacteria *Listeria monocytogenes* and *Bacillus cereus* were the most sensitive and resistant. Experiments showed that benzalkonium chloride was more effective against Gram-positive bacteria than against Gram-negative bacteria, except for *Bacillus cereus* which has the ability to form spores [41].

Dodecyl benzyldimethyl ammonium chloride shows antimicrobial activity against the Gram-negative bacterium *Pseudomonas fluorescens* [42].

Tetradecyl benzyldimethyl ammonium chloride can be used alone for the spectrophotometric determination of cobalt (II) [46] and for the preparation of modified analcimic zeolite, used in the determination of traces of cadmium [48].

Hexadecylbenzyl dimethyl ammonium chloride, used individually, shows antimicrobial activity against the bacterium *Pseudomonas aeruginosa* [49]. Hexadecylbenzyl dimethyl ammonium chloride was used in a study to evaluate the removal of cationic surfactants from aqueous solutions using activated carbon [50]

To prevent the transmission of the Covid-19 coronavirus during the SARS-COV-2 pandemic, chemicals with biocidal properties containing mainly benzalkonium chlorides were used to disinfect hands and surfaces [52].

After use, residual amounts of benzalkonium chlorides and their degradation products are discharged into sewage treatment plants or directly into surface water and groundwater. Benzalkonium chlorides belong to the category of emerging pollutants [53]. The presence of these compounds in the environment causes serious environmental problems, including ecological risks and damage to human health [54].

2.5. Industrial wastewater, domestic wastewater and surface water polluted with detergents

Benzalkonium chlorides are present in environmental samples worldwide. Studies on the presence of these compounds in environmental samples (wastewater, surface water) and in the activated sludge of the water treatment plant are relatively few. Pandemic and post-pandemic studies show that wastewater effluent samples from 12 treatment plants around the Minneapolis–Saint Paul metropolitan area (United States) were analyzed and concentrations of benzalkonium chloride were determined. The highest concentrations were obtained for C14-BAC which was detected in all analyzed samples and the highest concentration was 1.386 µg/L and for C12-BAC the highest concentration determined was 0.143 µg/L and for C16-BAC was 1.015 µg/L. The concentrations of these compounds were also determined in the sediments of the lake where the treated wastewater is discharged. The maximum concentrations determined were for C12-BAC of 0.127 mg/kg, for C14-BAC of 0.211 mg/kg and for C16-BAC it was 0.163 mg/kg [55]. This proves that the purified wastewater discharged into the lakes still contains benzalkonium chlorides which concentrate in the sediment.

In Germany, benzalkonium chlorides were found in the sludges of sewage treatment plants that used a primary mechanical and a secondary biological stage for wastewater treatment. The concentrations of 12-BAC found in sewage sludge were between 0.562 mg/kg and 38.6 mg/kg, while the concentrations of 14-BAC were between 0.055 mg/kg and 199.4 mg/Kg, and the concentrations of 16-BAC were between 0.010 mg/kg and 320.3 mg/kg. [56]. This proves that benzalkonium chlorides do not break down during wastewater treatment, they are concentrated in the sewage sludge.

In 2010, seawater was sampled from three locations in the north-east of England on the North Sea coast. The samples were analyzed by the SPE-LC–MS technique [57]. C12-BAC concentrations were below the method limit of determination, but didecyl dimethyl ammonium chlorides between 0.12-0.27 µg/L were determined.

As early as 2001, concentrations of C12-BAC and C16-BAC counterparts were determined in untreated wastewater and surface water in the United States [58]. C12-BAC and C14-BAC were measured in influentes concentrations up to 170 µg/L C12-BAC and 110 µg/L C14-BAC and in effluents up to 0.5 µg/L C12-BAC and 0.63 µg/L of C14-BAC.

In Romania, concentrations of benzalkonium chlorides were determined from domestic wastewater from office buildings, hospitals, car washes, as well as domestic wastewater from fuel station restrooms. The obtained results are presented in table 2.2.

Table 2.2. Concentrations of benzalkonium chlorides determined by different types of wastewater

	Concentration (µg/L)		
	C12-BAC	**C14-BAC**	**C16-BAC**
Purified wastewater	5,8	87,6	<7,6
Hospital wastewater	10,8	25,6	<7,6
Car wash waste water	44	9,4	<7,6
Fuel station waste water 4	<4,5	21,2	<7,6
Fuel station waste water 5	<4,5	259	9,4
Fuel station waste water 6	26,8	231	<7,6
Fuel station waste water 7	48	<5,6	135
Fuel station waste water 8	2700	146	<7,6
Household waste water, from the office building	<4,5	13,4	<7,6

As seen in Table 2.2 the concentrations of C12-BAC determined from the wastewater were determined in the range < 4.5 µg/L and 2700 µg/L. C14-BAC concentrations determined from the samples ranged from <5.6 µg/L to

259 µg/L. It is observed that the concentrations of C14-BAC are present in 8 of the 9 analyzed samples, while the presence of C16-BAC concentrations is determined only in 2 samples of the 9 analyzed samples, with concentrations of 9.4 µg/L and 135 µg/L [59].

CHAPTER 3. THE CURRENT STAGE REGARDING CONVENTIONAL TECHNIQUES FOR THE PURIFICATION OF WATER CONTAINING SURFACTANTS OF THE TYPE OF QUATERNARY AMMONIUM SALTS

3.1. General considerations

Conventional techniques for the removal of cationic surfactants from wastewater involve processes of adsorption, filtration, microfiltration and nanofiltration, chemical precipitation, photocatalytic degradation as well as biodegradation with the help of microorganisms, fungi and algae. In the conventional techniques used for the treatment of waters containing surfactants, individual surfactant concentrations are not monitored, but only the total organic load measured in total organic carbon, dissolved organic carbon or chemical oxygen consumption.

The conventional techniques found in the specialized literature studied are directed in two directions :

1. purification of water from treatment plants

2. the purification of gray water, which is industrial water that, through the use of appropriate purification techniques, can lead to the reuse of purified water in the production process as well as the recovery of the substances with which they were impurity, are the waste waters from laundries where water reuse is attempted purified and the partial recovery of the surfactant used in the washing process.

To achieve this objective, it is not enough to apply a single purification technique, hybrid purification techniques must be developed that contain a coagulation/flocculation technique followed by an adsorption technique.

3.2. Techniques based on the adsorption method

Conventional adsorbent materials used for the removal of surfactants found in the literature are :

- Ion exchange resin: Amberlite XAD-16[60], Three resins are strongly acidic having a sulfonate functional group (with trade names C150 H, Dowex 88, Marathon 1200 Na) and a weakly acidic resin with a carboxylic functional group (with trade name C104 plus) [61].
- Commercial activated carbons in different forms such as : Granular activated carbon [62], Activated carbon in powder form[63], Microporous and mexoporous activated carbon [64].
- Aerosil type silica [65].

The removal of surfactants from wastewater has been a priority and many techniques based on physical, chemical and biological methods have been tested, but adsorption is recognized as an effective and promising technique and is used in the tertiary treatment stage of wastewater.

On a large scale, the technique based on the adsorption method tends to be accepted because it exhibits high efficiencies in terms of surfactant removal. A great advantage of adsorbents is that they are easy to use and even cheap, most of them being very easy to modify to be used for a wide range of non-polar organic substances. From these considerations it can be said that the adsorption method is a cost-effective and ecological method [66-69].

The recycling or regeneration of adsorbent materials is the main advantage of the technique based on the adsorption method**.**

3.3. Techniques based on filtering methods

Membrane filtration systems are commonly used in sewage treatment plants to remove surfactants. These membrane filtration processes lend themselves to purifying waters with very high concentrations of cationic surfactants from their production plants. A microfiltration method on ceramic plates with a pore size of 0.14 μm demonstrated a removal of cationic surfactants with a efficiency of over 93% [70].

The nanofiltration method is used in particular for the purification of industrial waters, because after the application of this technology no waste water is discharged, moreover both surfactants and washing waters are recovered which are purified and reintroduced into the process [71].

The recovery of laundry wastewater through membrane filtration technology is increasingly being studied. In this context, an inclined filtration system was made for the purification of wastewater from a laundry in order to reuse both the purified water and the detergent [72].

3.4. Techniques based on coagulation/flocculation methods

Treatment of laundry wastewater in a pilot station was carried out using a conventional method of precipitation/coagulation, flocculation and adsorption on activated carbon. The coagulating agent used was aluminum sulfate. After adsorption on granular activated carbon, the purification efficiency was 93% [73].

Wastewater from the detergent industry is wastewater with low biodegradability due to the high concentrations of organic substances they contain. The wastewater resulting from the production of detergents has been successfully treated using a technology based on flocculation coagulation processes. The coagulants used were ferric chloride, polyaluminum chloride, aluminum sulfate, and a hybrid coagulant as coagulants, and the flocculants were three cationic, anionic, and neutral polyelectrolytes. Dissolved organic carbon purification yields were over 80% [74].

The electrocoagulation technique was used for the simultaneous removal of benzalkonium chloride (dodecyl benzyl dimethyl ammonium chloride) and microplastics. [75].

3.5. Techniques based on ozone pretreatment and activated sludge biodegradation

For the removal of benzalkonium chloride in the presence of nickel oxide nanoparticles, ozonation was used as pretreatment of a conventional activated sludge process from synthetic wastewater and influent from a sewage treatment plant. The ozone concentration was varied from 5 mg/L to 300 mg/L. The benzalkonium chloride concentration was 10 mg/L. The concentration of nickel oxide nanomaterial was 20 mg/L. The experiments were carried out in a cylindrical tank reactor with continuous stirring. During ozone degradation of benzalkonium chloride, a number of 12 intermediate degradation products resulted. The benzalkonium chloride removal efficiency was over 95% during ozonation in the presence of nickel oxide nanomaterials. At the end of the experiments, the toxicity of the treated water was also analyzed using the bacteria *Vibrio fisheri, Pseudomonas putida* and the protozoan *Tetrahymena thermophila*. Activated sludge was also used to analyze the toxicity of the treated wastewater for all biological communities. Thus, for benzalkonium chloride in untreated synthetic wastewater, toxicity was expressed as EC50 and was for Vibrio fisheri 0.26 mg BAC/L, for Pseudomonas putida 8.40 mg BAC/L, for the protozoa Tetrahymena thermophila it was 4.28 mgBAC/L and for the activated sludge bacteria it was 3.43 mg BAC/L. Both synthetic wastewater and sewage treatment plant wastewater treated with ozone at concentrations as low as 54 mg O3/L are non-toxic to both single bacteria and the bacterial consortium in the activated sludge [76].

3.6. Techniques based on biological methods

3.6.1. Biodegradation with the help of bacteria

Water treatment methods using bacteria are considered the most effective and economical for removing organic substances. The bacteria used can also be used in suspension or encapsulated/immobilized form. The advantage of using immobilized bacteria is that they are very easily separated from the treated wastewater. The bacteria used to remove surfactants from wastewater are: *Pseudomonas and Xantomonas* isolated from activated sludge [77], *Pseudomonas Fuorescens* TN4 [79], *Aeromonas hydrophila sp* [80]. *Pseudomonas putida* A[81].

3.6.2. Methods of biodegradation with the help of algae

A laboratory-scale technology was tested using microalgae from marine oil extraction wastewater for the biodegradation of benzalkonium chloride containing a mixture of alkylbenzyldimethylammonium chlorides with different alkyl chain lengths (C12-BAC and C14-BAC, mainly). The microalgal strains used were *Rhodomonas salina, Nannochloropsis oculata, Emiliania huxleyi, Dunaliella tertiolecta, Isochrysis galbana, Tetraselmis suecica*, *Dunaliella salina* and *Phaeodactylum tricornutum*. The concentration of benzalkonium chloride used was 5 mg/L. The benzalkonium chloride removal efficiency was 100% [88]

CHAPTER 4. PERSPECTIVES REGARDING NEW UNCONVENTIONAL WASTEWATER TREATMENT METHODS

After use, a large part of the cationic surfactants, especially benzalkonium chlorides, end up in wastewater from treatment plants where they can cause imbalances in the biological treatment stage by destroying the bacteria in the activated sludge. Having bactericidal properties, these pollutants are unlikely to be removed by conventional wastewater treatment techniques. It is necessary to develop unconventional methods for removing these pollutants from wastewater**.**

4.1. Techniques based on adsorption methods

The adsorbent materials used in these non-conventional techniques for removing surfactants from the class of quaternary ammonium salts are :

- natural inorganic materials: sepiolite[89], maghnite[90], montmorillonite [91]. Kaolinite [95]. Pyrite, [99].

- Activated carbons from waste - Activated carbon cloth[101].

- Industrial by-products: Municipal sludge from treatment plants [102]. Polyethylene microplastics[104],

Because pesticides, heavy metals, and cationic surfactants are found together in wastewater, an adsorption study of benzalkonium chloride surfactant, cationic herbicide paraquat, and cadmium metal on a montmorillonite was performed. Cationic surfactant was observed to increase herbicide adsorption capacity and not influence metal adsorption capacity [108**].**

4.2. Techniques based on advanced oxidation processes

Quaternary ammonium salt class surfactants are organic compounds with bactericidal and disinfectant properties that cannot be removed from wastewater by conventional techniques, as they are toxic to bacteria in activated sludge in the sewage treatment plant. As they are difficult biodegradable compounds, new, non-conventional techniques are being sought to remove them from wastewater, and studies demonstrate that the techniques based on advanced oxidation processes are suitable for the degradation of these pollutants.

The techniques based on advanced oxidation processes are classified according to the source of production of hydroxyl radicals in :

- techniques based on hydroxyl radical formation processes using ultraviolet radiation and oxygenated water (UV/H_2O_2), [112].

- techniques based on hydroxyl radical formation processes using ozone (O3), [115].

- techniques based on Fenton methods, [117].

- techniques based on photocatalytic methods, the titanium dioxide (TiO2) photocatalyst [137].

Techniques based on advanced oxidation processes alone do not always provide a high purification efficiency, and for this reason they must be combined

4.2.6. Combined techniques for removal of surfactants from wastewater

In recent years, biological and physicochemical treatment technologies have been investigated for the removal of surfactants from the wastewater matrix. However, due to the deficiency of these treatments to completely degrade cationic surfactants in wastewater, hybrid techniques have been used for the distinctive removal potential of different treatment processes. Hybrid systems combine several physical, chemical and biological methods for rapid and eco-efficient removal of cationic surfactants from wastewater. In most hybrid techniques, biological treatments are applied first and then physical or chemical treatments. Hybrid techniques combining activated sludge processes and physical processes such as ultrafiltration, reverse osmosis, and gamma radiation are considered cost-effective technologies and have better removal of trace organic pollutants [145]. If, in addition to biological and physical processes, a photocatalytic degradation process is also applied, the efficiency of removing these compounds increases greatly. One of the most used photocatalysts to accelerate the degradation process is TiO_2. TiO_2 photocatalysis is used as a pretreatment to improve the biodegradability of wastewater, or as a post-biodegradation, decontamination step to improve biodegradation. Biodegradation as the first step in the removal of cationic surfactants from wastewater is used when the wastewater contains a low concentration of cationic surfactants and sufficient nutrients and carbon to support the life of microorganisms. When the carbon level is reduced, photocatalysis can be used for the total removal of cationic surfactants or their degradation products from biologically treated wastewater. When the concentration of cationic surfactants is high and toxic to microorganisms in sewage treatment plant activated sludge, photodegradation is used to reduce their concentration until it becomes harmless to microorganisms [146].

The group of microorganisms capable of degrading cationic surfactants include Gram-negative bacteria *Pseudomonas spp. [147-149], Xanthomonas sp.[150], Aeromonas hydrophila sp.[151], Thalassospira sp*. and the Gram-positive bacteria *Bacillus niabensis* [152].

CHAPTER 6. EXPERIMENTAL RESEARCH ON METHODS OF MONITORING AND CONTROL OF SURFACTANTS IN WASTEWATER

6.1. Development of an HPLC-UV method for monitoring benzalkonium chlorides in wastewater

The experiments were carried out on an Agilent 1200 liquid chromatograph consisting of:

• quaternary pump with isocratic and gradient elution capable of supplying a mobile phase with up to 4 components, with variable flow rate;

• mobile phase vial support and membrane degasser;

• autosampler with a capacity of 100 positions and variable injection volume (0.1-100 µL);

• thermostat for maintaining a constant temperature in the chromatographic column;

• Acclaim Surfactant Plus chromatographic column, 3µm, 3.6x150mm (Thermo Scientific);

• UV-VIS detector (DAD) with variable wavelength and ability to simultaneously record up to 8 different wavelengths;

• Agilent ChemStation software for data acquisition, processing, reporting.

The optimal HPLC separation parameters of benzalkonium chlorides established experimentally are as follows:

- Column: Acclaim Surfactant Plus, 3 □m, length 150 mm, inner diameter 3 mm

- Column temperature: 30°C

- Injection volume: 20 µL

- Mobile phase: Ammonium acetate 0.2 M: Acetonitrile = 50:50 (v/v)
- Mobile phase flow rate: 0.5 mL/min
- Elution: isocratic
- UV detection: λ = 262 nm for the three cationic surfactants
- Duration of separation: 5 minutes
- Linearity range: 1 mg/L and 100 mg/L
- Quantification limits of the method: 4.5 µg/L for C12-BAC, 5.6 µg/L for C14-BAC, 7.6 µg/L for C16-BAC.

6.4. Experimental research on the separation process of cationic surfactants by solid phase extraction (SPE)

sample concentration procedure was developed by extraction using a DIONEX AUTOTRACE 280 Automated SPE Purification System using SPE cartridges with Strata-X polymeric absorbent (Phenomenex) (500 mg/6 mL, 33µ polymeric reversed phase).

The developed method was tested on wastewater from office buildings, a hospital, a car wash, as well as from gas stations.

CHAPTER 7. EXPERIMENTAL RESEARCH ON THE APPLICATION OF NANOMATERIALS AS AN ADSORBENT FOR THE PURPOSE OF WASTEWATER PURIFICATION CONTAINING CATIONIC SURFACTANTS LIKE QUATERNARY AMMONIUM SALTS

7.1. Experimental research for testing the magnetite nanomaterial in order to develop unconventional techniques for the removal of the cationic surfactant - benzalkonium bromide from wastewater

In order to demonstrate the adsorbent capacities of the magnetite nanomaterial for the cationic surfactant - benzalkonium bromide (BB), both kinetic and adsorption studies were carried out, and the influence of pH at pH=6 and pH=9 was also studied

Kinetic studies were performed by adding 25 mg of Fe_3O4 nanomaterial to each 250 mL BB solution of different concentrations: 5 mg/L(BB1), 10 mg/L(BB2) and 20 mg/L(BB3), then the samples they were mixed at 200 rpm for 1; 2; 4; 6; 24 and 48 hours. Benzalkonium bromide concentrations were analyzed as mg total organic carbon per liter (mg C/L)

Adsorption studies were performed by adding Fe_3O_4 nanomaterial amounts of 25 mg, 20 mg, 15 mg, 10 mg, and 5 mg at a concentration of 5 mg/L belzalkonium bromide in a volume of 250 mL wastewater. The samples were mixed at 200 rpm for 2 hours. Benzalkonium bromide concentration reported in mg total organic carbon per liter (mg C/L) was analyzed using a TOC analyzer. The effect of pH on the nanomaterial removal efficiency was determined by interacting 25 mg of Fe_3O_4 nanomaterial with different concentrations of benzalkonium bromide (5 mg/L, 10 mg/L, and 20 mg/L) for 2 h. The purification efficiency was higher at pH=9.

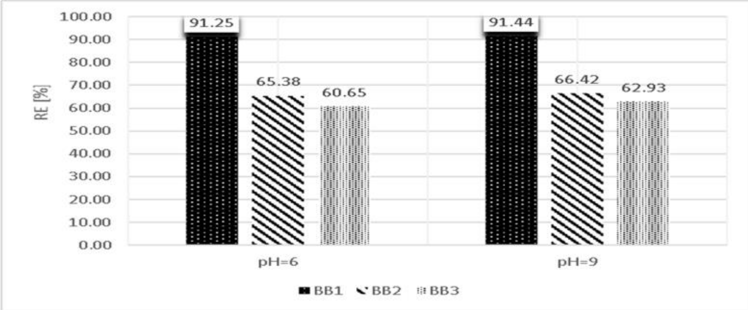

Fig. 7.2. The influence of pH in the purification efficiency η purification by nanomaterial

The scavenging efficiency of benzalkonium bromide increases with increasing amount of magnetite nanomaterial during 2 hours at pH=9 for amounts of Fe_3O_4 nanomaterial between 0.005g and 0.025g as can be seen in figure 7.3.

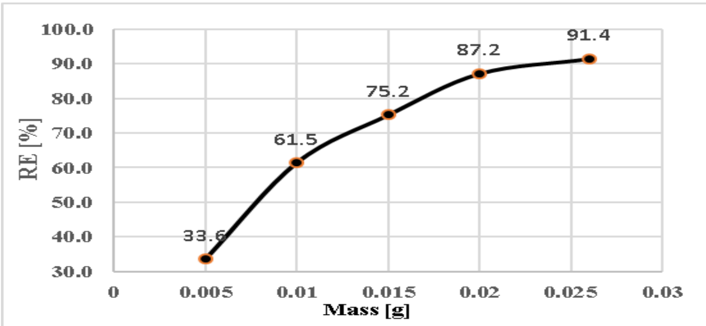

Fig. 7.3. Purification efficiency of benzalkonium bromide

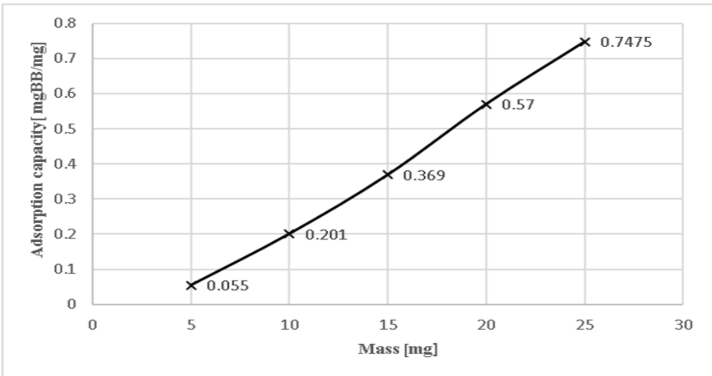

Fig 7.4. *Capacitate de adsorbție BB1 funcție de masa de nanomaterial de magnetita Fe_3O_4*

The experimental data of the benzalkonium bromide adsorption study were used to calculate the adsorption capacity of the nanomaterial represented in figure 7.4.

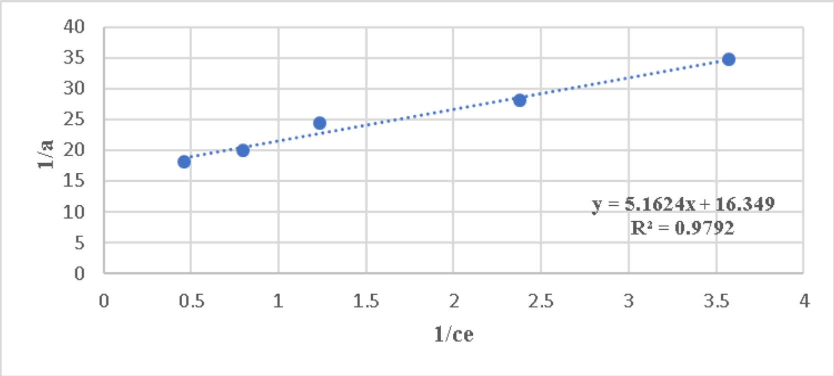

Fig. 7.5. *izoterma de adsorbție Langmuir*

The experimental data correspond to the Langmuir model.

7.2. Experimental research for testing the magnetite nanomaterial in order to develop unconventional techniques for the removal of the cationic surfactant - benzethonium chloride from wastewater

Kinetic studies were performed by adding 0.05 g of magnetite nanomaterial to 500 mL of wastewater with benzethonium chloride concentrations of 2 mg/L and 20 mg/L. The mixtures were homogenized at 200 rpm for 1, 2, 4, 6, 24 and 48 hours. During the experiments, samples were taken for analysis. Surfactant concentrations were measured with the spectrophotometer SPECORD 205 / UV VIS, at a wavelength of 217 nm.

The effect of the initial concentration of benzethonium chloride cationic surfactant was studied to determine its scavenging efficiency on the magnetite nanomaterial used.

The treatment efficiency of benzethonium chloride from wastewater in relation to time were presented in Figure 7.8.

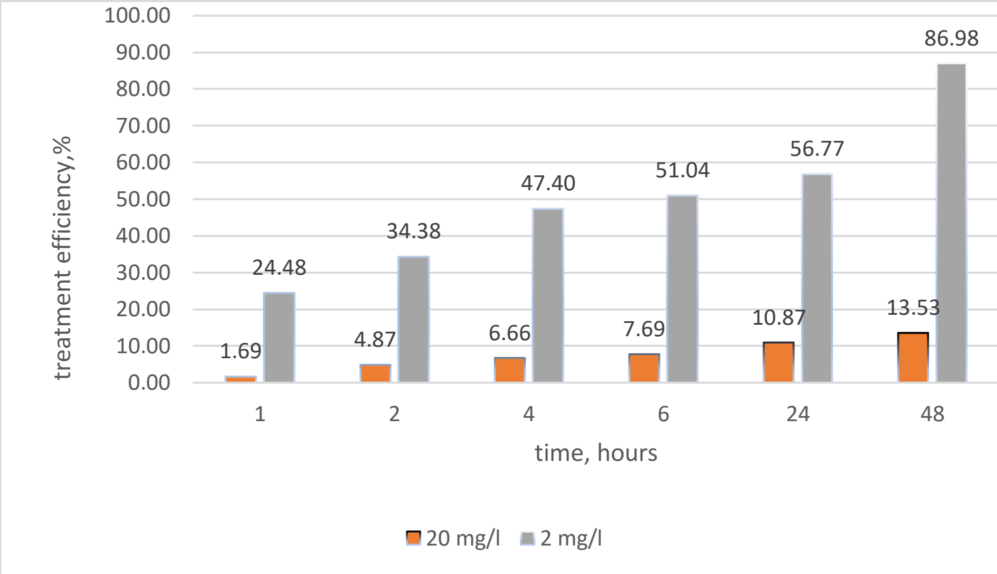

Fig. 7.8. Treatment efficiencies of benzethonium chloride from wastewater as a function of time

As can be seen in figure 7.8, the maximum treatment efficiency of benzethonium chloride obtained was 87% for wastewater containing 2 mg/L of benzethonium chloride and 0.05 g of magnetite nanomaterial, after a contact time of 48 hours.

7.3. Experimental research for testing the ZEOLIT-ZSM-5 nanomaterial in order to develop unconventional techniques for the removal of dodecyl benzyldimethyl ammonium chloride surfactant from wastewater

Kinetic studies were performed by adding 0.05 g of zeolite to 100 mL of dodecyl benzyldimethyl ammonium chloride (C12-BAC) at concentrations of 10 mg/L 20 mg/L and 50 mg/L. The mixtures were homogenized at 200 rpm for 60 minutes. During the experiments, samples were taken for analysis. Surfactant concentrations were measured with the SPECORD 205 / UV VIS spectrophotometer at a wavelength of 207 nm.

Influence of pH. To investigate the effect of pH on C12-BAC adsorption, experiments were performed at three pH values: 4, 6, and 10. The concentration of C12-BAC was 10 mg/L.

The adsorption studies were carried out by adding amounts of zeolite of 100, 50, 25, 10 and 5 mg to a concentration of 10 mg/L of C12-BAC in a volume of 100 mL. The samples were mixed at 200 rpm for 60 minutes. Surfactant concentrations were measured with the SPECORD 205 / UV VIS spectrophotometer at a wavelength of 207 nm.

The effects of pH on the purification efficiency of zeolite were determined by interacting the amount of 50 mg of zeolite with the concentration of 10 mg/L of C12-BAC at three pH values: 4, 6 and 10, for 60 minutes . The highest value of C12-BAC purification efficiency was obtained at pH=10 as can be seen in figure 7.10.

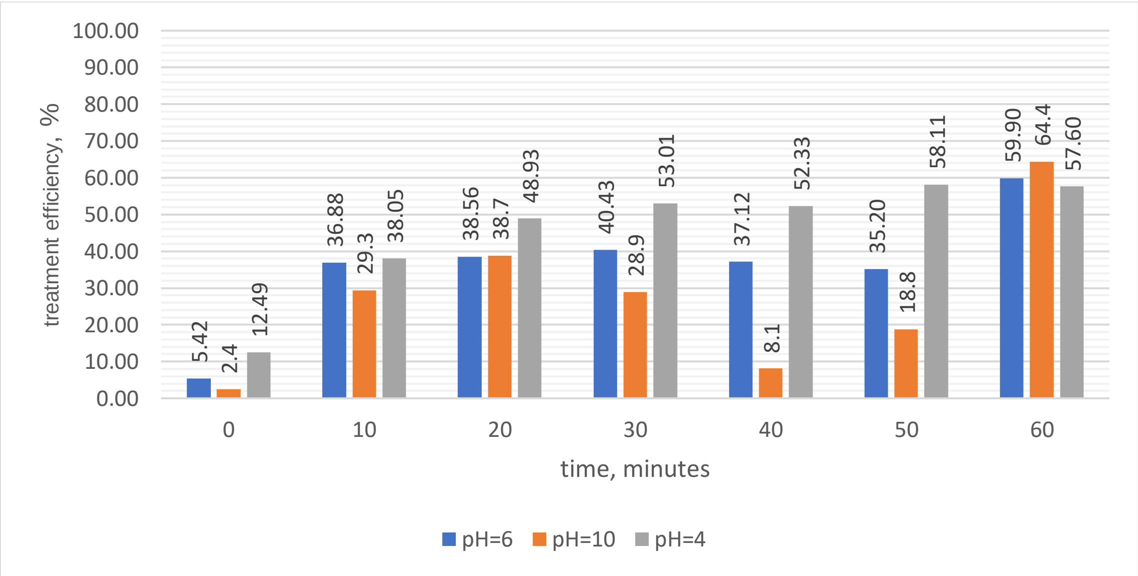

Fig. 7.10. The influence of pH in the efficiency of C12-BAC purification by zeolite for the concentration of 10 mg/L

The purification efficiency of C12-BAC on different amounts of zeolite showed that it increased with the amount of zeolite as can be seen in figure

7.11.

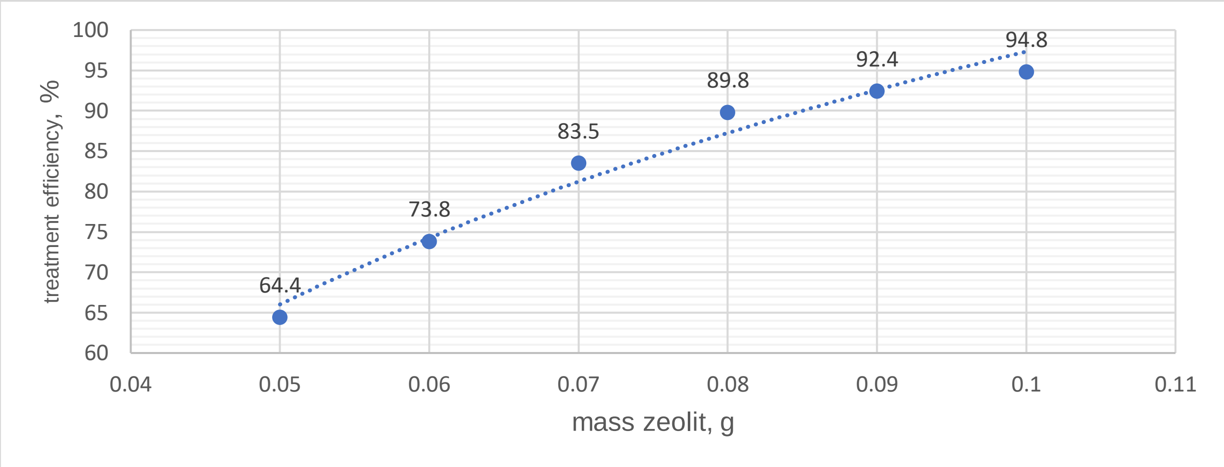

Fig. 7.11. Removal efficiency of C12-BAC from wastewater over 60 minutes at pH=10 for different amounts of zeolite (0.05 to 0.1 g)

Experimental data from the adsorption study of C12-BAC were used to calculate the adsorption isotherm plotted in Figure 7.12

The concentration of C12-BAC adsorbed on the zeolite at equilibrium was determined experimentally and was calculated with the following equation:

$$a = \frac{(Ci - Ce) * V}{m}$$

Where:

- Ci and Ce were the concentrations of C12-BAC in the initial and equilibrium wastewaters (mg/L),

- m was the mass of zeolite (g),

- V was the volume of the C12-BAC solution initially used in the study (L).

The adsorption capacity of the zeolite increased with the increase in the amount of zeolite used in the experiments as in figure 7.12

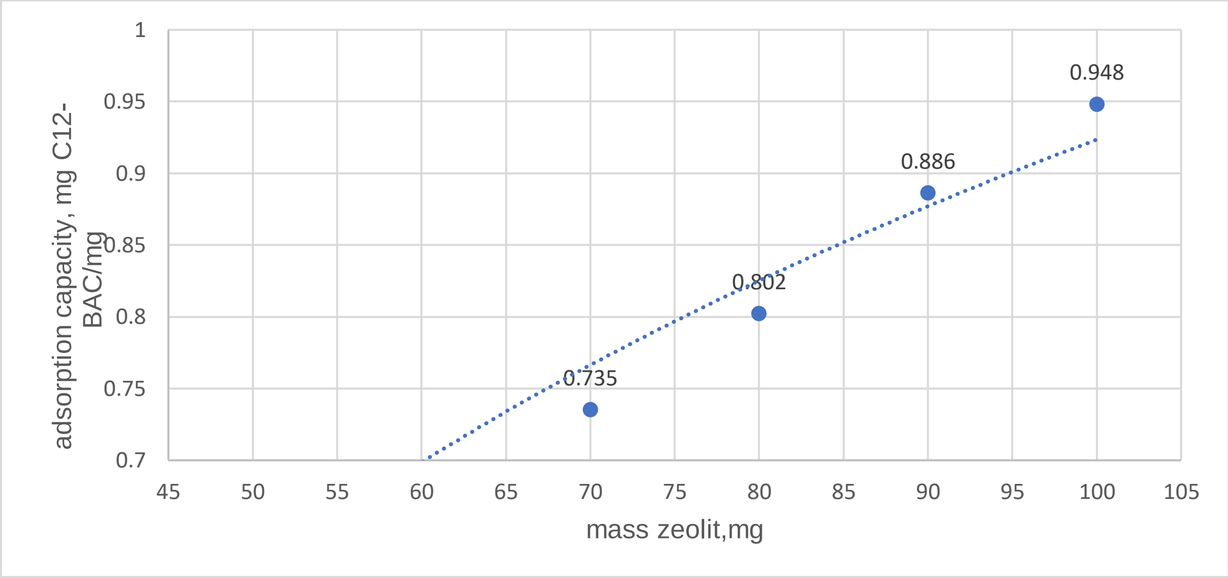

Fig. 7.12. Adsorption capacity of C12-BAC as a function of zeolite mass

In all experiments, the increase of C12-BAC adsorbed on the zeolite increased as the amount of zeolite added increased.

After 60 minutes, the concentration of C12-BAC adsorbed on the zeolite was 9.1 mg/L from the initial concentration of 10 mg/L, which corresponds to a zeolite adsorption capacity of 18.2 mg C-12-BAC /g zeolite, of 12.2 mg/L from the initial concentration of 20 mg/L which corresponds to an adsorption capacity of 24.4 mg C12-BAC /g zeolite, and 19.1 mg C12-BAC/L for the initial concentration of 50 mg/L which corresponds to an adsorption capacity of 38.2 C12-BAC mg/g zeolite, as can be seen in the figure. 7.13.

The C12-BAC removal efficiency decreases with increasing C12-BAC concentration for the same amount of adsorbent. That is, for C12-BAC concentrations of 10 mg/L, 20 mg/L, and 50 mg/L, the scavenging efficiencies were 91.1%, 61.1%, and 38.2%, respectively.

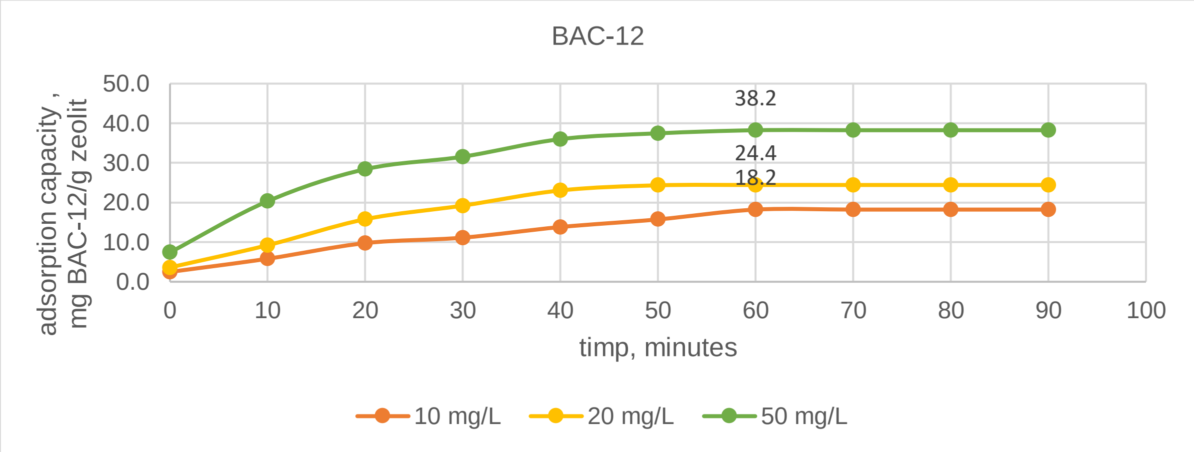

Fig. 7.13. Adsorption capacity of 0.050 g zeolite for different concentrations of C12-BAC

As can be seen in Fig. 7.13 the adsorption capacity of zeolite is moderate throughout the contact time, after 60 minutes it remains constant for another 30 minutes, which means that the adsorption equilibrium has been reached after 60 minutes. The shape of the adsorption curve is similar for all three tested concentrations.

7.5. Conclusion

Removal of surfactants such as quaternary ammonium salts from wastewater using adsorbent materials, especially nanomaterials, offers better performance compared to conventional techniques.

A variety of adsorbent materials have been developed for surfactants. Two adsorbent nanomaterials were used in the present study: the magnetite nanomaterial Fe_3O_4 and the zeolite nanomaterial ZSM-5. These were used to demonstrate their adsorption capacities for the cationic surfactants benzalkonium bromide, benzethonium chloride and benzyl dodecyl dimethyl ammonium chloride. The results obtained for the magnetite nanomaterial support the possibility of its application for the elimination of cationic surfactants such as quaternary ammonium salts from wastewater.

The maximum benzalkonium bromide removal efficiency was 91.4% using 25 mg magnetite nanomaterial for 2 h interaction at pH= 9.

The experimental data fit very well with the Langmuir model, the correlation coefficient (R^2) being 0.9792. The adsorption process of benzalkonium bromide follows first-order kinetics. The removal efficiency of benzalkonium bromide increases with increasing amount of magnetite.

The maximum benzethonium chloride removal efficiency obtained was 87% using the magnetite nanomaterial of 50 mg and the benzethonium chloride concentration of 2 mg/L for the contact time of 48 hours.

The removal of benzalkonium chloride on zeolite-type adsorbents gives rise to the formation of new organo-zeolite adsorbents that are used for the removal of metals or non-polar or weakly polar organic substances that could not be adsorbed on the solid surface of the zeolite. For example, benzalkonium chloride has been used as a cationic surfactant to modify the surface of a natural mordenite zeolite so that it is suitable for Congo red adsorption [162] and for the adsorption of stearyl dimethyl benzyl ammonium chloride on natural zeolite tuff, with organo-zeolite formation, can be used as a filter in wastewater treatment [163].

CHAPTER 8. HYBRID TECHNIQUES FOR THE REMOVAL OF SURFACTANTS FROM WASTEWATER USING THE SEMICONDUCTOR NANOMATERIAL TiO2 THROUGH THE CONTINUOUS PHOTOCATALYSIS PROCESS OF BIODEGRADATION WITH THE HELP OF BACTERIAL STRAINS

8.1. Experimental research on the testing of the TiO_2 nanomaterial with a catalytic role in order to develop unconventional techniques for the removal of cationic surfactants such as quaternary ammonium salts from wastewater

The photocatalytic activity of the TiO_2 nanomaterial in powder form and in film form on benzalkonium chloride cationic surfactants (dimethyl tetradecyl ammonium chloride (C14-BAC) and dimethyl hexadecyl ammonium chloride (C16-BAC)) was determined.

8.1.1 Purification by photocatalytic degradation with TiO_2 powder

The photocatalytic experiment was carried out in four Berzelius beakers of 150 m/L. In beaker 1, 100 mL of C14-BAC solution with a concentration of 10 mg/L and 0.1 g of TiO_2 photocatalyst powder were introduced, in beaker 2, 100 mL of C14-BAC solution with a concentration of of 10 mg/L, in beaker 3 were introduced 100 mL of C16-BAC solution with a concentration of 10 mg/L and 0.1 g of TiO_2 photocatalyst powder, in beaker 4 were introduced 100 mL of C16-BAC solution with a concentration of 10 mg/L. During the experiment, the solutions of C14-BAC and C16-BAC were homogenized by mixing with a magnetic stirrer and the UV lamp used was positioned sideways. All experiments were performed at room temperature. During the experiment, samples were taken at shorter intervals in the first part of the experiment and at longer intervals in the second part of the experiment. The collected samples were stored at 4°C and analyzed by the HPLC-DAD method.

By determining the concentrations of C12-BAC and C14-BAC at different time intervals, the photocatalytic performance of the TiO_2 nanomaterial was determined. The degradation efficiency was calculated using the formula:

$$\eta \% = \frac{c_{0-}c_t}{c_0} x\, 100$$

where c0 and ct represent the surfactant concentration value at time 0 and time t, respectively.

Figures 8.1 and 8.2 plots the degradation efficiency of C14-BAC and C16-BAC as a function of time in the absence and presence of TiO_2 powder.

C14-BAC and C16-BAC can undergo autodegradation under UV light irradiation. To confirm this, a blank test was performed under UV light irradiation without using a catalyst. The control test showed 5.2% degradation for C14-BAC and 4.8% C16-BAC respectively, which is a negligible amount. The percent degradation after 46 hours for C14-BAC was 95.0% and for C16-BAC was 98.9%.

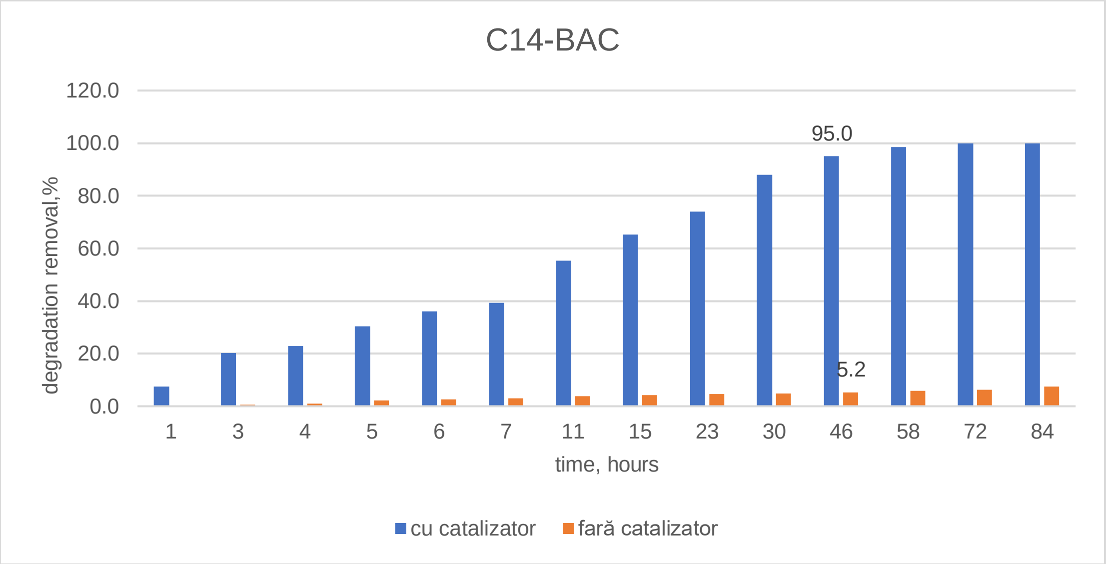

Figure 8.1. Degradation of C14-BAC in the absence and presence of TiO2 powder under UV light irradiation.

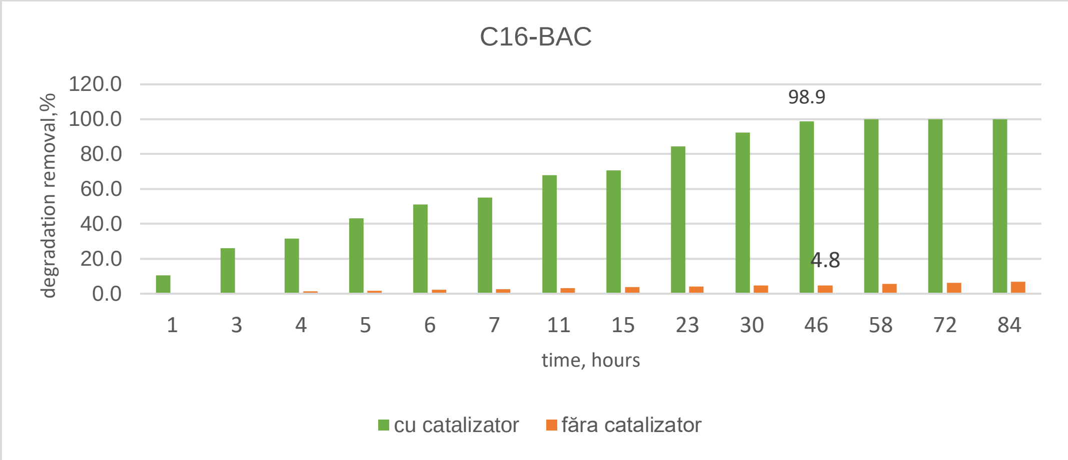

Figure 8.2. Degradation of C16-BAC in the absence and presence of TiO_2 powder under UV light irradiation.

Degradation of C14-BAC and C16-BAC occurs according to first-order kinetics, defined by the equation below:

$$C_t = C_0 \cdot e^{-kt}$$

where k (hour-1) is defined as a compound degradation rate constant.

This constant (k) can be calculated from the slope of the line obtained by plotting -ln (C / C0) against the time of irradiation time (t), as can be seen in Figure 8.3.

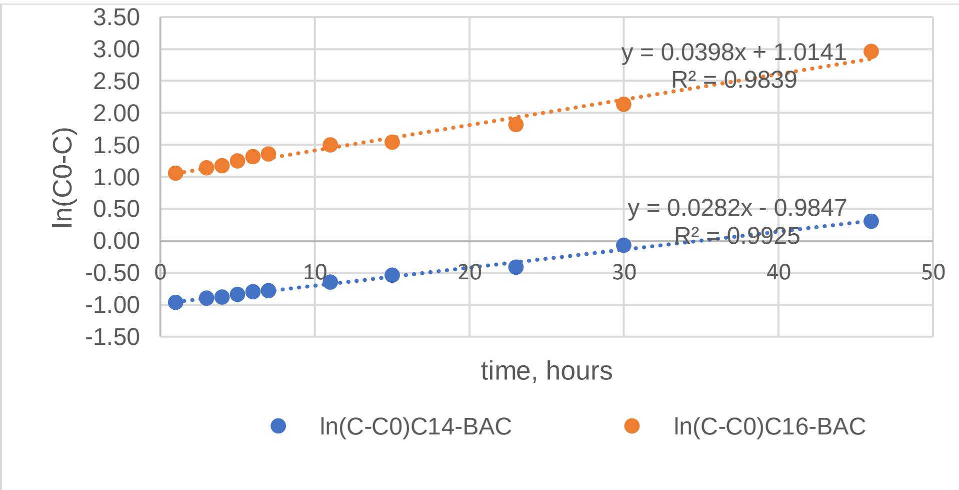

Fig. 8.3. Plot of first-order equations of photocatalytic degradation of C14-BAC and C16-BAC for TiO_2 powder

The correlation coefficients (R^2) were 0.9839 for C14-BAC and 0.9925 for C16-BAC, indicating that the degradation of these compounds follows the first-order kinetic model.

The half-life (t1/2) was determined using the equation below [164]:

$$t_{1/2} = \frac{\ln 2}{K}$$

The kinetic data from Figure 8.3 regarding the degradation rate constant K and the half-life, t1/2, for the photocatalytic degradation of C14-BAC and C16-BAC are listed in Table 8.1.

Table 8.1. Kinetic data for the degradation of C14-BAC and C16-BAC with TiO2 powder

cationic surfactant	k, hour^{-1}	$t_{1/2,\ hour}$	R^2
C14-BAC	0.0398	7.56	0.9839
C16-BAC	0.0282	10.67	0.9925

The photocatalytic degradation efficiency of C14-BAC and C16-BAC after 46 h was 95.0% and 98.9%, respectively.

The half-life ($t1_{/2}$) for C14-BAC was 7.56 hours and for C16-BAC was 10.67 hours.

During irradiation, in the presence of TiO_2 photocatalyst, for both C14-BAC and C16-BAC, a decrease in concentration was observed compared to irradiation without catalyst. As can be seen from Figures 8.1 and 8.2, the degradation efficiency is over 95% in the presence of TiO_2 catalyst.

8.1.2 Treatment by photocatalytic degradation using TiO_2 film

The photocatalytic activity of the TiO_2 film was demonstrated by a series of laboratory experiments.

Experiment 1:

150 mL of wastewater with a concentration of 10 mg/L of C14-BAC was subjected to UV degradation for 84 hours without a catalyst.

- 150 ml of wastewater with a concentration of 10 mg/L of C14-BAC was subjected to UV degradation in the presence of the TiO_2 film photocatalyst for 84 hours.

Experiment 2:

- 150 mL of wastewater with a concentration of 10 mg/L of C16-BAC was subjected to UV degradation for 84 hours without a catalyst

- 150 ml of wastewater with a concentration of 10 mg/L of C16-BAC was subjected to UV degradation in the presence of the TiO_2 film photocatalyst for 84 hours.

During the experiment, the solutions of C14-BAC and C16-BAC were homogenized by mixing with a magnetic stirrer and the UV lamp used was positioned sideways.

The determination of C14-BAC and C16-BAC surfactant concentration was performed using an HPLC-DAD chromatographic method, and the results obtained are presented in table 8.2

Table 8.2. C14-BAC and C16-BAC concentrations obtained with TiO2 film

Without catalyst		With TiO_2 film	Without catalyst	With TiO_2 film
hours	**Concentration C14-BAC (mg/L)**		**Concentration C16-BAC (mg/L)**	
i	9.91		9.10	6.53
1	9.89	9.82	9.10	6.43
2	9.88	9.40	9.10	6.40
3	9.87	9.15	9.10	6.37
4	9.83	8.34	8.99	6.21
5	9.83	7.83	8.86	6.49
6	9.82	7.64	8.84	5.41
7	9.81	7.14	8.76	5.14
8	9.71	6.62	8.74	4.77
10	9.65	6.46	8.71	2.41
14	9.65	3.37	8.67	1.29

Table 8.2. C14-BAC and C16-BAC concentrations obtained with TiO2 film- cont

Without catalyst		With TiO_2 film	Without catalyst	With TiO_2 film
hours	Concentration C14-BAC (mg/L)		Concentration C16-BAC (mg/L)	
18	9.65	3.10	8.66	1.31
22	9.65	2.60	8.66	0.83
26	9.63	1.47	8.66	0.58
30	9.6	1.19	8.64	0.46
34	9.6	0.86	8.60	0.21
46	9.59	0.50	8.55	< 0,1
58	9.5	0.36	8.53	< 0,1
64	9.49	< 0,1	8.52	< 0,1
72	9.41	< 0,1	8.53	< 0,1
78	9.41	< 0,1	8.52	< 0,1
84	9.40	< 0,1	8.46	< 0,1

Figures 8.4 and 8.5 show the degradation efficiencies for the two surfactants C14-BAC and C16-BAC

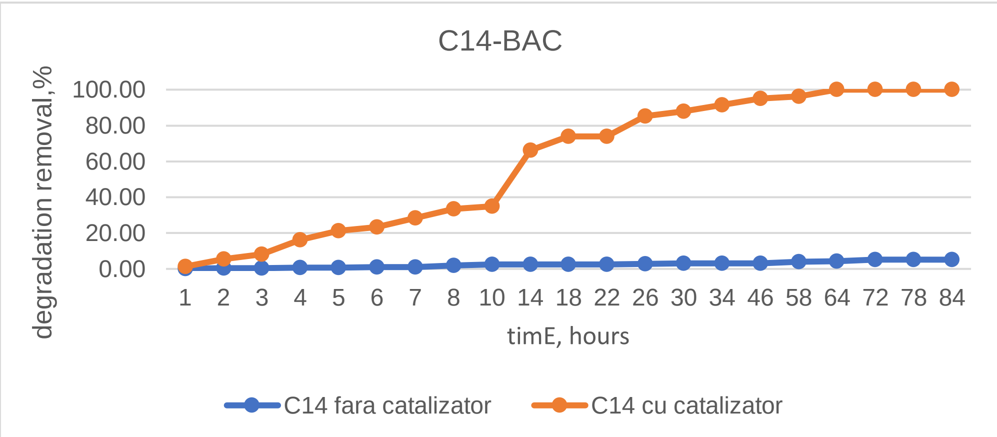

Figura 8.4. *Eficiența de degradare a C14-BAC funcție de timp*

As can be seen in figure 8.4, the degradation efficiency of C14-BAC in the presence of the TiO2 film catalyst is 99.9% after 64 hours of exposure to UV radiation, while the degradation efficiency of C14-BAC without the catalyst, only at exposure to UV radiation decreases insignificantly during the experiment, after 84 hours being only 5.15%.

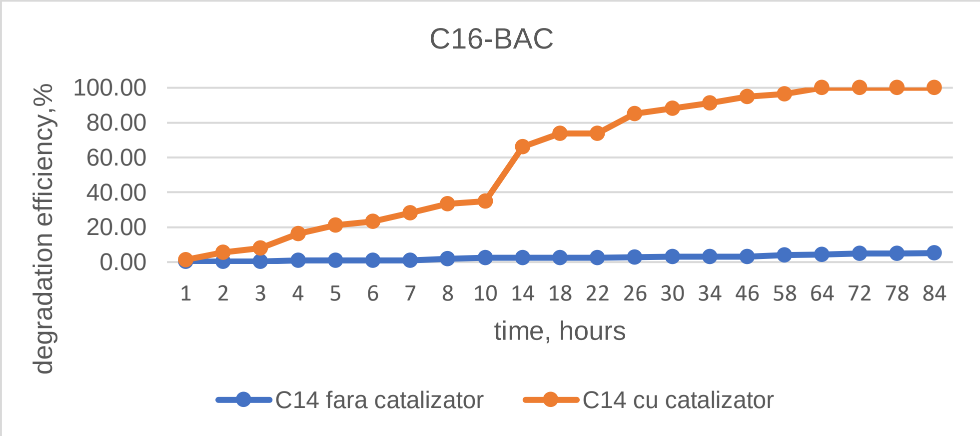

Figure 8.5. Degradation efficiency of C16-BAC as a function of time

As can be seen in figure 6.16, the removal efficiency for C16-BAC in the presence of the TiO2 film catalyst is 99.9% after 58 hours of exposure to UV radiation, while the removal efficiency of dimethyl hexadecyl ammonium chloride C16- BAC without catalyst, only when exposed to UV radiation, decreases insignificantly during the experiment, after 84 hours being only 7.08%.

The degradation of C14-BAC and C16-BAC is carried out according to the first-order kinetics, defined by the equation [164]:

$$C_t = C_0 \cdot e^{-kt}$$

where k (hour-1) is defined as a compound degradation rate constant.

This constant (k) can be calculated from the slope of the line obtained by plotting -ln (C / C0) versus the irradiation time (t), as can be seen in Figure 8.6

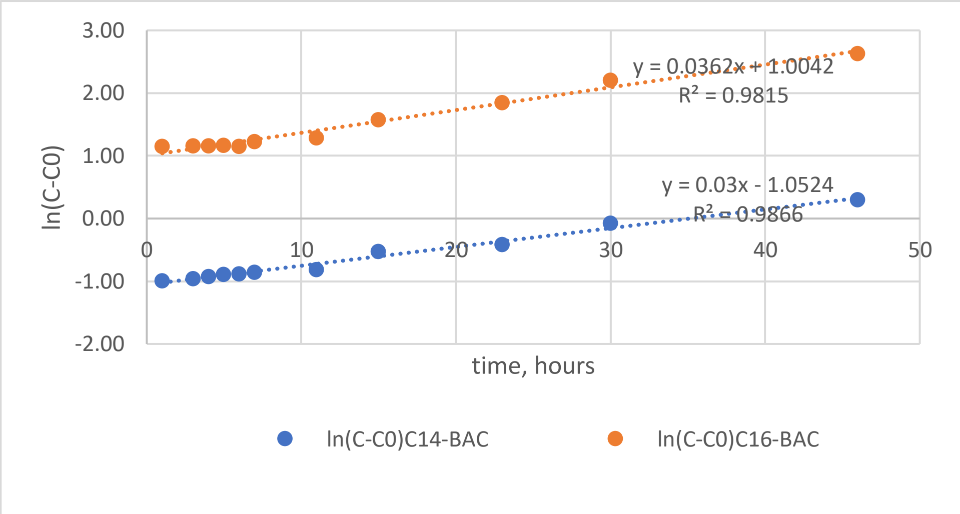

Fig 8.6. Plot of first-order equations of photocatalytic degradation of C14-BAC and C16-BAC for TiO2 film

The correlation coefficients (R^2) were 0.9815 for C14-BAC and 0.9966 for C16-BAC, indicating that the degradation of these compounds follows the first-order kinetic model.

The half-life (t1/2) was determined using the equation below [164]:

$$t_{1/2} = \frac{\ln 2}{K}$$

The kinetic data resulting from Figure 8.6 regarding the degradation speed constant K and the half-life, $t_{1/2}$, for the photocatalytic degradation of C14-BAC and C16-BAC are listed in Table 8.3

Table 8.3. Kinetic data for the degradation of C14-BAC and C16-BAC with TiO2 film

cationic surfactant	**k, oră$^{-1}$**	**$t_{1/2}$, oră**	**R^2**
C14-BAC	0.0362	8.31	0.9815
C16-BAC	0.0300	10.03	0.9866

The photocatalytic degradation efficiency of C14-BAC and C16-BAC after 46 h was 95.0% and 98.9%, respectively.

The half-life ($t_{1/2}$) for C14-BAC was 8.31 hours and for C16-BAC was 10.03 hours.

During irradiation, in the presence of TiO_2 photocatalyst, for both C14-BAC and C16-BAC, a decrease in concentration was observed compared to irradiation without catalyst. As can be seen from Figures 8.4 and 8.6, the degradation efficiency is over 95% in the presence of the TiO_2 catalyst.

8.2. Experimental research using bacteria found in sewage treatment plant activated sludge to develop biodegradation techniques for the removal of cationic surfactants such as quaternary ammonium salts from wastewater

8.2.1 Experimental research on the toxicity of cationic surfactants on activated sludge

This experimental study was conducted to evaluate the effect of surfactants on the respiration of activated sludge collected from a municipal wastewater treatment plant (WTP).

The effects on activated sludge microorganisms were determined by measuring their respiration rate under defined conditions in the presence of different concentrations of surfactants. Activated sludge respiration rate was measured using an oxygen electrode every 15 min within 3 h of sludge exposure to surfactant according to OCSPP guideline 850.3000 [165].

The concentration of C14-BAC used in the experiments was 1 mg/L and 10 mg/L. The test solutions and the control sample were prepared by combining 16 mL of culture medium with different volumes of surfactant stock solution and water to a volume of 300 mL. All mixtures were aerated for several minutes to saturate the solutions with O2 above 60-70%. The test was then started by adding appropriate volumes of activated sludge slurry (microbial inoculum) giving a concentration of 1.5 g suspended solids/L in the test mixture and a total volume of 500 mL.

After the addition of the inoculum, vials of test and control mixtures were capped and incubated at approximately 20°C with shaking, without aeration, and the oxygen concentration (mgO_2/L) was measured every 15 min for 3 h.

The surfactant solutions were sampled at regular intervals (after every hour) during the experiment. After collection, samples were centrifuged and from the supernatant, C14-BAC concentrations were determined.

The C14-BAC removal efficiency decreases with time, from 50% to 35% for C1 (1 mg/L) and from 33% to 24% for C2 (10 mg/L), as seen in Figure 6.1, After 3 hours, the removal rate increases, which can be related to the fact that they have a very long structural chain and their removal requires more time. This situation can be attributed to the adsorption of C14-BAC on the activated sludge, due to the stronger interaction of the electric charge with the chemical compounds of the activated sludge.

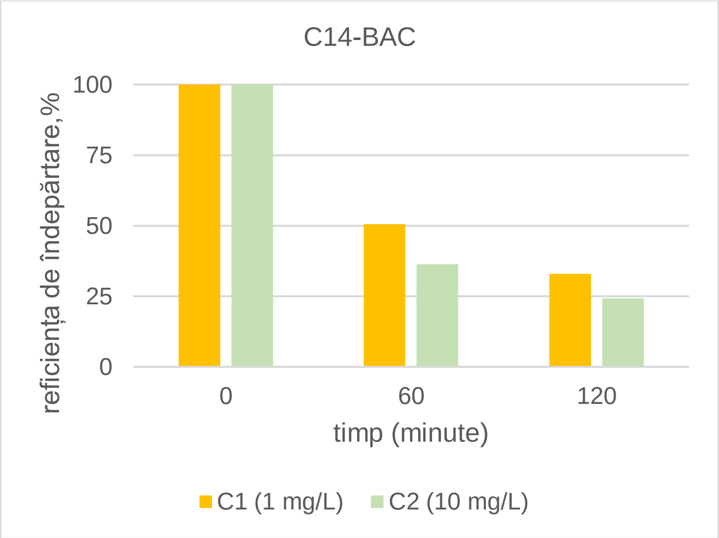

Fig. 8.13. Removal efficiency of C14-BAC from wastewater with activated sludge

The results showed that inhibition of microbial respiration was modulated by surfactant and the degree of inhibition was time-dependent. The cationic surfactant, C14-BAC had a strong respiratory inhibition effect at 10 mg/L, reaching up to 20% inhibition as can be seen in figure 8.14.

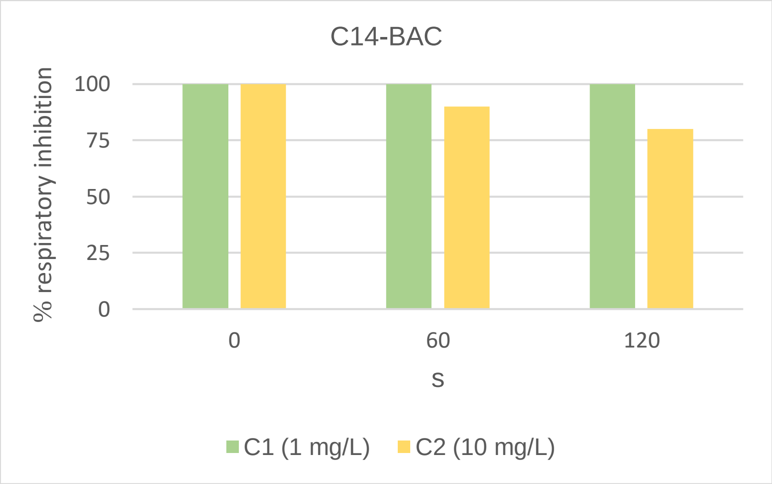

Fig. 8.14. Inhibition of microbial respiration by C14-BAC on activated sludge

Cationic surfactants, C14-BAC have an effect on the microbial community in the activated sludge involved in the wastewater treatment procedure. Inhibition of the microbial respiration process is an important sign of the degree of surfactant pollution that could reduce the efficiency of the treatment plant. The presence of surfactants with high charges (cationic surfactants) in the activated sludge of the sewage treatment plant can increase the negative biochemical processes, such as decreasing the respiration of the microorganism and interrupting the entire biological treatment process.

8.2.2 Experimental research on the assessment of the aquatic toxicity of benzalkonium chlorides using the species *Daphnia mangna* and *Selenastrum capricornutum*

he aquatic toxicity screening of benzalkonium chlorides (C12-BAC, C14-BAC, C16-BAC) was carried out according to OECD 202/ SR EN ISO 6341:2013 and OECD 201/ SR EN ISO 8692:2012 methods, MicroBioTest kits, Belgium .

Benzalkonium chlorides C12-BAC, C14-BAC and C16-BAC determined acute toxic effects on Daphnia mangna and Selenastrum capricornutum. According to the REACH Regulation, the tested compounds fall into the ACUTE DANGER (short-term) toxicity class for the aquatic environment, Acute toxicity Category 1 – VERY TOXIC with EC50 values ≤ 1 mg/L. The results obtained are similar to those reported [166-167].

8.2.3. Bacterial degradation of cationic surfactants in wastewater

During biological wastewater treatment, cationic surfactants are adsorbed on biomass or biodegraded by activated sludge microorganisms. Microorganisms use surfactants as a source of carbon and energy. Biodegradation of quaternary ammonium salts occurs in the presence of microorganisms under aerobic conditions. The group of microorganisms capable of degrading quaternary ammonium salts includes gram-negative bacteria and gram-positive bacteria.

Preliminary experiments for the degradation of a cationic surfactant (dodecylbenzyldimethyl chloride C12-BAC) were carried out using activated sludge from a sewage treatment plant.

Experiments were performed in 1.5 L glass Erlenmayer beakers stirred with a Teflon-coated stir bar and aerated with compressed air.

All experiments were performed with a mixed aerobic bacterial culture from activated sludge incubated in the absence (control) or presence of 5 mg/L (C1) and 10 mg/L (C2) cationic surfactant.

The solutions were inoculated with 2 mL of the microbial inoculum. Incubation was carried out for five days and aliquots were taken periodically for surfactant quantification and microbiological analyses. The following types of bacteria were determined: total coliform bacteria (CT), faecal coliform bacteria (CF) and *Escherichia coli (E.coli)*.

Quantitative dosages of C12-BAC were obtained from homogenous samples and filtered samples to determine the amount of degraded substance and the amount of adsorbed substance.

The results are presented in Table 8.6 and Figure 8.15, where MC represents the 10 mg/L C12-BAC solution without the bacterial inoculum, C1O represents the concentration of 5 mg/L C12-BAC with the homogeneous bacterial inoculum, C1F is the concentration of 5 mg/ L C12-BAC with filtered bacterial inoculum, C2O is the concentration of 10 mg/L C12-BAC with homogeneous bacterial inoculum, C2F- the concentration of 10 mg/L C12-BAC with filtered bacterial inoculum.

As can be seen in figure 8.15 after 120 hours in the solutions of the experiments with the bacterial inoculum the concentration of C12-BAC is below the detection limit of the method.

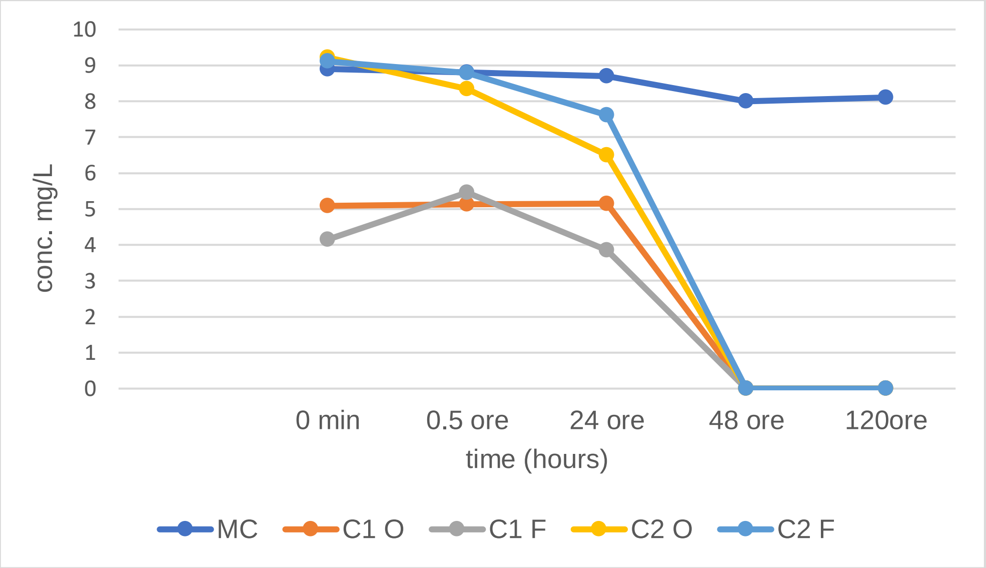

Fig 8.15. The variation of concentrations of solutions subject to degradation as a function of time

Table 8.6 Monitored C12-BAC concentrations at time point

Time/Concentration	MC	C1O	C1F	C2O	C2F
0 min	8.9	5.09	4.15	9.22	9.11
0.5 hours	8.8	5.46	5.18	8.79	8.34
24 hours	8.7	5.15	3.85	7.63	6.5
48 hours	8	<0.1	<0.1	<0.1	<0.1
120 hours	8.1	<0.1	<0.1	<0.1	<0.1

After 24 hours, the treatment efficiencies were calculated, which are 99.9% for C12-BAC concentration of 5 mg/L and 52% for C12-BAC concentration of 10 mg/L as shown in Figure 8.16.

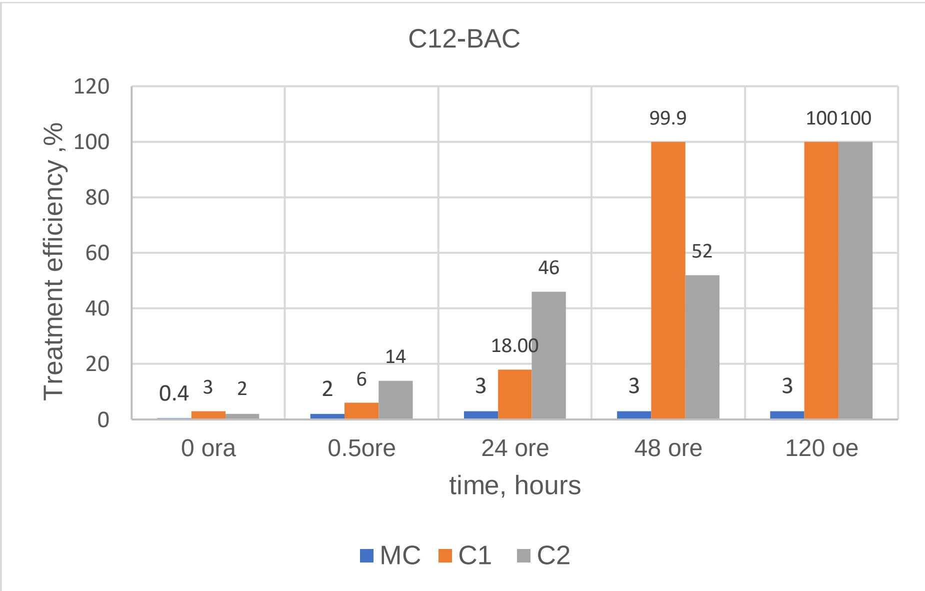

Figure 8.16. Treatment efficiency as a function of time for the two concentrations of C12-BAC

The results of C12-BAC biodegradation showed a clear involvement of bacterial communities, which possibly used the surfactants as an energy source by metabolizing them. If metabolism has occurred, the number of colonies should increase compared to control bacteria (incubated without surfactant).

Table 8.6 The values of the types of bacterial strains detected during the experiments

	CT (UFC/100 mL)		CF (UFC/100 mL)		E.Coli (UFC/100 mL)	
	30 min	120 ore	30 min	120 ore	30 min	120 ore
M	242000	150000	30	1658	10	500
AC1	72700	134000	529	200	100	100
AC2	20100	1120000	249	8300	100	500

Quantification of total coliforms (CFU/100 mL) in the presence of surfactants showed an overall increase in the bacterial growth pattern. The ratio of CFU/100mL between surfactant-incubated bacteria and control bacteria (no surfactant incubation) showed that higher concentrations of cationic surfactants stimulated bacterial growth compared to lower concentrations as seen in Figure 8.17. Incubation time was directly related to bacterial growth and decreased surfactant concentration.

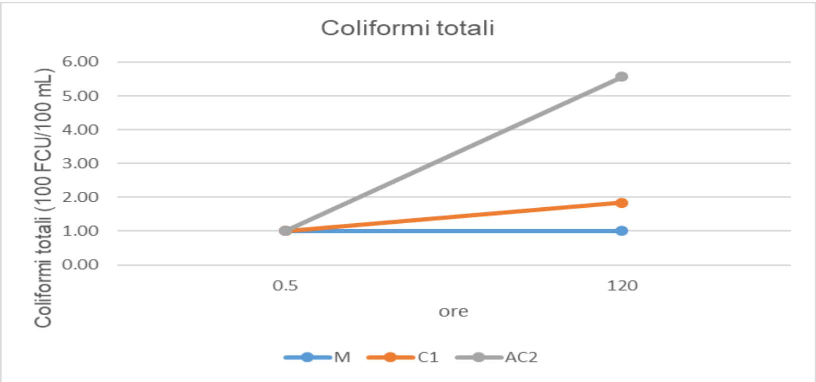

Fig. 8.17. Growth of total coliforms in the presence and absence of cationic surfactant

Faecal coliforms are part of total coliforms and the following tests showed more specifically whether the faecal bacterial group played a role in the biodegradation of surfactants as seen in Figure 8.18.

The results showed the same pattern of growth activation for the higher concentrations. Lower concentrations of surfactants had the same range of values as the control.

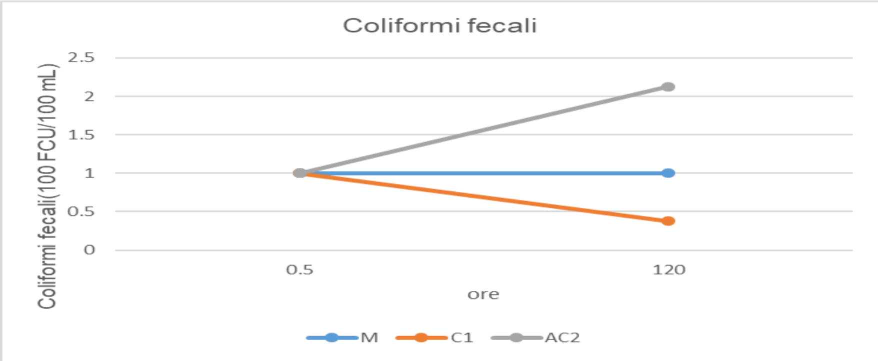

Fig. 8.18. *Creșterea coliformilor fecali în prezența și absența surfactanțior cationici.*

Escherichia Coli (E. coli) bacteria, part of total coliforms, behaved differently in the presence of surfactants. Cationic surfactants increased bacterial growth in direct proportion to increasing concentration as can be seen in Figure 8.19. This result could be related to the fact that the 22 mg/L cationic surfactant (benzalkonium chloride) reduced the sludge activity of microorganisms by half.

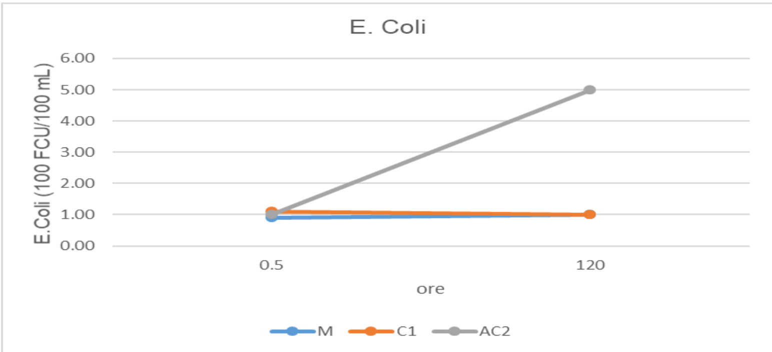

Fig. 8.19. *Creșterea bacteriilor E. coli în prezența și absența surfactanților cationici.*

Biodegradation of the cationic surfactant -C12-BAC was successfully achieved in the presence of active sewage sludge microorganisms. Total coliform bacteria and their subgroups *Escherichia Coli (E. coli)* and Faecal Coliforms played an active role in cationic biodegradation. The biodegradation process was efficient, in 48 hours almost all the surfactant biodegraded.

8.2.4. Techniques for the removal of cationic surfactants such as quaternary ammonium salts from wastewater using TiO_2 film photocatalyst and bacterial strains

Treatment of waste water with organic compounds with emerging properties, such as quaternary ammonium salts (benzalkonium chlorides), is poorly carried out, which leads to their discharge into receiving waters, where they can cause endocrine-disrupting effects and the ability to induce the proliferation of strains highly resistant microbes in the environment.

Due to their toxicity on activated sludge in sewage treatment plants and their persistence, in the treatment of municipal and industrial wastewater, large amounts of benzalkonium chlorides could disrupt the biological processes of microorganisms, making the biodegradation step ineffective, and therefore, large amounts of them would could reach from the waste water discharged directly into the rivers. Their effective removal from wastewater depends on several processes, including photochemical and biological degradation.

The chronic problem of chemicals such as quaternary ammonium salts, difficult to degrade biologically and in some cases even toxic, is addressed by describing an experimental study undertaken to investigate the integrated chemical photocatalytic treatment (TiO_2/UV) and biological (with the help of bacteria) of benzalkonium chlorides: (12-BAC, C14-BAC and C16-BAC.

Preliminary experiments were carried out in the laboratory for the degradation of surfactants using the TiO_2 photocatalyst deposited on plates in the form of a film, preliminary experiments were carried out in the laboratory to determine the efficiency of using some bacterial strains in biodegradation studies, and finally hybrid experiments combining photocatalysis and biodegradation.

8.2.4.1. Technique for removing C14-BAC from wastewater using TiO_2 photocatalyst and bacterial strains (*E.coli*)

Two experiments were performed. The 2000 mL test solution made in peptone culture medium was divided into 1000 mL for each experiment.

Experiment 1: 1000 mL of test solution was divided into 250 mL

1. 500 ml solution without catalyst
2. 500 ml glass plate with TiO2 film

These two solutions were subjected to UV radiation for 6 hours, after which they were each divided into 250 mL as follows:

1.1 250 mL solution without catalyst

1.2 250 mL solution without catalyst to which 20 mL culture medium with E*. coli* bacteria were added

2.1 250 mL TiO_2 deposited plate solution

2.2 250 mL of TiO_2 deposited plate solution to which 20 mL of culture medium with *E. Coli* bacteria were added.

These 4 solutions were stirred at 100 rpm overnight.

Experiment 2: 1000 mL of test solution was divided into 250 mL

1.1 250 mL solution without catalyst

1.2 250 mL solution without catalyst to which 20 mL of culture medium with E. Coli bacteria were added.

2.3 250 mL TiO_2 deposited plate solution

2.4 250 mL solution with a plate deposited with TiO_2 to which 20 mL culture medium with *E. coli* bacteria were added

These 4 solutions were stirred at 100 rpm overnight.

Next, the 4 solutions were subjected to UV radiation for 6 hours. The solutions were irradiated using a device with 4 lamps, and the exposure was lateral.

50 mL of each solution was sampled and C14-BAC concentration was determined at baseline, after 6 h of UV irradiation and overnight. The number of *E.coli* bacteria was also determined.

The purification efficiencies were calculated for each experiment separately and the results are presented in figure 8.20.

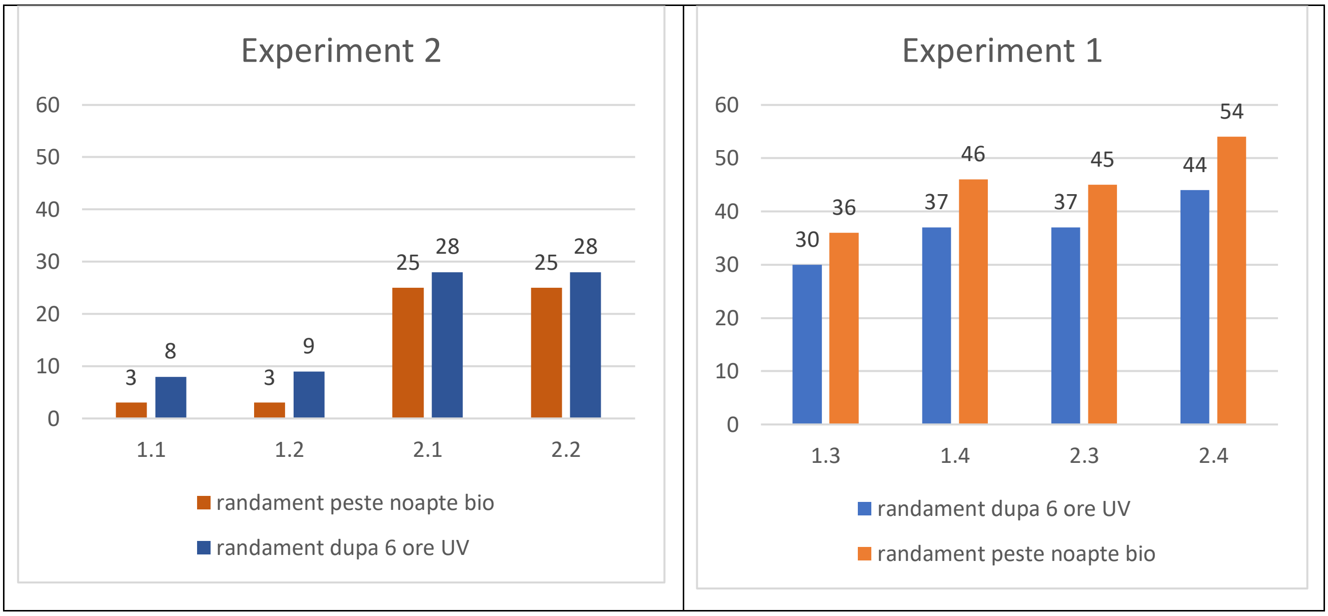

Figura 8.20. *Eficiențele de degradare pentru C14-BAC obținute în cele două experimente*

From figure 8.20 it is observed that the higher degradation efficiencies are obtained in experiment 2, that is, the degradation technique with the first photocatalytic step followed by the biological step is more efficient, because quaternary ammonium salts are bio-recalcitrant in nature and cause the death of microorganisms. The lower yields in the first experiment are due to the fact that, in addition to the surfactant concentration, the peptone concentration with which the inoculum is prepared must also be degraded.

Studies related to the removal of quaternary ammonium salts from water are very rare and are mostly limited to biological treatment with activated sludge. However, quaternary ammonium salts are biorecalcitrant in nature and cause the death of microorganisms. This method requires a long adaptation time and is only applicable to low concentrations of quaternary ammonium salts less than 10 mg/L.

8.2.4.2. Hybrid techniques for removal of benzalkonium chlorides from wastewater using photocatalytic treatment step with TiO_2 photocatalyst and biological step with bacterial strains

Starting from the preliminary degradation experiments with the bacteria found in the activated sludge of the sewage treatment plant, namely total coliform bacteria, faecal coliform bacteria and *Escherichia coli*, it was observed that the most effective in the biodegradation process and the most resistant were the bacteria *E.coli*. That is why they were selected. For the preliminary research carried out in the laboratory on the surfactant C14-BAC, the treatment method was chosen with the first stage of photodegradation with the TiO_2 film catalyst followed by the second stage of biodegradation with the help of *E.coli* bacteria.

Further experimental research proceeded from photocatalytic treatment followed by biodegradation techniques for benzalkonium chloride, a mixture of C12-BAC, C14-BAC and C16-BAC.

To increase the removal efficiency of the three cationic surfactants, a biological step was used after the photocatalysis step.

In the biological stage, for each liter of solution, 10 mL of the bacterial inoculum (*E coli*. in peptone water) was added. The use of pure strains of the E. coli type was motivated by the presence of this bacterial strain in the activated sludge used in the biodegradation of surfactants in the first experimental stage of degradation with the help of bacteria. The efficiency of biodegradation of surfactants in the presence of activated sludge, which contains in its composition a significant amount of *E. coli* bacteria, suggests a specificity of this strain in the biodegradability process.

After the incubation time, 10 mL of bacterial suspension was added over different surfactant solutions. The mixture of *E. coli* bacterial strain and supernatants was homogenized for 1 minute and then samples were taken up to 24 hours. The samples taken were analyzed both from the microbiological point of view of the bacterial density and from the point of view of the biodegradability of the surfactants. The microbiological analyzes consisted of the analysis of 100 mL of the bacterial mixture sample and surfactants, using the Most Probable Number Colilert-18 method for the determination of E. coli. Also, the samples containing surfactant and bacterial strain were analyzed after 24 h of contact by the same analysis method (Colilert 18). The solutions were left for 12 hours in the presence of bacteria, after which the concentration of each surfactant was determined using the HPLC-DAD chromatography method.

After 12 hours of biodegradation in the presence of *E.coli* bacteria for all three cationic surfactants, the degradation yields increase considerably, reaching 98.1% for C12-BAC, 97.9% for C14-BAC and 97.3% for C16-BAC

8.3. Conclusion

The degradation of surfactants from the class of quaternary ammonium salts was achieved using a hybrid method composed of a photodegradation step with the help of the TiO_2 film photocatalyst and a biodegradation step with the help of *E.Coli* bacteria.

The degradation removal obtained by this method were over 95% for all three cationic surfactants, namely 98.1% for C12-BAC, 97.9% for C14-BAC and 97.3% for C16-BAC.

This demonstrates that the hybrid method developed in the laboratory in this PhD thesis can be successfully applied to cationic surfactants from the class of quaternary ammonium salts.

CHAPTER 9. FINAL CONCLUSIONS. ORIGINAL CONTRIBUTIONS. FUTURE PROSPECTS

9.1. FINAL CONCLUSIONS

The doctoral thesis with the title "Unconventional techniques for the removal of detergents from waste water" includes studies and research whose main objective was the testing of nanomaterials with an adsorbent role and a TiO_2 semiconductor nanomaterial in order to develop unconventional techniques for the removal of cationic surfactants from the class of quaternary ammonium salts from wastewater, as well as the development of a method for their combined, integrated photocatalytic chemical (TiO_2/UV) and biological (with the help of bacteria) treatment.

Cationic surfactants in the class of quaternary ammonium salts are relatively little studied. The cationic surfactants used in experimental research to develop non-conventional methods for their removal from wastewater were:

o Benzethonium chloride

o Benzalkonium bromide

o 3 Benzalkonium chlorides namely benzyl dodecylbenzyl dimethyl ammonium chloride (C12-BAC), benzyl tetradecylbenzyl dimethyl ammonium chloride (C14-BAC) and benzyl hexadecylbenzyl dimethyl ammonium chloride (C16-BAC).

We chose these cationic surfactants because they have bactericidal properties, they are active ingredients in many disinfection and cleaning products for both domestic and industrial use, especially for cleaning surfaces in hospitals and the food industry. Due to these multiple uses, increasingly higher concentrations reach the sewage treatment plants. Current treatment plants reduce the level of pollution in waste water mainly by two methods:

mechanical and biological by using activated sludge loaded with microorganisms that purify the water through the process of biodegradation.

Cationic surfactants are organic compounds with bactericidal properties and it is very unlikely that they can be removed from the sewage treatment plant in the biological stage. For these reasons, it is necessary to find the most effective methods for removing surfactants from wastewater and to develop accurate, sensitive and reproducible methods for the analysis of cationic surfactants at very low trace concentrations in wastewater and surface water.

The specialized literature studied is very poor in research related to the methods of determining surfactants from environmental samples. Regarding the removal methods of cationic surfactants found in the studied literature, the removal methods with the help of adsorbent materials are the most. The adsorbent materials most used to remove cationic surfactants are mainly natural and synthetic zeolites, activated carbons immobilized on different materials, in traces from waste water and in the aquatic environment.

In order to fulfill the objectives of the doctoral thesis, we developed in the laboratory methods for removing surfactants using magnetite adsorbent nanomaterials and synthetic zeolite ZSM-5. With the help of benzalkonium bromide and benzethonium chloride we tested the adsorbent material properties of the magnetite nanomaterial, and with the help of benzalkonium chlorides we tested the adsorbent material properties of the ZSM-5 synthetic zeolite.

In order to monitor the concentrations of benzalkonium chlorides, we adapted from the existing methods in the literature an existing method for determining the 3 benzalkonium chlorides C12-BAC, C14-BAC and C16-BAC by the HPLC/DAD technique.

The research activities carried out during the doctoral internship led to the development of an unconventional hybrid technology for the removal of cationic surfactants using two treatment steps: the first step is photocatalysis with the help of the TiO_2 photocatalyst and the second step is biodegradation with the help of *E.Coli* bacteria. The degradation efficiency obtained by this method were over 95% for all three cationic surfactants, namely 98.1% for C12-BAC, 97.9% for C14-BAC and 97.3% for C16-BAC.

The preliminary research that led to this hybrid method was carried out through individual biodegradation studies of surfactants with the help of bacteria from the activated sludge of the sewage treatment plant, namely total coliform bacteria, faecal coliform bacteria and *E.coli*. Of these, the most effective and resistant was *E.coli* and for these reasons it was chosen for the biodegradation step.

The TiO_2 photocatalyst was used to degrade benzalkonium chlorides using UV radiation from two types of UV lamps. The TiO_2 photocatalyst was used in the powder and film degradation experiments. The results of the experiments showed that regardless of the form in which it is presented, the degradation efficiency are comparable. The advantage of the TiO_2 film is that the analyzed waste water no longer needs to be filtered or centrifuged. When TiO_2 was used for the concentration of 5 mg/L for all three benzalkonium chlorides the 12 hours of photodegradation give photodegradation efficiency of 98% for C12-BAC, 97.2% for C14-BAC and 96.8% for C16-BAC, while for the concentration of 10 mg/L, photodegradation efficiency of 48.5% for C12-BAC, 43.5% for C14-BAC and 40.3% for C16-BAC were obtained. These results led to the conclusion that for concentrations higher than 5 mg/L an additional treatment step is required which was decided to be the biodegradation method with the help of *E.coli* bacteria.

9.2 ORIGINAL CONTRIBUTIONS

Through the research studies carried out, the contributions in the field of environmental engineering were summarized in:

- the selection and testing of some cationic surfactants from the class of quaternary salts with bactericidal properties that were used for the development of unconventional wastewater treatment techniques with surfactants using two nanomaterials with an adsorbent role: the magnetite nanomaterial and the ZSM-5 zeolite nanomaterial and a adsorbent material coal active in powder form.

The original contributions concern research carried out for the advanced treatment stage of a treatment plant (tertiary stage)

- the development of an unconventional hybrid technique for the removal of cationic surfactants in two treatment steps: the photocatalytic step carried out with the help of the TiO_2 photocatalyst and the biological step carried out with the help of *E. Coli* bacterial strains.

9.3 FUTURE PROSPECTS

- For the magnetite adsorbent materials used in the experimental research, no desorption tests were carried out in order to reuse it.

- ZSM-5 zeolite adsorbent material together with cationic surfactants form a new adsorbent material that can be used to remove non-polar substances such as drugs or pesticides.

- Transfer of the hybrid technology obtained at the pilot level to demonstrate the reliability of the degradation method.

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