National University of Science and Technology POLITEHNICA Bucharest
Faculty of Biotechnical Systems Engineering
Doctoral School of Biotechnical Systems Engineering
Field of Environmental Engineering

SUMMARY OF PHD THESIS

ECOTECHNOLOGIES APPLIED IN ADVANCED WATER TREATMENT PROCESSES

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CONTENT

FOREWORD

The PhD thesis entitled "Ecotechnologies applied in advanced processes specific to water treatment" aims to remove pollutants from wastewater using econanotechnologies based both on the use of environmentally friendly materials in adsorption and photocatalysis processes and the use of algae.

The PhD thesis is structured in 6 chapters, developed in 125 pages, contains 60 figures and graphs and a bibliography of 151 references.

The PhD thesis contains a synthesis of the theoretical studies and experimental research carried out by the author on the application of ecotechnologies in advanced water treatment processes involving the use of environmentally friendly materials and algae.

In chapter I of the PhD thesis entitled "THE IMPORTANCE OF THE THEME. OBJECTIVES OF THE PhD THESIS" the proposed and achieved objectives are described, highlighting the importance of the chosen topic and its necessity in the scientific and social context.

Chapter II of the PhD thesis entitled "LITERATURE REVIEW ON INDUSTRIAL WASTEWATER" consists of four sub-chapters and presents the current state of scientific research on industrial wastewater. This chapter is based on a comprehensive review of the literature highlighting the environmental problems of: waters polluted with heavy metals, waters polluted with dyes, waters polluted with medicines, waters polluted with detergents and their sources.

Chapter III of the PhD thesis entitled "LITERATURE REVIEW OF INDUSTRIAL WATER TREATMENT TECHNOLOGIES" describes both conventional industrial water treatment technologies, with reference to chemical, physical and biological technologies, and non-conventional industrial water treatment ecotechnologies, describing the following categories: (a) nanotechnology applied to water treatment by photocatalysis used for the photodegradation of dyes, herbicides, polymers, drugs and detergents; (b) ecotechnology applied to water treatment based on adsorption; (c) biodegradation ecotechnology using algae.

Chapter IV entitled "METHODOLOGY OF EXPERIMENTAL RESEARCH" details the working method that underpinned the experimental research presented in the PhD thesis.

Chapter V, "EXPERIMENTAL RESEARCH", is composed of six sub-chapters and presents the description of experiments and results for the development of the following ecotechnologies:

a) Photocatalysis-based ecotechnology applied to remove detergents from wastewater using TiO_2;

b) Activated carbon-based ecotechnology applied to remove detergents from wastewater;

c) Adsorption-based ecotechnology applied for the removal of drugs from wastewater using activated carbon;

d) Photocatalysis-based ecotechnology for removing drugs from wastewater;

e) Algae-based ecotechnology for the removal of lead ions from wastewater investigating the algae *Sargassum fusiforme* and *Enteromorpha prolifera*;

f) Plant for the removal of organic pollutants from wastewater based on photocatalysis.

In Chapter VI , "ORIGINAL CONTRIBUTIONS IN THE FRAMEWORK OF THE DOCTORATE THESIS. FINAL CONCLUSIONS. PERSPECTIVES", the own contributions made in the framework of the PhD thesis, its general conclusions and future perspectives are presented.

The doctoral thesis concludes with a list of published articles, the conferences attended and the references consulted for the thesis.

The experimental research data obtained from the research was used to publish seven articles in national and international journals.

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

1.1. Importance of the theme

Due to population growth and rising living standards, there is an increasing demand for water. The quality of water resources is deteriorating daily due to the continuous use of chemical compounds in various industries, hospitals etc..

The most toxic pollutants are found in industrial wastewater, which is currently subject to treatment technologies with many drawbacks.

For this reason, it has been decided to investigate and develop new unconventional eco-technologies for water treatment, based on recent research in the field of nanotechnology on nanomaterials (TiO2, ZnO), adsorbents of the ecological material type (activated carbon) and algae used as biomaterials with a dual role: as adsorbent and absorbent.

Some of the arguments highlighting the importance of this PhD thesis include the advantages of using nanomaterials in purification processes, such as:

- They have a large specific surface area, thus having the ability to retain a large amount of wastewater pollutant using a small amount of material;
- Possibility to be regenerated and reused a large number of times in a treatment technology;
- No or low toxicity of nanomaterials studied in eco-treatment technologies (ZnO, TiO_2);
- Possibility of achieving high purification yields;
- Economic efficiency as it eliminates the costs of purchasing chemical reagents consumed during purification technologies;
- Lack of waste from conventional purification technologies that require further treatment.

The arguments related to the use of environmentally friendly material such as activated carbon for water treatment purposes are as follows:

- Lack of toxicity to humans and the environment;
- Ability to be regenerated and reused in treatment technologies.

  Câteva dintre avantajele utilizării algelor în ecotehnologia propusă pentru epurarea apei sunt următoarele: lipsa toxicității fiind un biomaterial care se găsește în mediul înconjurător, potențialul de a juca rol atât de adsorbant cât și de absorbant al poluanților existenți în apa uzată.

The need to study the application of nanotechnology for the removal of some organic compounds in the class of dyes, detergents and drugs from wastewater because of the toxic effects they have on human health when they enter the human body from the environment.

The relevance of the studies in the PhD thesis related to the realization of ecotechnologies used for the removal of emerging organic compounds from the class of dyes, detergents, drugs and heavy metals from wastewater is supported by the following assumptions:

- Preventing their negative impact on humans and the environment;
- Possibility of achieving high treatment yields;
- Use of environmentally friendly and cost-effective technologies.

Currently, both nationally and internationally, clean, economically and technologically efficient technologies that do not result in waste requiring further treatment and disposal are being investigated. Such technologies can be considered as those developed in the framework of the PhD thesis based on the use of environmentally friendly materials such as UV-activated semiconductor nanomaterials (e.g. TiO_2, ZnO) with a photocatalytic role, activated carbon with an adsorbent role and algae with the dual role of bioadsorbent and bioabsorbent.

The importance of developing such ecotechnologies is due to the need to overcome three of the disadvantages of conventional biological treatment for the removal of emerging organic compounds from wastewater: low yield, large amounts of sludge resulting from the biological treatment step and long treatment times.

1.2. Objectives of the PhD thesis

The objectives of the PhD thesis were the following:

- development of an eco-technology using the semiconductor nanomaterial TiO_2 as a photocatalyst for the degradation of emerging organic pollutants such as detergents (dodecyl benzyldimethyl ammonium chloride (C12-BAC), $C_{21}H_{38}ClN$, dimethyl tetradecyl ammonium chloride (C14-BAC), $C_{23}H_{42}ClN$ and dimethyl hexadecyl ammonium chloride (C16-BAC), $C_{25}H_{46}ClN$ from water to CO_2 and H_2O;
- development of an eco-technology using the semiconductor nanomaterial ZnO as a photocatalyst for the degradation of emerging organic pollutants such as drugs (paracetamol) from wastewater to CO_2 and H_2O;
- development of an eco-technology based on the use of the ecological material activated charcoal to remove medicines (paracetamol, diclofenac, ketoprofen and ibuprofen) from wastewater;
- development of an eco-technology based on the use of ecological activated carbon material for the removal of the detergent dodecyl benzyldimethyl ammonium chloride (C12-BAC), $C_{21}H_{38}ClN$ from wastewater;

- development of an eco-technology based on algae used for the removal of lead ions from wastewater, investigating the algae *Sargassum fusiforme* and *Enteromorpha prolifera*;
- realization of a treatment plant that removes organic pollutants such as detergents from wastewater by photocatalysis using TiO_2 nanomaterial.

CHAPTER 2. LITERATURE REVIEW ON INDUSTRIAL WASTEWATER

2.1. Water polluted with heavy metals

Heavy metal pollution of water is a major problem for the environment and human health. There are various approaches, both commercial and non-commercial, to address this problem in the context of ever-evolving technological progress [1, 2].

The main sources of heavy metal pollution of water include:

1. Waste from landfills;
2. Urban waste water;
3. Municipal wastewater;
4. Mining waste;
5. Industrial wastewater, such as from the galvanic, electronic and metal finishing industries.

As the amount of metals generated from technological activities continues to increase, the issue of their removal from wastewater becomes of paramount importance. Aquatic ecosystems are facing metal concentrations that exceed the limits set in water quality standards, which are designed to protect the environment, animal species and human health [2].

Some examples of sources of water pollution containing lead ions are:

(a) Battery processing: This industry involves the use of lead in batteries. During the manufacturing process, improper handling of used batteries or waste can lead to leakage of lead ions into the environment, including water.

(b) Oil industry: Some oil operations may contain traces of lead. Discharges of wastewater from refineries or oil facilities may contribute to lead pollution of water.

(c) Paint industry: Paints and varnishes often contain lead compounds, and runoff or spills from manufacturing processes or waste disposal can introduce lead into surrounding waters.

(d) Automotive industry: The production and maintenance of vehicles may involve the use of lead in various components, such as car batteries. Leakage or improperly managed waste may end up in surface waters.

(e) Aeronautical industry: Some aeronautical applications may involve the use of lead, for example in aircraft batteries. Any leakage or improper disposal of these components may contribute to lead pollution of water.

(f) Manufacture of explosives: In the production of explosives, substances containing lead may be used. Any spillage or accidental release may introduce lead into the environment.

(g) Steel industry: Although lead is not a common component in the steel industry, some secondary processes or auxiliary materials may contain lead. Improper storage or disposal of these materials can lead to lead pollution of water.

It is important that these industries comply with strict environmental regulations and adopt appropriate management practices to minimise lead pollution and protect the environment and human health.

Some examples of sources of copper ion water pollution in different industries:

(a) Mining industry: During the extraction of copper ores, copper can be released into the environment. This copper can end up in surface waters through rainwater run-off or improper management of mining waste.

(b) Textile industry: Some manufacturing processes in the textile industry involve the use of copper compounds such as dyes. Wastewater discharges from these processes may contain copper ions and lead to water pollution.

(c) Metallurgical industry: Waste containing copper may be produced in metallurgical processes, such as the processing of copper or other metals. Improper disposal or leakage from these processes can lead to water pollution.

(d) Steel industry: Although the main metal processed in the steel industry is iron, there are some secondary operations or auxiliary materials that may contain copper. Improper disposal of these materials can introduce copper into the aquatic environment.

(e) Paint industry: Certain types of paints and varnishes may contain copper-containing pigments or additives. Wastewater discharge from the paint production process can introduce copper into the environment.

To minimise copper pollution, these industries must adopt appropriate waste management and wastewater treatment practices in accordance with environmental regulations to protect water quality and aquatic ecosystems.

Sources of manganese pollution may include the following:

(a) Mining: The mining industry can contribute to manganese pollution of water by releasing manganese-containing mineral wastes and tailings into the environment.
(b) Alloy production: Production of alloys involving the use of manganese can generate manganese-containing wastes and emissions that may end up in water sources.
(c) Commodity processing: Some commodity processing processes, such as metal processing, may involve the use of manganese-containing compounds or materials. Improper disposal of these materials can contribute to manganese pollution of water.
(d) Iron-manganese operations: The production and processing of iron-manganese can release manganese into the environment, particularly if proper waste management practices are not followed.
(e) Welding: Welding processes may involve the use of manganese-containing materials. Emissions or leakage from these operations may contribute to manganese pollution of water.
(f) Agrochemical production: Some chemicals used in the agrochemical industry may contain manganese. Discharges of wastewater from this industry can introduce manganese into the aquatic environment.

There are other human activities that can contribute to manganese pollution of water, such as the use of chemicals in industry or agriculture, improper waste management and other industrial or commercial processes involving manganese.

To minimise manganese pollution, it is important to comply with environmental regulations, adopt proper waste management practices and carry out appropriate wastewater treatment to prevent excessive accumulation of manganese in water sources [2].

CHAPTER 3. LITERATURE REVIEW ON INDUSTRIAL WATER TREATMENT TECHNOLOGIES

3.1. Conventional industrial water treatment technologies

3.1.1. Tehnologii chimice

Chemical precipitation is an efficient and widely used technique in industry due to its operational simplicity and economy. In these processes, chemicals react with heavy metal ions to form insoluble precipitates. These precipitates can be separated from the wastewater by sedimentation or filtration. After this stage, the treated water can be decanted and then discharged into the environment or disposed of in a suitable manner. Conventional chemical precipitation methods include hydroxide precipitation and sulphur precipitation [18].

The most commonly used chemical precipitation technique is the precipitation of metal hydroxides, due to its relative simplicity, low cost and ease of pH control. The solubility of various metal hydroxides is minimised in a pH range between 8.0 and 11.0. Flocculation and sedimentation processes are used to remove metal hydroxides. A variety of hydroxides have been used for the precipitation of metals from wastewater, guided by low cost and ease of handling [18].

Various chemical precipitation techniques for the removal of Cu(II) and Cr(VI) ions from wastewater were investigated and evaluated. For this purpose, $Ca(OH)_2$ and NaOH were used to initiate the precipitation process. Cr(VI) was also reduced to Cr(III) using ferrous sulphate. For optimal precipitation of Cr(III), it was observed that the optimal pH is 8.7 with the addition of $Ca(OH)_2$, and the chromate concentration was significantly reduced from 30 mg/L to 0.01 mg/L. For copper, the optimum pH for precipitation was approximately 12.0 for both $Ca(OH)_2$ and NaOH, and resulted in a reduction of the copper concentration from 48.51 mg/L to 0.694 mg/L. The initial high concentrations of chromium, copper, lead and zinc in the effluents were significantly reduced to levels of 0.08; 0.14; 0.03 and 0.45 mg/L, respectively [19].

In addition, the precipitation process of metal hydroxides has been improved by adding coagulants such as iron salts and organic polymers to increase the efficiency of heavy metal removal from wastewater. This type of chemical coagulation and precipitation has been successfully used for the treatment of synthetic waters containing Zn, Cd, Mn and Mg.

3.2. Photocatalysis-based ecotechnology applied for the removal of detergents from wastewater using TiO_2

Wastewater containing the three cationic surfactants C12-BAC (benzyl-dodecyl-dimethylazanium chloride, $C_{21}H_{38}ClN$), C14-BAC (benzyl-dimethyl-tetradecylazanium chloride, $C_{23}H_{42}ClN$) and C16-BAC (benzyl-dimethyl-tetradecylazanium chloride, C23H42ClN) working concentrations of 5 mg/L and 10 mg/L were analysed ($C_{25}H_{46}ClN$, benzyl-hexadecyl-dimethylazanium;chloride).

Laboratory studies were carried out for the disintegration of the three surfactants using a TiO_2 film as a photocatalyst on the plates. Laboratory experiments were also conducted to degrade the surfactants using bacteria. In conclusion, hybrid experiments combining photocatalysis with biodegradation were conducted.

The TiO_2 catalyst was deposited on plastic plates that were immersed in the 15-litre reactor. Three UV lamps of 30W each were inserted between the TiO_2 plates. The solution volume in the reactor was 10 litres. Water samples were taken from the reactor every hour. The experimental results are shown in the figures below.

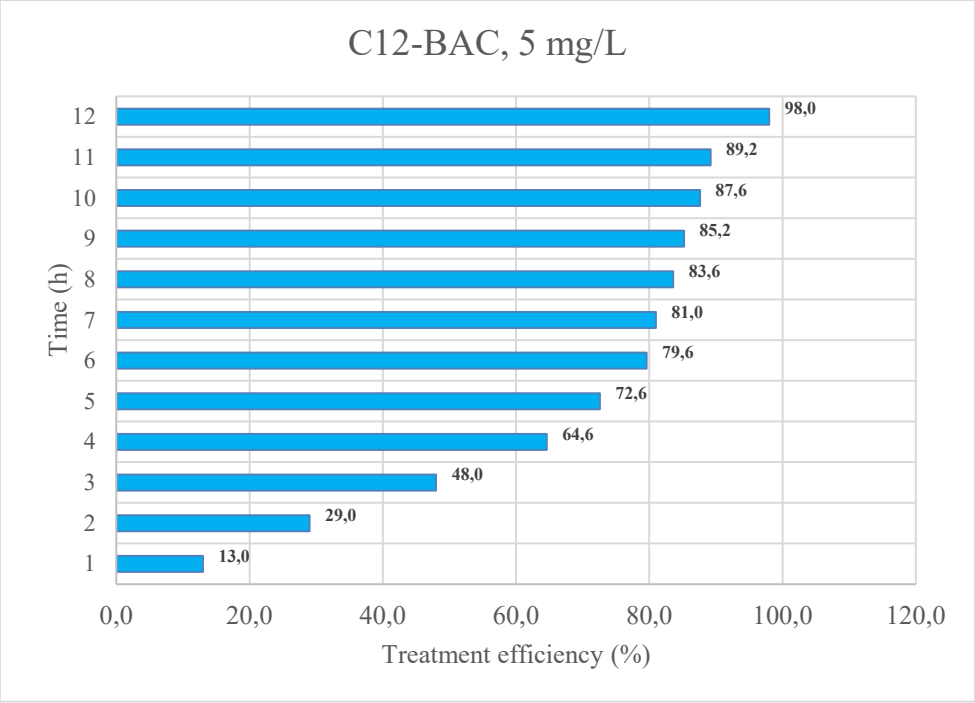

Figure 5.1. Variation of treatment yield over time for photocatalysis applied to wastewater containing C12-BAC -5 mg/L.

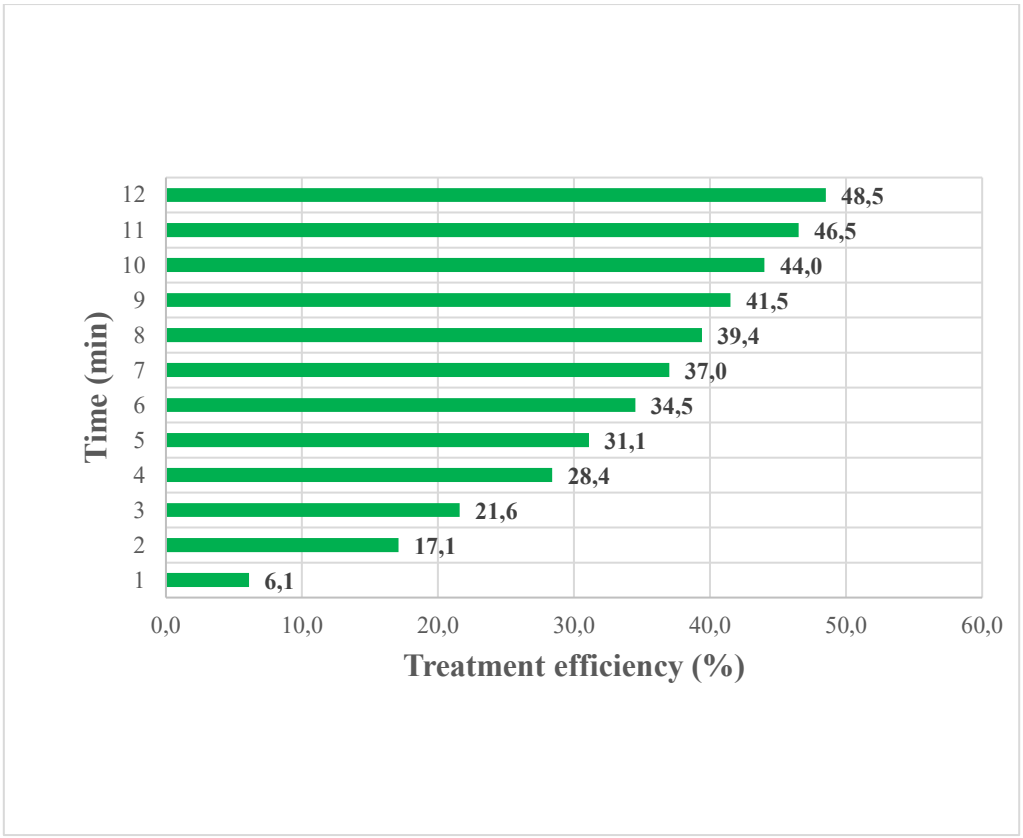

Figure 5.2. Variation of treatment yield over time for photocatalysis applied to wastewater containing C12-BAC -10 mg/L.

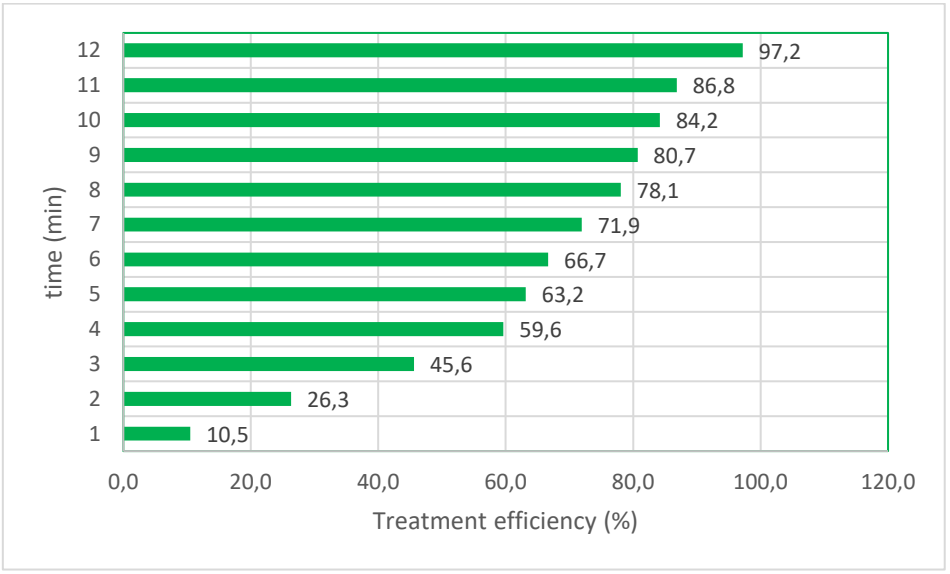

Figure 5.3. Variation of treatment yield over time for photocatalysis applied to wastewater containing C14-BAC -5 mg/L.

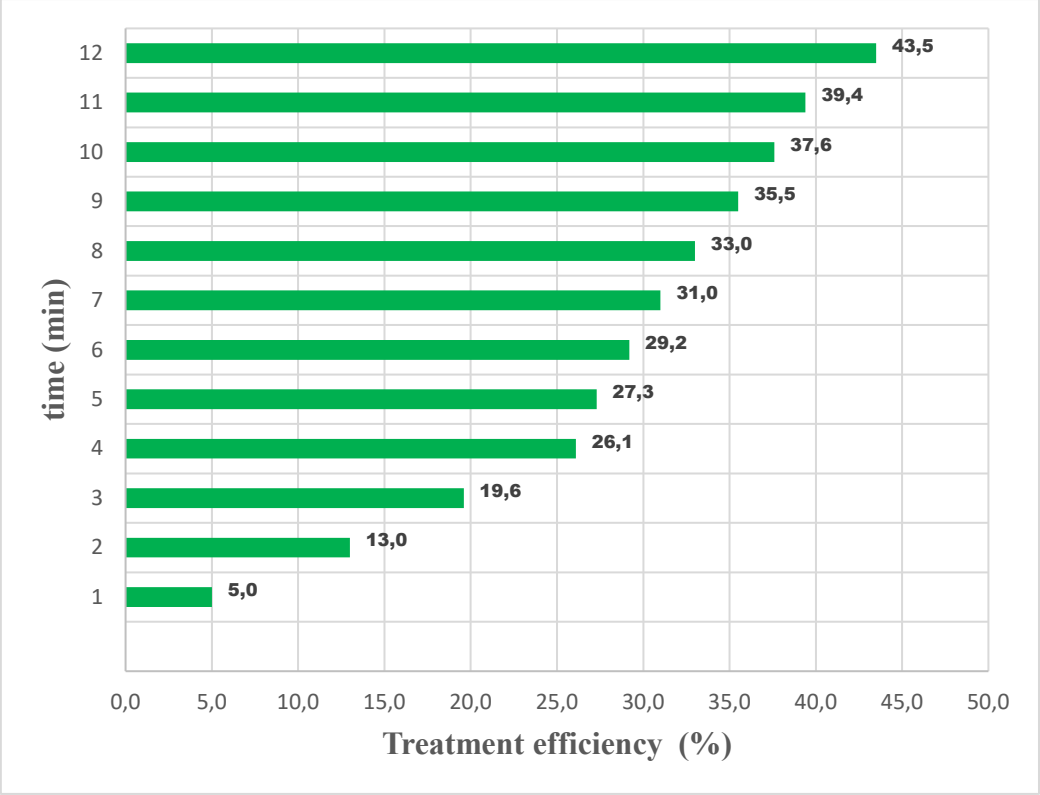

Figure 5.4. Variation of treatment yield over time for photocatalysis applied to wastewater containing C14-BAC -10 mg/L.

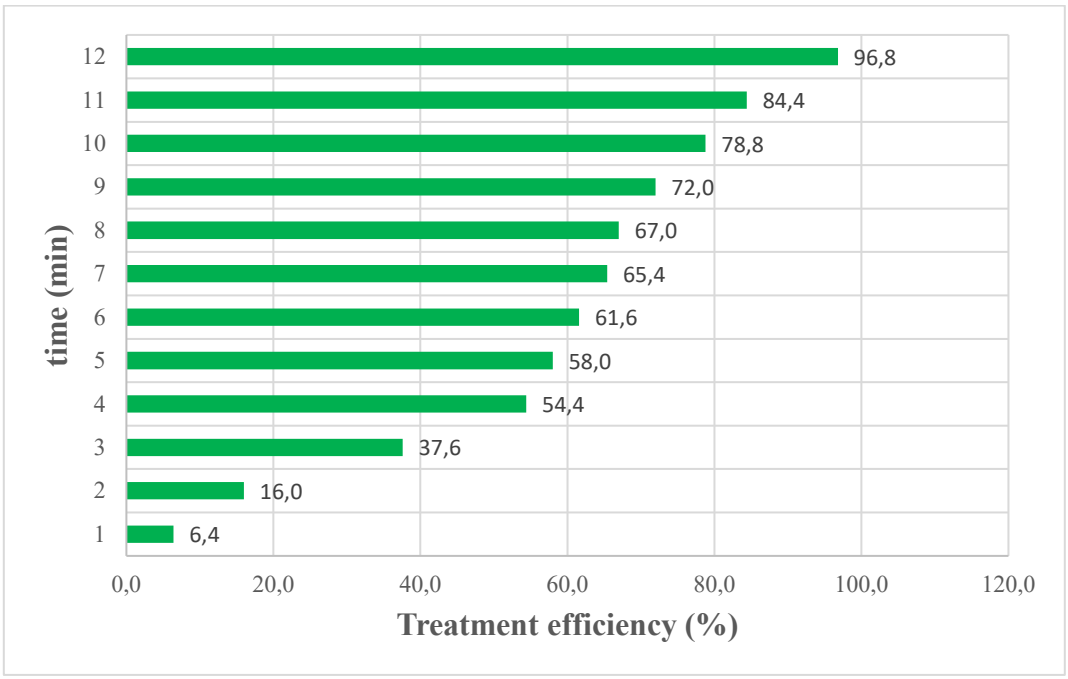

Figure 5.5. Variation of treatment yield over time for photocatalysis applied to wastewater containing C16-BAC -5 mg/L.

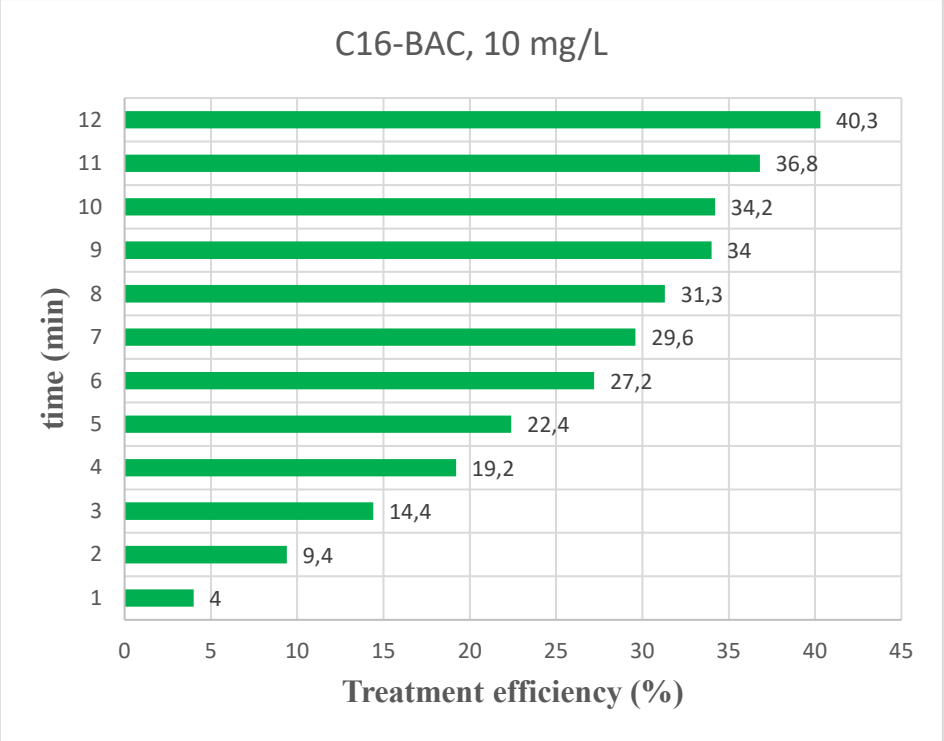

Figure 5.6. Variation of treatment yield over time for photocatalysis applied to wastewater containing C14-BAC -5 mg/L.

The scrubbing yield increases with decreasing number of carbon atoms in the long chain of compounds in the order C16-BAC, C-14-BAC, C12-BAC. For an initial concentration of 5 mg/L for all three cationic surfactants, the 12-hour photodegradation process resulted in the removal of 98% of C12-BAC, 97.2% of C14-BAC and 96.8% of C16-BAC. At a concentration of 10 mg/L, the removal efficiency is found to be 48.5% for C12-BAC, 43.5% for C14-BAC and 40.3% for C16-BAC.

3.3. Activated carbon-based ecotechnology applied to remove detergents from wastewater

Activated carbon was chosen for the removal of detergents from water because it has several advantages: it is non-toxic, renewable, reusable and cheap.

The activated carbon (denoted PAC) used in the purification studies was purchased from Trace Elemental Instruments and has the following characteristics: particle size between 10 and 50 µm, specific surface area of 256 m^2/g, pore size of 12.7 Å and total pore area of 870 m^2/g.

The detergent class compound present in synthetic wastewater was C12-BAC, and its analysis during the depletion ecotechnology study.

C12-BAC analysis: the chromatographic method used for the determination of C12-BAC concentrations was developed in another paper [35], and the equipment used was an Agilent 1200 liquid chromatograph equipped with a DAD detector operating at a wavelength of 262 nm and an Acclaim Surfactant Plus chromatographic column, 3 μm, length 150 mm, inner diameter 3 mm. The operating parameters of the method were: column temperature of 30°C, injection volume of 20 μL, mobile phase of 0.2 M ammonium acetate:acetonitrile in 50:50 (v/v) ratio, mobile phase flow rate of 0.5 ml/min, elution time for C12-BAC was 2.4 min.

Kinetic studies

Kinetic analyses were performed by mixing 250 mg of PAC with 500 ml of synthetic wastewater containing C12-BAC at concentrations of 50 mg/L, 100 mg/L and 250 mg/L. The mixtures were stirred at 250 rpm for 60 minutes, and samples were taken at 10-minute intervals for analysis.

Influence of pH

To examine the influence of pH on the adsorption process of C12-BAC, experiments were conducted using the same concentration of 50 mg/L of C12-BAC and two different amounts of adsorbent material, 200 mg and 250 mg respectively, at three different pH levels: pH=4, pH=6 and pH=10.

Adsorption studies

C12-BAC is adsorbed on an adsorbent material, i.e. PAC (powdered activated carbon).

The experiments were carried out in 500 ml of synthetic wastewater with a concentration of 50 mg/L of C12-BAC. Three amounts of adsorbent material were used for C12-BAC adsorption: 100 mg, 200 mg and 250 mg. The experiments were carried out at pH=10. The mixtures were homogenized at 250 rpm for 60 minutes. Samples were taken every 10 minutes and analysed.

The removal efficiency (RE) can be determined using the following equation:

$$RE\% = 100\ x\ \left(1 - \frac{C_t}{C_i}\right) \quad (3)$$

where:

C_t and C_i are the concentration of C12-BAC at time t and at the initial time.

The amount of C12-BAC adsorbed on the adsorbent material used was calculated using the following equation:

$$Qe = \frac{(Ci - Ce) * V}{m} \quad (4)$$

where:

- Q_e - adsorption capacity at equilibrium (mg/g);

- C_i is the initial concentration of C12-BAC in the wastewater (mg/L);

- C_e is the equilibrium concentration of C12-BAC in the wastewater (mg/L);

- m is the mass of adsorbent material (g);

- V is the initial volume of C12-BAC used in the study (L).

Sorption isotherms are used to explain adsorption processes and, in addition, to calculate the adsorption capacity of the adsorbent material used, using mathematical modelling. The most commonly used adsorption isotherm models are the Langmuir and Freundlich isotherms.

The Langmuir isotherm is based on the following mathematical equation [37]:

$$Q_e = \frac{Q_{max} K_L c_e}{1 + K_L c_e} \quad (5)$$

where:

- What is the equilibrium C12-BAC concentration (mg/L);

- K_L is the equilibrium constant of the Langmuir model (L/mg);

- Q_e is the adsorption capacity at equilibrium (mg/g);

- Q_{max} is the maximum adsorption capacity (mg/g);

- 1 was the maximum occupied adsorption capacity for a given set of conditions to equilibrate the entire monomolecular layer, mg/g;

The Freundlich isotherm equation is based on the following mathematical equation [38].

$$Q_e = K_F \, x \, C_e^{\frac{1}{n}} \quad (6)$$

where:

- K_F is the adsorption capacity determined by the Freundlich equation (mg/g);

- 1/n is the Freundlich parameter as a function of adsorption intensity;

- C_e is the equilibrium C12-BAC concentration (mg/L).

The purification efficiency calculated for each concentration of C12-BAC was 92.3% for the concentration of 50 mg C12-BAC/L, 67.5% for the concentration of 100 mg C12-BAC/L and 39.92% for the concentration of 250 mg/L, respectively, as shown in Figure 5.8. For wastewater containing a concentration of 50 mg/L C12-BAC and PAC adsorbent material, after 60 minutes of contact time, the concentration determined was 0.40 mg C12-BAC/L. The adsorption capacity of PAC was 0.20 mg C12-BAC/mg PAC. For a concentration of 100 mg C12-BAC/L in the wastewater, the concentration remaining in the treated wastewater was 0.38 mg C12-BAC/mg PAC, and the adsorption capacity of PAC was 0.38 mg C12-BAC/mg PAC. For wastewater containing 250 mg C12-BAC/L, 26 mg C12-BAC/L was determined in the wastewater, corresponding to an adsorption capacity of PAC of 0.90 mg C12-BAC/mg PAC.

As can be seen in Figure 5.8., the removal efficiencies are above 90% for all three wastewater concentrations used in the experiments.

Influence of pH

The effects of pH on the removal efficiency of C12-BAC using powdered activated carbon were determined by interacting 200 mg and 250 mg of adsorbent material with a concentration of 50 mg/L of C12-BAC at three pH values, i.e. pH=4, pH=6 and pH=10. The results of the quantitative determination of C12-BAC showed that at pH=4 the removal efficiency was less than 50%, at pH=6 the removal efficiency was more than 50% and at pH=10 the removal efficiency was more than 90%, as shown in Figure 5.9.

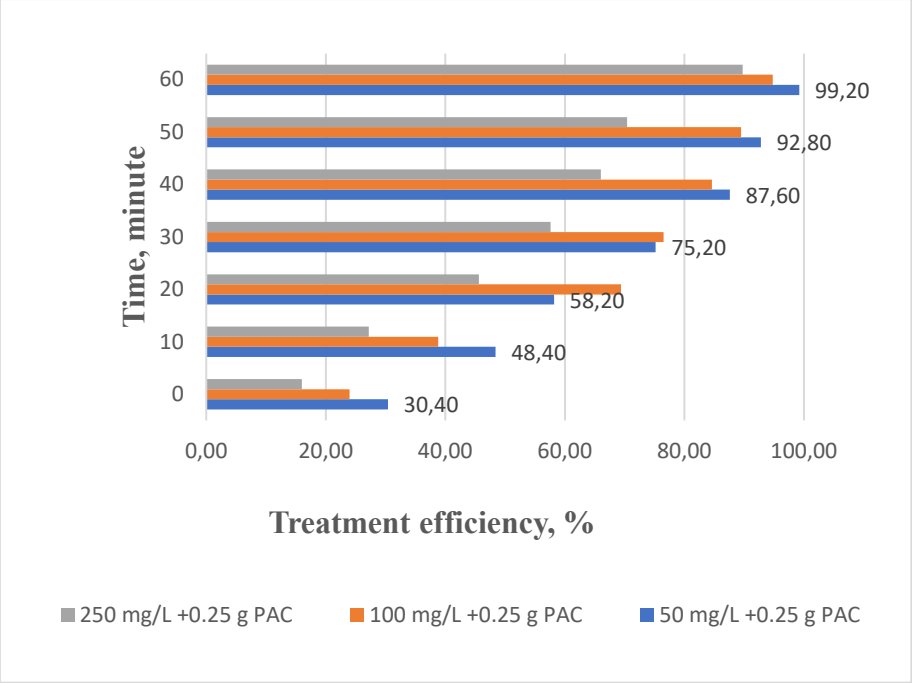

Figure 5.8. Removal efficiency of C12-BAC using 250 mg of activated carbon adsorbent material.

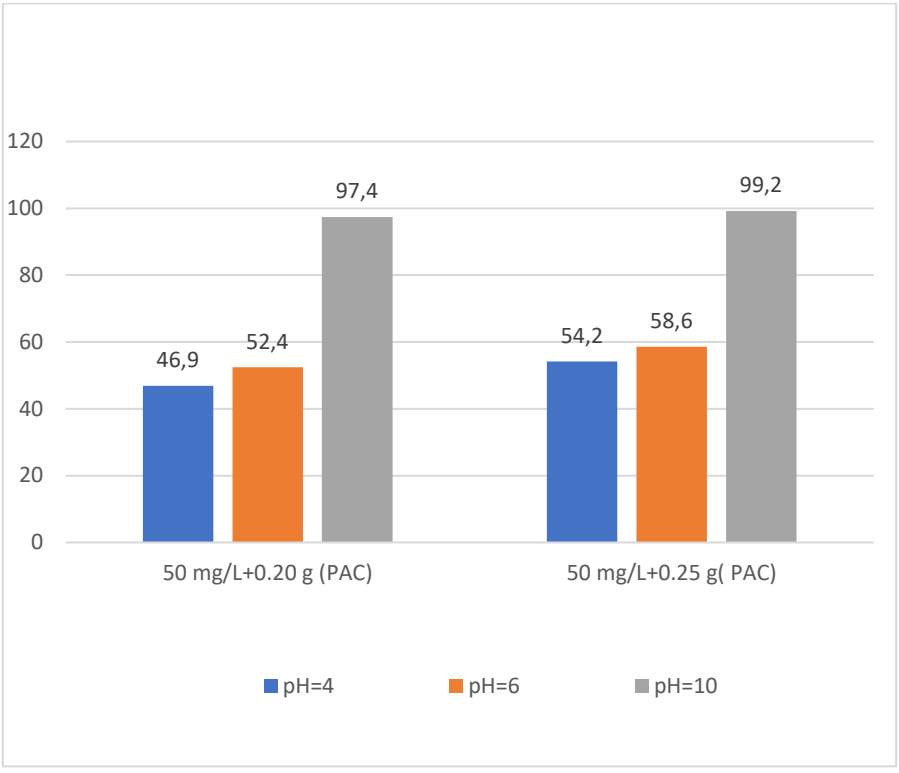

Figure 5.9. Influence of pH on the efficiency of C12-BAC purification by activated carbon.

Adsorption studies

The removal efficiency of C12-BAC on different amounts of PAC material increased with increasing amount of adsorbent material (Figure 5.10). The experimental data obtained in the adsorption study were used to calculate the adsorption isotherms for each adsorbent material used.

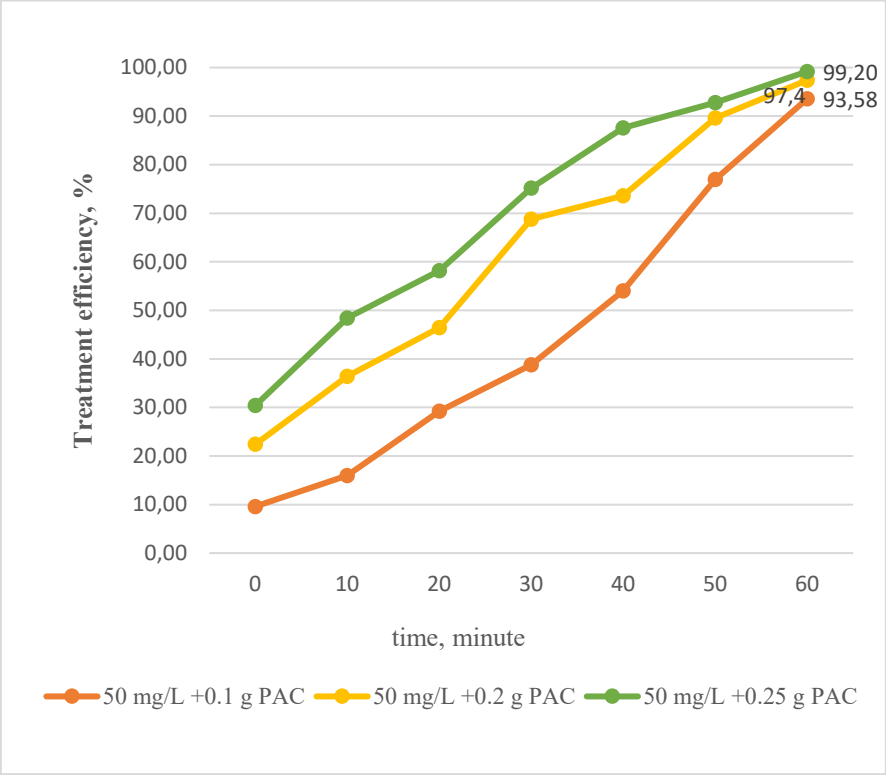

Figure 5.10. Treatment efficiency of C12-BAC as a function of time for different amounts of activated carbon material.

The adsorption capacity of the activated carbon material increased with the contact period (Figure 5.11).

The Langmuir isotherm proposes that adsorption occurs on homogeneous active sites of a monolayer adsorption surface with a finite number of identical sites, with no interactions between adsorbed molecules.

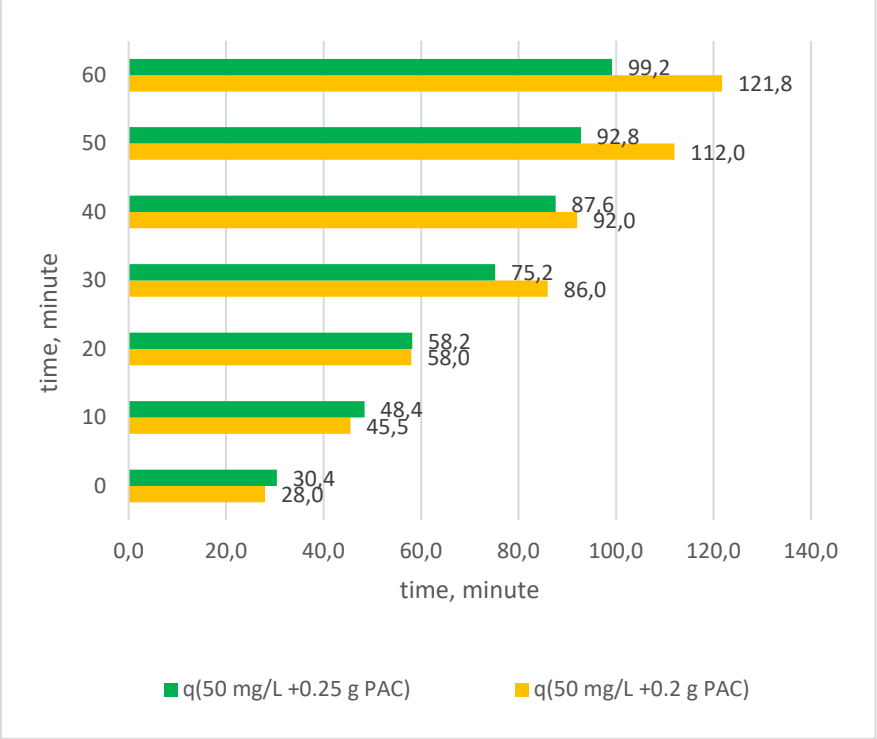

Figure 5.11. Adsorption capacity (mg/g) of activated charcoal ecomaterial over time.

The Freundlich isotherm model can be used for multilayer adsorption on heterogeneous sites. Heterogeneous adsorption occurs when the pollutant penetrates the adsorbent material in such a way that adsorption is continuously increasing and adsorption equilibrium is not reached [39].

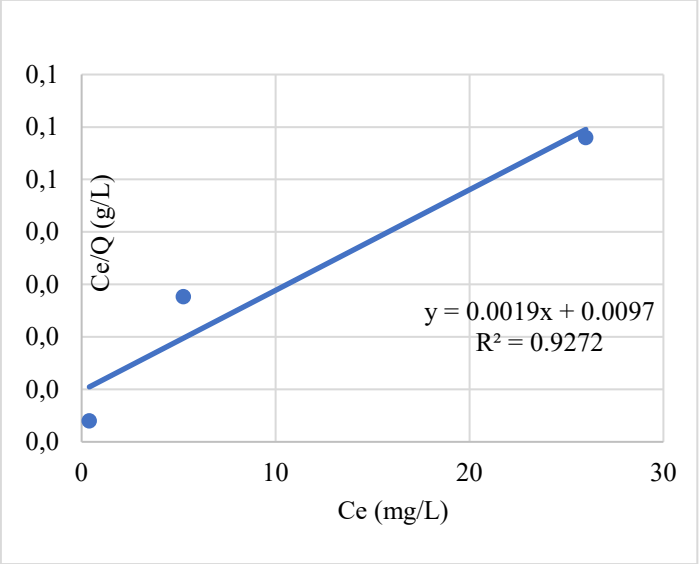

Figure 5.12. Langmuir isotherm for PAC.

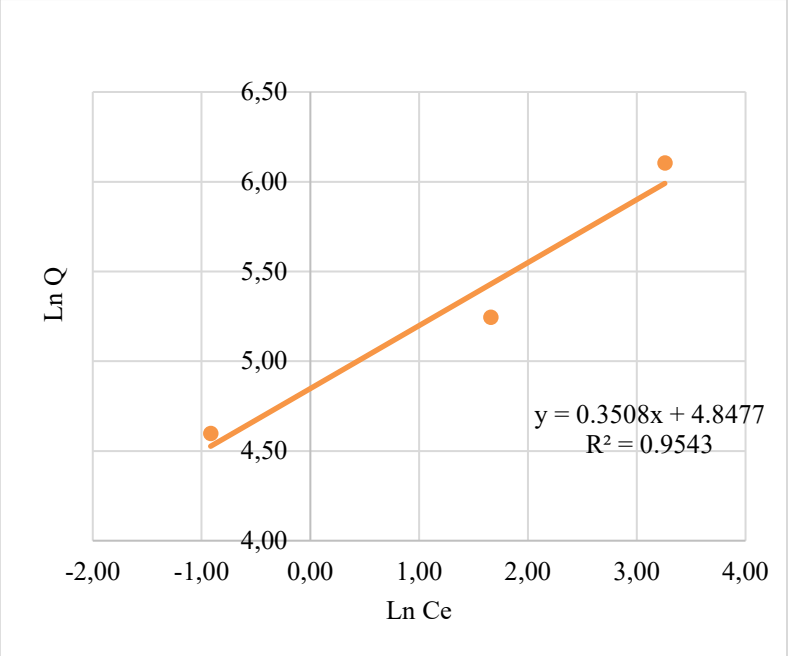

Figure 5.13. Freundlich isotherm for PAC ecomaterial.

Table 5.2. Langmuir and Freundlich adsorption parameters.

Adsorbant material	**Langmuir parameters**			**Freundlich parameters**		
	Q_{max} (mg/g)	K_L (L/mg)	R^2	K_F (L/g)	1/n	R^2
PAC	526	0.196	0.9272	2.85	127	0.9543

As can be seen in Table 5.2, the correlation coefficients (R2) and isotherm parameter values used show that all adsorption data for the adsorbent material PAC fit the Freundlich model better. These results support that the adsorption of C12-BAC on wastewater PAC ecomaterial occurs on heterogeneous sites.

C12-BAC adsorption increases with increasing wastewater pH, and maximum C12-BAC adsorption is obtained at pH 10.

The adsorbent eco-material activated carbon (PAC) had the highest adsorption capacity of 526 mg/g and the removal efficiency was 99.2% for 250 mg of adsorbent material at a concentration of 50 mg C12-BAC/L and pH =10.

The correlation coefficients (R2) and isotherm parameter values for the PAC adsorbent ecomaterial fit better with the Freundlich model, which is applied to explain adsorption for heterogeneous surface.

3.4. Adsorption-based ecotechnology applied for the removal of drugs from wastewater using activated carbon

The aim of this chapter was to highlight the use of activated carbon material for the removal of anti-inflammatory drugs from a synthetic wastewater. The drug products studied were acetaminophen (ACF), diclofenac (DCF), ibuprofen (IBF), ketoprofen (KET) which belong to the class of non-steroidal anti-inflammatory drugs (NSAIDs).

The removal of several NSAIDs from wastewater collected from hospitals was lower due to hydrophobic substances and oil interference found in the samples used, microextraction (3) and adsorption, HPLC-UV [11-12]. The adsorption mechanisms of naproxen (NAP), acetaminophen (ACT) and clofibric acid (active metabolite CFA) on porous silica-based materials were examined.

Advances in nanotechnology offer opportunities to treat wastewater much more efficiently and quickly using affordable nanomaterials. Due to their unique surface characteristics and structure, nanomaterials are suitable and effective adsorbents for the removal of drug residues from wastewater [1].

The quantities of drugs entering the treatment plants may differ depending on the physical and chemical properties of the drug. Due to their hydrophobic properties and stability, NSAIDs (non-steroidal anti-inflammatory drugs) can remain in the aqueous phase, which is why they can be found in surface waters at concentrations up to ng/l [143]. Several methods have been applied to treat or remove NSAIDs from the aquatic environment.

Photocatalytic degradation [144]: Photocatalytic degradation was determined by sunlight of TiO2. This was achieved by an ultrasonic bath assisted process and their structural, photocatalytic and optical properties were characterized. Optimization of the photocatalytic degradation method involved experiments that were influenced by dose, pH and initial drug concentration. The results of the photocatalytic experiments showed that there was approximately 99% photodegradation of ketorolac tromethamine (NSAID) solution at a concentration of 10 mg/L with an optimized amount of TiO2, 0.5 g/L and pH=4.4. under sunny conditions.

Biodegradation [145, 146, 147]: Laboratory tests were conducted with four NSAIDs (naproxen, ibuprofen, diclofenac and ketoprofen) under different aerobic, anaerobic, anoxic

and sulphate-reducing conditions to assess abiotic and biotic degradation of a surface water. The results of the experiment showed that the removal of the compounds decreases as the concentration of dissolved oxygen in the surface water decreases. The study showed that all compounds can be biodegradable under aerobic conditions and their dissipation half-life can be between 1.6 - 20.1 days. Dissipation half-lives for ketoprofen and naproxen increase with a correlation coefficient of 2 under conditions tested in the absence of oxygen.

Biofiltration [148], COD (chemical oxygen demand): The study shows the possible use of zebra mussels for the removal of pharmaceutical contaminants that cannot be completely removed from wastewater. The mussels are resistant to anthropogenic and natural stresses, have filtering capacity and could be used to bioaccumulate lipophilic contaminants. The data demonstrated the ability of these molluscs to reduce concentrations of some pharmaceuticals, suggesting a possible evaluation of the biofiltration process in wastewater management.

This flotation-electrocoagulation process has been used to remove NSAIDs (diclofenac, ketoprofen and ibuprofen) from wastewater. Cetyltrimethylammonium ammonium bromide (CTAB), a cationic surfactant, was added as a foaming agent, and NSAID removal was significantly improved, over 45% in wastewater systems with single NSAIDs. For the removal of several pharmaceutical NSAID compounds, the concentration of CTAB used for good removal was equal to the sum of the molar concentrations of all NSAIDs.

The materials used in this study were purchased from Sigma-Aldrich. The purity of paracetamol was ≥95.0%, ibuprofen ≥97.0%, ketoprofen ≥99.0% and diclofenac ≥99.0%. Solvents used for total organic carbon (TOC) analysis were purchased from Honeywell. Activated charcoal material was purchased from Trace Elemental Instruments, with particle sizes ranging from 10 to 50 μm. The carbon material has the following characteristics: specific surface area 604m2/g, total pore volume 12.7cm3/g and average micropore radius 870Å.

Adsorption experiments were conducted using synthetic wastewater with three different concentrations of anti-inflammatory drugs (1mg/L; 5mg/L and 10 mg/L), at two different pH values (4 and 6), using three different amounts of activated carbon material for the adsorption process (0.1g, 0.5g and 1g). All experiments were carried out in Erlenmeyer flasks (100mL) using a temperature controlled orbital shaker (100 min-1 shaking speed) for 120 minutes. Experiments were performed at room temperature (25±20C).

The removal efficiency was calculated using the following equation (7):

$$\eta = \frac{C_i - C_f}{C_i} * 100 \quad (7)$$

where: C_i - initial concentration of anti-inflammatory drugs (mg/L);

C_f - final concentration of anti-inflammatory drugs (mg/L).

Desorption studies were applied to highlight drug residues retained on the adsorbent material and the possibility of using this material in further removal studies. The desorption procedure was as follows: 1mg/L samples loaded with synthetic pollutants were stirred with 50 ml of HCl at different concentrations (0.1M; 0.3M and 0.5M) on a mechanical shaker (90 minutes at 150 rpm). The supernatant obtained was centrifuged and analysed by TOC.

The desorption of drug residues from activated carbon materials was calculated using the following equation (8):

$$\text{Desorption } (\%) = \frac{\text{Cd}}{(\text{Q}*\text{m})} * 100 \quad (8)$$

where:
C_d is the concentration of drug residue desorbed from the adsorbent material (mg/L);
Q is the adsorption capacity (mg/g);
m(g) is the mass of adsorbent material applied in the experiment.

Carbon organic total (TOC)

Residues of pollutants in synthetic wastewater were monitored using the TOC (total organic carbon) technique. Another means of measuring organic matter in wastewater is TOC, which is mainly applied to low concentrations of organic matter. This TOC is achieved by injecting a known amount of sample into a high temperature furnace or chemical oxidation medium. The organic carbon is oxidised to carbon dioxide in the presence of a catalyst. The carbon dioxide produced was measured quantitatively using an infrared analyser. Acidification and aeration of the sample before analysis eliminates errors due to the presence of inorganic carbon. The test can be performed quickly and is becoming increasingly popular.

The performance parameters of the TOC method are as follows: limit of detection (0.1mg/L), limit of quantification (0.3mg/L) and expanded uncertainty of the analytical method 12%. The name of the equipment used for the experiments is Shimadzu Analyzer TOC TN LCPN.

Adsorption studies

The removal efficiency of drug residues (paracetamol, diclofenac, ketoprofen and ibuprofen) from a synthetic wastewater was studied at pH 4 and 6, at three pollutant concentrations (1mg/L, 5mg/L and 10mg/L) and at three adsorbent dosages (0.1g; 0.5g and 1g). The main results are shown in Figures 5.14..a - 5.14.d and Figure 5.15.

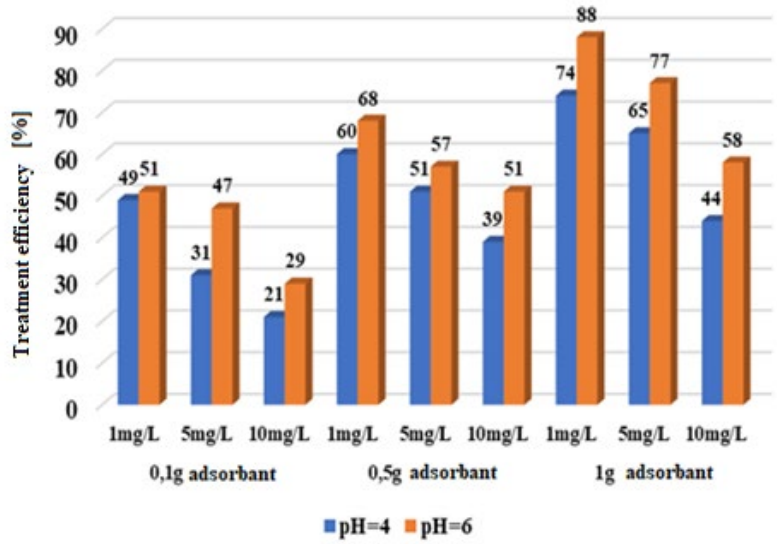

Figure 5.14.a. Effect of pH on the removal of paracetamol residues at different concentrations and doses of adsorbent.

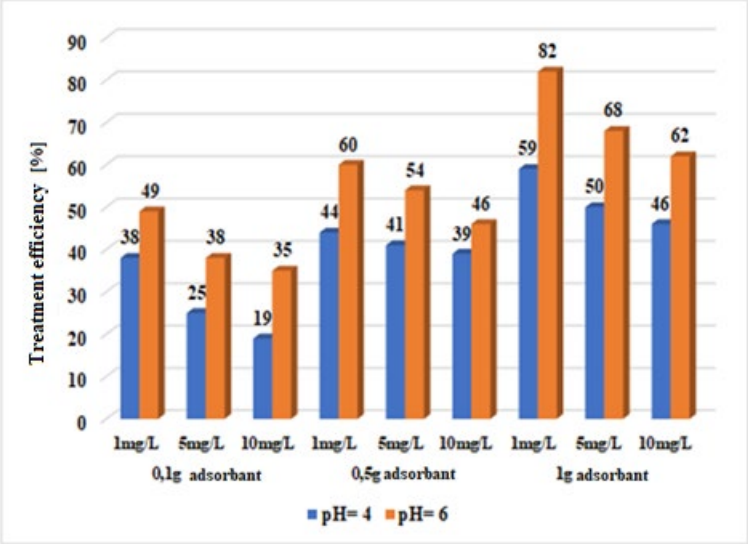

Figure 5.14.b. Effect of pH on removal of diclofenac residues at different concentrations and doses of adsorbent.

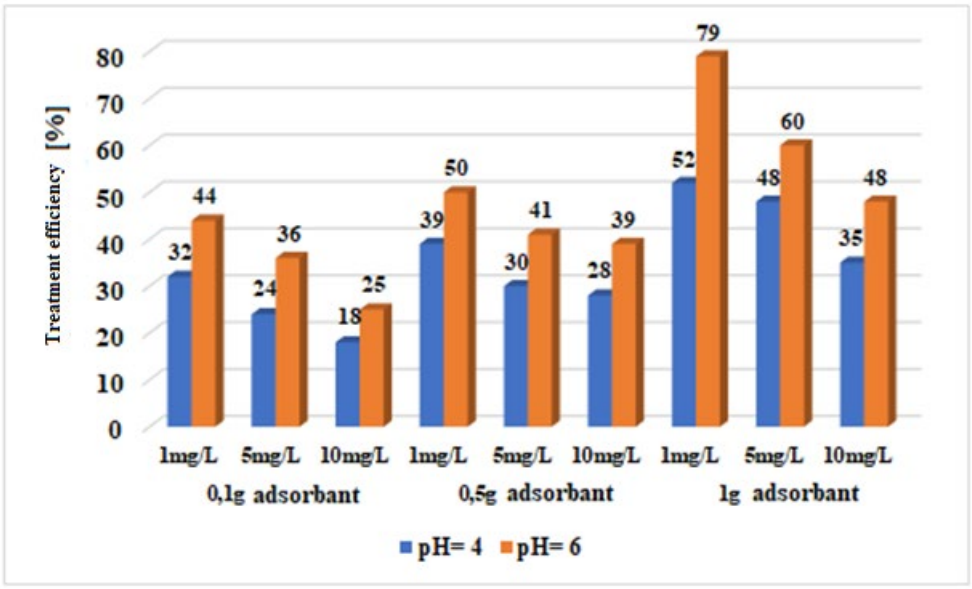

Figure 5.14.c. Effect of pH on the removal of ketoprofen from wastewater at different concentrations and doses of adsorbent.

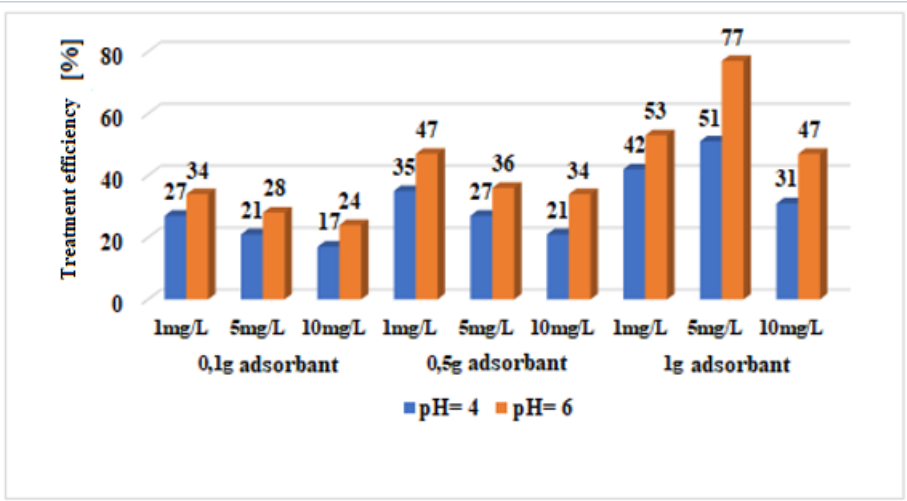

Figure 5.14.d. Effect of pH on ibuprofen removal from wastewater at different concentrations and adsorbent dosages.

Adsorbent dosing is very important in adsorption studies. Activated carbon (adsorbent material) has a higher specific surface area ($604 m^2/g$) which allowed all adsorption processes on its sites. With 1 g of adsorbent material, at pH=6, the highest removal efficiency results were obtained compared to 0.1 g of adsorbent material, also at pH=6, which showed the lowest removal efficiency, as shown in Figures 5.14.a - 5.14.d.

The results obtained for the four drug residues are as follows, with an adsorbent dose of 1g, an initial concentration of 1mg/L and pH=6 (Figure 5.14.a - 5.14.d): acetaminophen (88%) > diclofenac (82%) > ketoprofen (79%) > ibuprofen (77%).

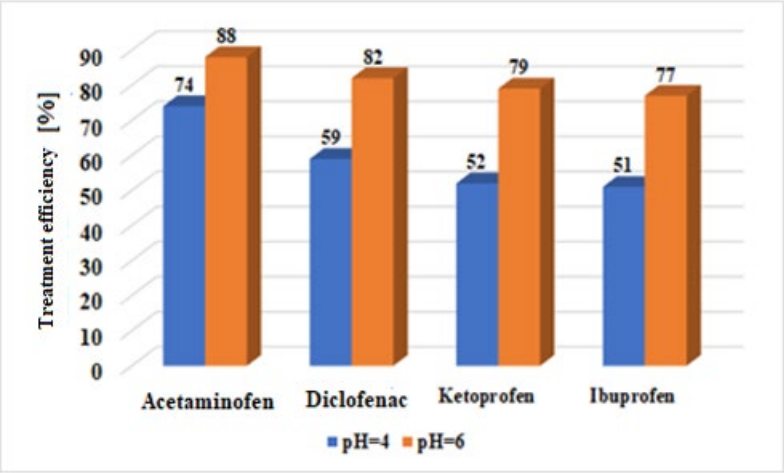

Figure 5.15. Effect of pH on drug residue removal at different pollutant concentrations and adsorbent dosages.

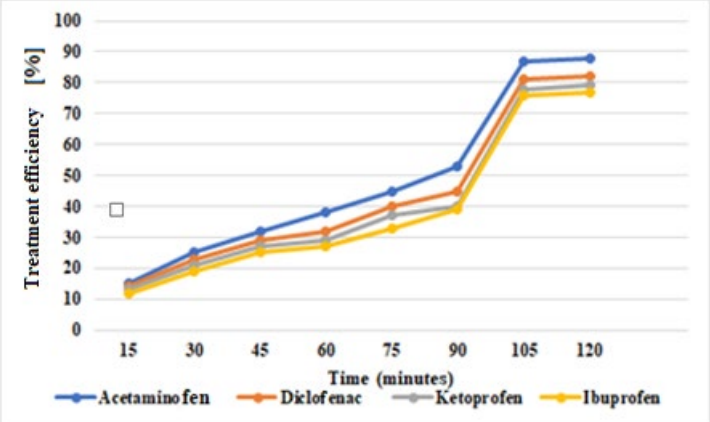

Figure 5.16. Removal efficiency as a function of contact time.

Figure 5.15. showed the importance of the pH value of wastewater in the treatment process. In all cases, the treatment efficiency was maximum. However, pH 6 is much more advantageous for the removal of drug residues from wastewater, with a shorter treatment time (120 minutes).

These studies aim to highlight the importance of determining TOC (total organic carbon) for a low concentration of organic matter in wastewater. The effect of the contact period on synthetic wastewater at pH 6 was studied and the results are shown in Figure 5.16. The removal efficiency of four drug residues showed high values at pH 6 and low values at pH=4. After a contact time of 120 minutes, the adsorbent material becomes saturated and no

longer adsorbs the drug residues. The equivalence point is reached and the adsorption process ends.

Langmuir and Freundlich adsorption isotherms

To best describe the adsorption process the Langmuir and Freundlich mathematical models are used which are described elsewhere [149].

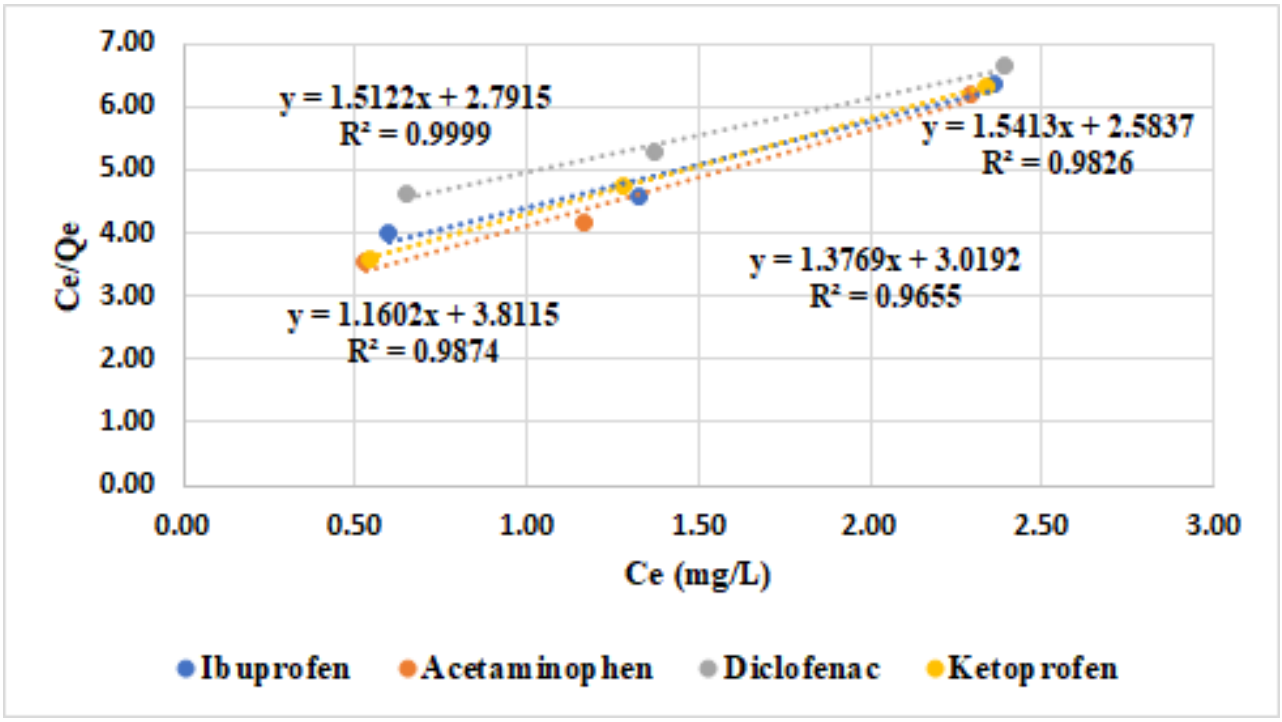

Figure 5.17. Langmuir isotherm for drug residues adsorbed on activated carbon material.

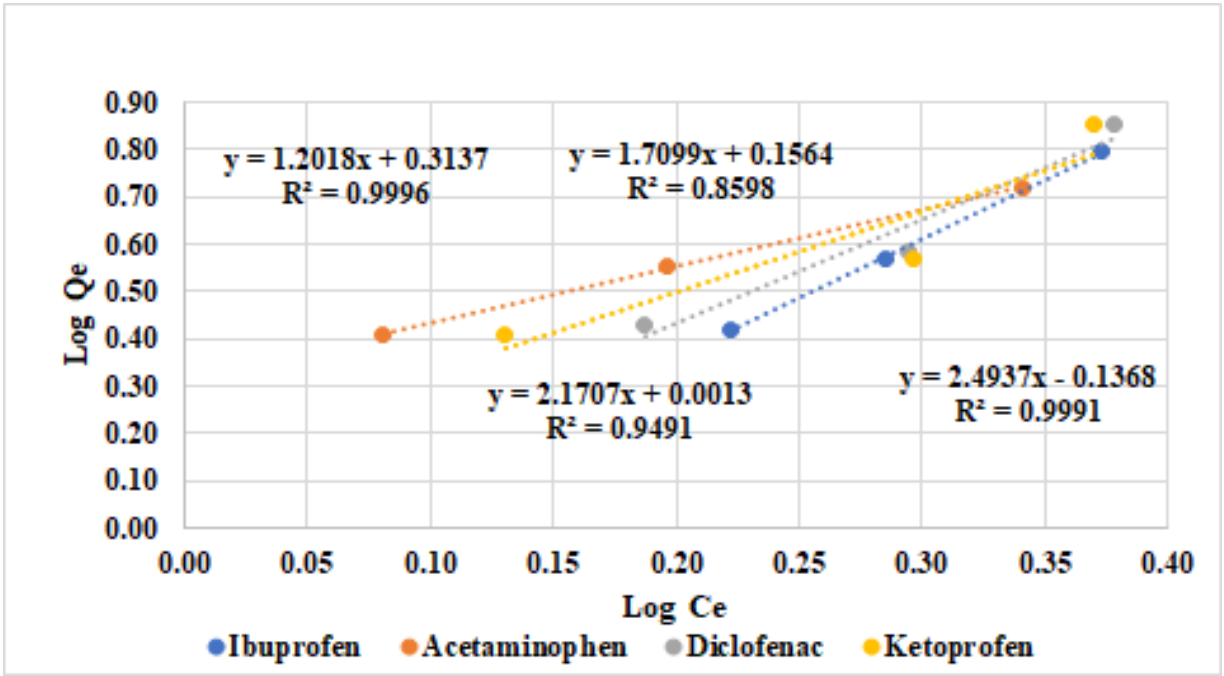

Figure 5.18. Freundlich isotherm for drug residues adsorbed on activated carbon material.

Table 5.3. Langmuir and Freundlich adsorption parameters.

	Langmuir parameters				Freundlich parameters		
Drug residues	Q_{max}(mg/g)	K_L (L/mg)	R_L	R^2	K_F (L/g)	1/n	R^2
Acetaminophen	0.64	1.62	0.28	0.9826	1.20	0.31	0.9996
Ibuprofen	0.70	2.70	0.10	0.9655	2.49	0.14	0.9991
Diclofenac	0.85	3.23	0.41	0.9874	1.55	0.21	0.9491
Ketoprofen	0.66	1.85	0.18	0.9999	1.71	0.16	0.8598

The experimental conditions for the Langmuir and Freundlich isotherms are: initial pollutant concentration 1mg/L, pH=6 and adsorbent dose of 1g. Experimental data shown in Figures 5.17. and 5.18. and in Table 5.3. showed that the Langmuir isotherm model fits very well the experimental data for diclofenac (R^2=0.9874) and ketoprofen (R^2=0.9999), and the Freundlich models fit very well the data for the drug residues paracetamol (R^2=0.9996) and ibuprofen (R^2=0.9991), based on the correlation factor (R^2).

Desorption studies

The results of the desorption studies are shown in Figure 5.19:

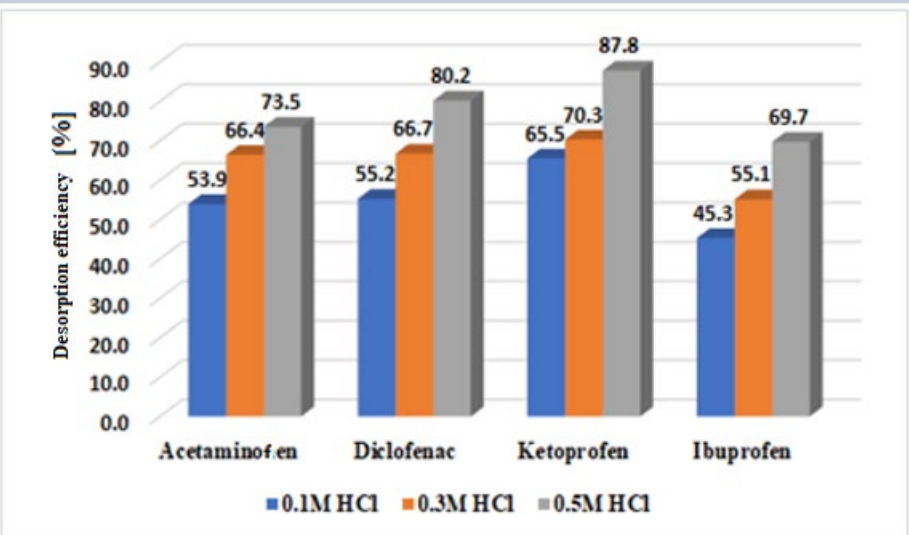

Figure 5.19. Desorption studies.

As can be seen in Figure 5.19, ketoprofen residues (87.8%) are very well desorbed in the presence of 0.5M HCl solution, followed by diclofenac (80.2%), paracetamol (73.5%) and

ibuprofen (69.7%) residues. All experiments were performed using 1g of adsorbent material and 1mg/L synthetic pollutant solutions. The desorption time was 90 minutes for all pollutants tested in this study. All experiments showed that the adsorbent material used in this study can be reused in other adsorption studies. Our activated carbon material is inexpensive and environmentally friendly.

This study aims to highlight the use of the TOC technique for wastewater at very low concentrations of organic pollutants, as well as the use of activated carbon as an adsorbent material for drug residues.

Anti-inflammatories such as paracetamol (acetaminophen), diclofenac, ketoprofen and ibuprofen end up in the city sewer and break down under certain environmental conditions. Residues of medicines or their by-products formed in waste water must be monitored in accordance with the legislation in force.

From the experiments presented in this chapter, it was found that the removal efficiency of drug residues from synthetic wastewater was maximum. In the case of synthetic wastewater with pH 6, using a quantity of 1g of adsorbent material, the required treatment time was 120minutes for initial drug residue concentrations of 1mg/L. Two mathematical models were used to describe the adsorption processes. Based on the correlation factor (R^2), it can be concluded that the Langmuir model fits well the data for diclofenac and ketoprofen and the Freundlich model fits well the data for paracetamol and ibuprofen.

Since organic pollutants in synthetic wastewater are relatively fixed, the accuracy of sample detection is assured with the TOC technique.

The results obtained in this study also indicate the feasibility of using activated carbon as an adsorbent material for the removal of drug residues from wastewater.

3.5. Photocatalysis-based ecotechnology for removing drugs from wastewater

Photocatalysis, which is based on semiconductors such as TiO_2 or light-activated ZnO, is a powerful technique for initiating chemical reactions [14]. However, the widespread use of TiO_2 has raised cost concerns, leading to a growing interest in alternative photocatalysts. ZnO has emerged as a promising alternative due to its similar attributes, versatility and photodegradation mechanism, which in some cases provides superior photocatalytic performance [15].

Photodegradation experiments: The photocatalytic experiment was conducted in the presence of two different doses of ZnO used as photocatalyst and acetaminophen (AMP) under UV irradiation. The pollutant solutions are obtained by diluting the AMP stock solutions.
Pollutant analysis: Pollutant residues in synthetic wastewater were effectively evaluated using the total organic carbon analysis technique (TOC).

The TOC method has specific performance parameters: a detection limit of 0.1 mg/l, a quantification limit of 0.3 mg/l and an expanded analytical method uncertainty of 12%. The experimental equipment used in these investigations is called Shimadzu Analyzer TOC TN LCPN.

The removal efficiency (RE) can be determined using the following equation:

$$RE\% = \left(\frac{C_i - C_t}{C_i}\right) x\ 100 \quad (9)$$

where C_t and C_i are the MPA concentration at time t and at baseline.

Photodegradation tests

In a typical experiment, different doses of ZnO nanoparticles were placed in contact with two 150 ml containers of 10 mg/L AMP solutions. In the experiment, the surfactant solution was homogenized using a magnetic stirrer and the UV lamp was placed on its side. The experiments were performed at room temperature. To determine the concentration of AMP removed, samples were taken at 15-minute intervals at the beginning of the experiment and at longer intervals at the end. Samples taken were kept at 4°C until analysis.

Photodegradation efficiency was determined using TOC analysis, an invaluable method for measuring organic constituents in wastewater, especially when low concentrations involve placing a known amount of sample in a high-temperature oven or chemical oxidation environment. In this controlled environment, the organic carbon undergoes oxidation to carbon dioxide, catalysed by a catalyst.

The resulting carbon dioxide is meticulously quantified using an infrared analyser. By preparing the sample through acidification and aeration prior to analysis, any potential errors resulting from the presence of inorganic carbon are effectively mitigated. This method boasts a fast turnaround and is steadily gaining popularity.

Figures 5.20. and 5.21 show the photodegradation efficiency for AMP when using 0.1 g ZnOg and 0.2 g.

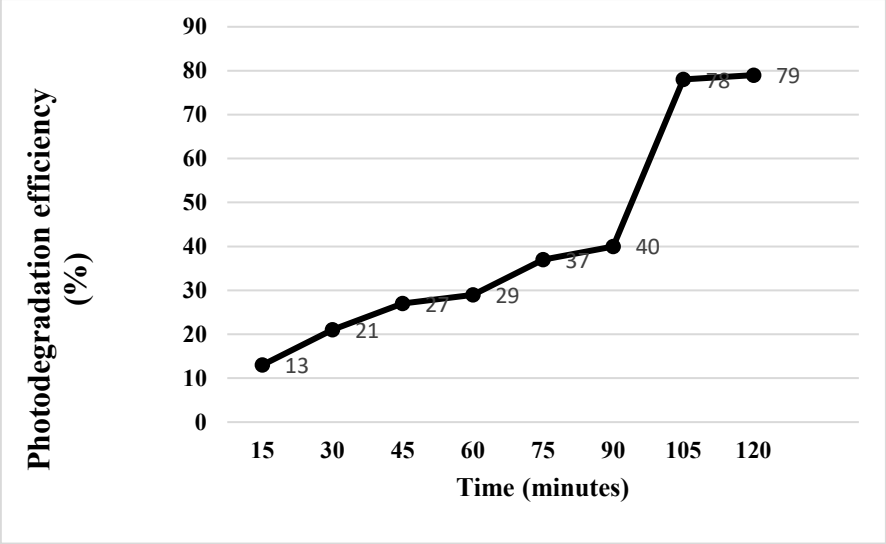

Figure 5.20. Time-dependent removal efficiency for paracetamol contained in wastewater for 0.1 g ZnO

It was observed that photodegradation in the first 90 minutes increased at a slower rate for both ZnO doses, reaching only 40% during this time for the 0.1 g photocatalyst and 53% for the 0.2 g, respectively.

After this time, the efficiency increased rapidly and stabilized at 79% and 88% after 120 minutes of contact time.

When a higher dose of ZnOg is used, the photodegradation efficiency for AMP is higher due to the increase in the number of active sites on the photocatalyst surface as a result of increasing the dose of ZnO.

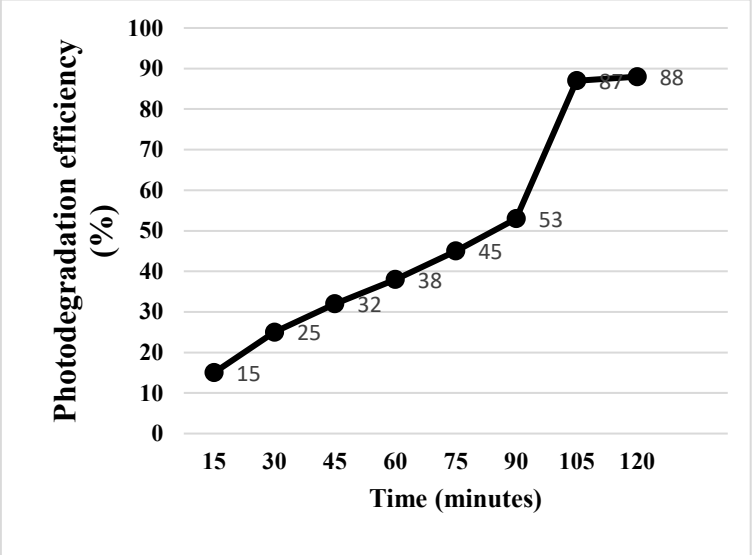

Figure 5.21. Photodegradation efficiency as a function of time for acetaminophen contained in wastewater for 0.2 g ZnO

By increasing the dose, the number of free radicals (-OH and O22-) in the solution is also increased, leading to increased photodegradation of the wastewater sample [22].

ZnO photocatalyst prepared by green synthesis precipitation method using grapefruit extract was tested for the purpose of removing acetaminophen from waste water. Structural and morphological analyses suggested that the material is in the form of a fine powder with aggregates ranging in size from 50-150 nm. XRD analysis confirmed the presence of characteristic ZnO peaks, suggesting that the preparation of ZnOg was successful.

The ZnO photocatalyst had the highest degradation efficiency of 88% after 120 min of contact with 200 mg of material, for a solution with a concentration of 10 mg/L acetaminophen.

3.6. Algae-based ecotechnology used to remove lead ions from wastewater

Various techniques have been investigated and applied for the removal of metal ions from wastewater, such as coagulation/flocculation, ion exchange, photocatalysis, flotation, electro-remediation, solvent extraction, biological sludge, and others [306, 307]. Each of these methods has both advantages and disadvantages [308]. However, absorption is largely preferred by researchers because of its high efficiency in removing pollutants, ease of use and relatively low energy consumption [309]. The use of biomass sources as absorbent materials in water treatment processes contributes to promoting circular economy concepts and supporting environmental sustainability [310 - 312]. Studies on algae used in water purification have shown that they are significantly effective in removing heavy metal ions [313]. The main benefits of using biomass in the removal of metal ions from wastewater include high metal sorption capacity, favourable economics, and wide availability in the natural environment [314, 315].

In recent years, special attention has been paid to the use of biotechnology to remove heavy metal ions from wastewater. Biosorption is an alternative based on the use of certain natural materials of biological origin, including fungi, bacteria, algae, yeasts, etc.

Biosorbent materials have shown remarkable abilities to remove metal ions, being effective even when concentrations of these ions in wastewater are extremely low. Their efficiency is particularly high, making them suitable for the treatment of large quantities of water containing low concentrations of metal ions [318].

There is a lot of research focusing on the use of biosorbent materials to remove organics and metal ions from wastewater. These biosorbents can fall into various categories such as fungi (e.g. *Rhizopus arrhizus*), bacteria (e.g. *Bacillus subtillis*), algae (such as *Sargassum*

fusiforme and *Enteromorpha prolifera*), yeasts (e.g., *Saccharomyces cerevisiae*), agricultural wastes (such as *maize stalks*), industrial wastes (such as *Saccharomyces cerevisiae* waste biomass from the food industry and fermentation processes), and other polysaccharide materials [319].

Algae can be divided into two categories, namely microalgae and unicellular macroalgae. Macroalgae belong to the kingdoms *Plantae* and *Chromista* and are photosynthetic multicellular aquatic organisms [320]. Depending on their pigments, macroalgae are classified into three categories: green algae (*Chlorophyta*), brown algae (Phaeophyceae) and red algae (*Rhodophyta*) [321, 322].

Marine algae comprise about 250 genera and 1 500 species. The second largest species of seaweed are brown algae [323, 324]. *Sargassum fusiforme* belongs to the order *Fucales*, family *Sargassaceae*. It is an edible brown seaweed that can be found in the temperate Pacific Northwest. *Sargassum fusiforme* is distributed along the coasts of Korea, Japan and China. [325, 326]. Această algă conține diverși nutrienți complecși și, prin urmare, a fost utilizată ca medicament terapeutic și aliment esențial de mii de ani [327].

Algae can be divided into two distinct categories: microalgae and unicellular macroalgae. Macroalgae, being photosynthetic multicellular aquatic organisms, are found in the kingdoms Plantae and Chromista [320]. Depending on their pigmentation, macroalgae are grouped into three main categories: green algae (Chlorophyta), brown algae (Phaeophyceae) and red algae (Rhodophyta) [321, 322].

In the world of seaweeds, there are about 250 genera and 1,500 species, and brown algae are the second most numerous category [323, 324]. Sargassum fusiforme, which belongs to the family Sargassaceae and belongs to the order Fucales, is an edible brown seaweed. This species can be found in temperate areas of the Pacific Northwest and has a distribution along the coasts of Korea, Japan and China [325, 326]. Sargassum fusiforme is known for its rich content of complex nutrients and has been used as a therapeutic remedy and essential food source for thousands of years [327].

Enteromorpha, a green alga belonging to the class Chlorophyceae and order Ulvales, is part of a genus containing several species of green algae such as E. prolifera, E. linza, E. intestinalis, E. compressa and E. flexuosa. In the Chinese Yellow Sea, E. prolifera has been shown to be the dominant species. This alga has been used both as a functional food source and as a traditional medicine [330 - 334].

To remove lead ions from wastewater, 1 g of algae was used. The initial concentration of lead ions was 1.86 mg/L. The treatment process was carried out under continuous stirring at room temperature. Samples were taken using the PhotoLab S12.

Treatment efficiencies were calculated using the formula:

$$\eta = \frac{C_i - C_f}{C_i} * 100 \quad (10)$$

where:

η – treatment efficiency, %;

C_i- initial lead ion concentration, mg/L;

C_f - final lead ion concentration, mg/L.

Tables 5.5. and 5.6. present the working conditions and the results of experimental research on the ecotechnology of lead ion removal from wastewater using the algae *Sargassum fusiforme* and *Enteromorpha prolifera* in native, coarse and wetted form. Samples were taken at 8, 16, 24, 32 and 40 hours of contact. The results have been published in the literature.

Using the results in Tables 5.5. and 5.6., the following graphs were produced. The results have been presented graphically in Figures 5.30. and 5.32. representing the variation of lead ion concentrations over time and in Figures 5.31. and 5.33. representing the variation of purification yields over time.

Figure 5.30. shows the gradual decrease of lead ion concentrations in wastewater from the initial concentration of 1.84 mg/L to the final concentrations of 0.02; 0.01 and 0.06 over 600 minutes of contact time when using Sargassum fusiforme algae in native, coarse and wetted form, respectively.

Table 5.5. Lead ion concentrations and purification yields testing *Sargassum fusiforme* algae.

Algae type	Time [min]	C_i [mg/L]	C_f [mg/L]	Yield [%]
***Sargassum fusiforme* – native form**	0	1,86	1,86	0,00
	120		1,52	18,28
	240		0,87	53,23
	360		0,20	89,25
	480		0,04	97,85
	600		0,02	98,92
***Sargassum fusiforme* – rough form**	0	1,86	1,86	0,00
	120		1,38	25,81
	240		0,83	55,38
	360		0,04	97,85
	480		0,03	98,39
	600		0,01	99,46
***Sargassum fusiforme* - wet form**	0	1,86	1,86	0,00
	120		1,69	9,14
	240		1,20	35,48
	360		0,45	75,81
	480		0,25	86,56
	600		0,06	96,77

Table 5.6. Lead ion concentrations and purification yields testing the algae *Enteromorpha prolifera.*

Algae type	Time [min]	C_i [mg/L]	C_f [mg/L]	Yield [%]
***Enteromorpha prolifera* – native form**	0	1,86	1,86	0,00
	120		1,54	17,20
	240		1,06	43,01
	360		0,60	67,74
	480		0,25	86,56
	600		0,00	100,00
***Enteromorpha prolifera* – rough form**	0	1,86	1,86	0,00
	120		1,61	13,44
	240		1,44	22,58
	360		1,21	34,95
	480		0,92	50,54
	600		0,00	100,00
***Enteromorpha prolifera* - wet form**	0	1,86	1,86	0,00
	120		1,68	9,68
	240		1,01	45,70
	360		0,78	58,06
	480		0,34	81,72
	600		0,04	97,85

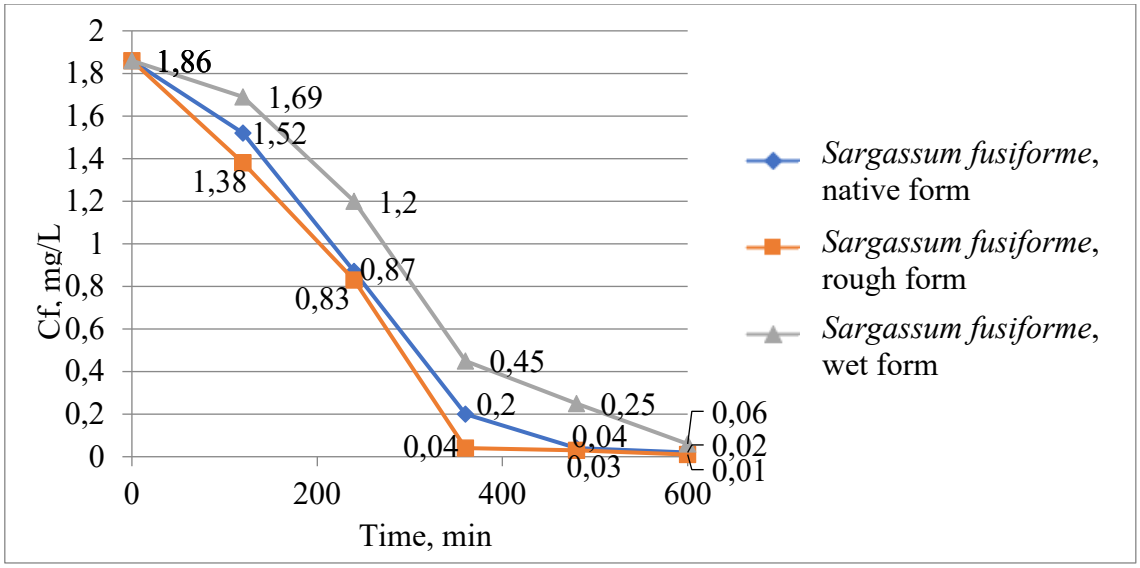

Figure 5.30. Variation of Pb(II) ions in wastewater over time in a treatment system containing Sargassum fusiforme for C_i =1.86 mg/L.

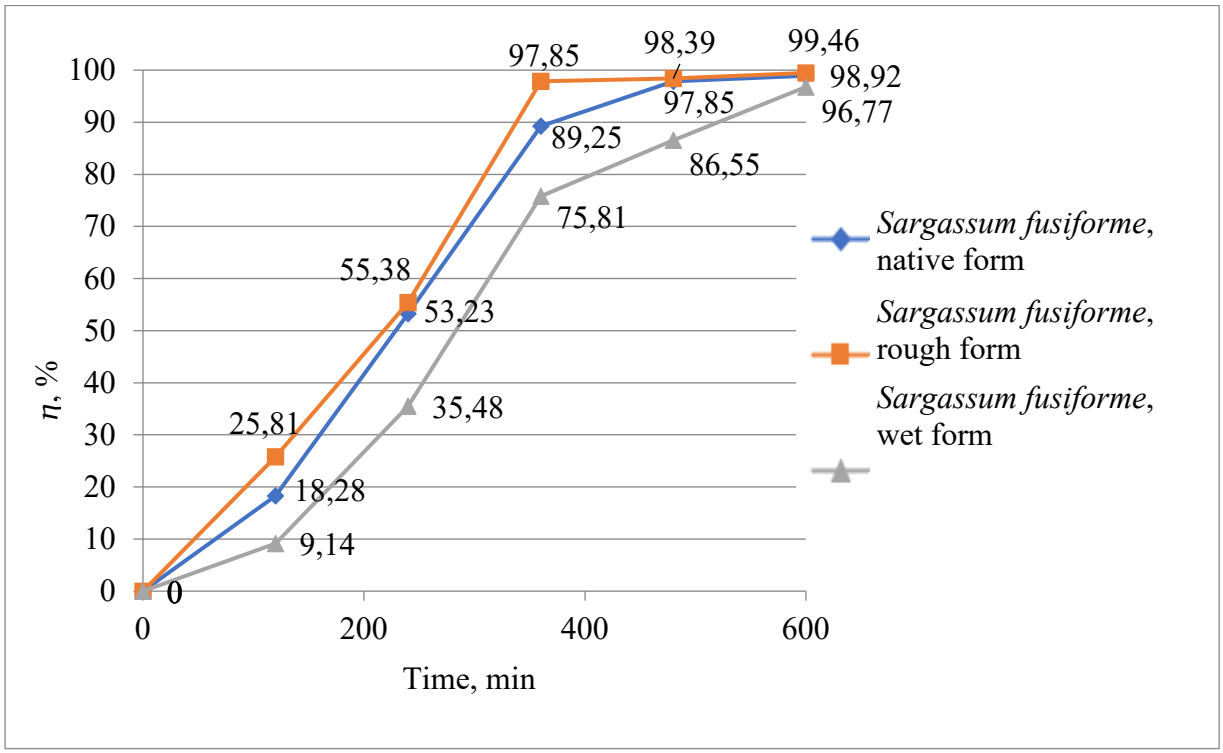

Figure 5.31. Variation of treatment yield over time for wastewater containing Pb(II) ions, C_i = 1.86 mg/L.

The increase in treatment yield by the phytoremediation process for the removal of lead ions from wastewater is shown in Figure 5.31. At the end of the process, the treatment yield closest to the maximum yield (i.e. 99.46%) was obtained using coarse-form Sargassum

fusiform algae. However, in all three cases, the purification yields were similar, i.e. 99.46, 98.92 and 96.77 % using Sargassum fusiform algae in coarse, native and wetted form, respectively.

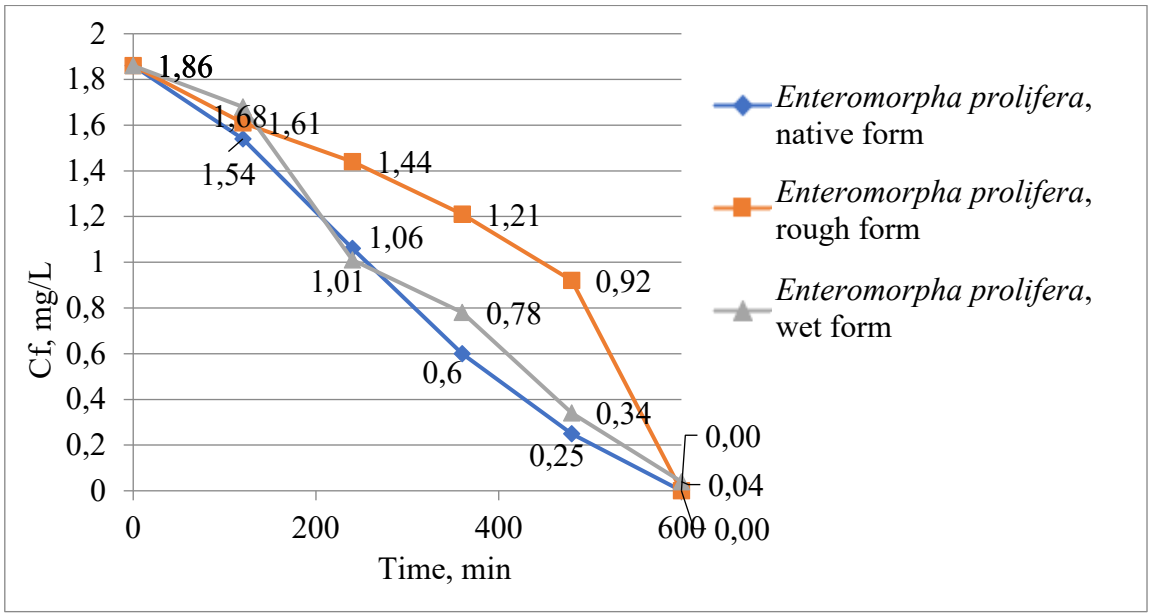

Figure 5.32. Variation of Pb(II) ions in wastewater over time in a treatment system containing *Enteromorpha prolifera* for C_i =1.86 mg/L.

Lead ion concentrations gradually decreased until lead ions were completely removed from wastewater when *Enteromorpha proliferfera* was used in its native, coarse form. The final concentration of lead ions in wastewater when using *Enteromorpha prolifera* algae in its coarse form was 0.04 mg/L (Fig. 5.32).

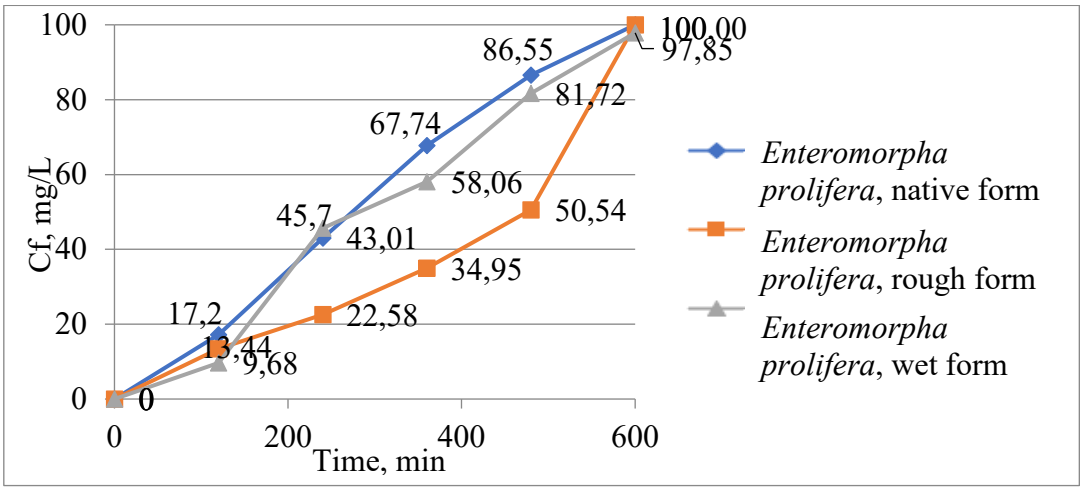

Figure 5.33. Variation of purification efficiency over time for wastewater containing Pb(II) ions , C_i = 1,86 mg/L.

Maximum purification yields were obtained using *Enteromorpha prolifera* algae in native and coarse form in a time of 600 minutes (Figure 5.33.).

The comparison of the percentage of purification obtained using the two types of algae presented above, in the three forms studied, for the removal of lead ions from wastewater is shown in Figure 5.34.

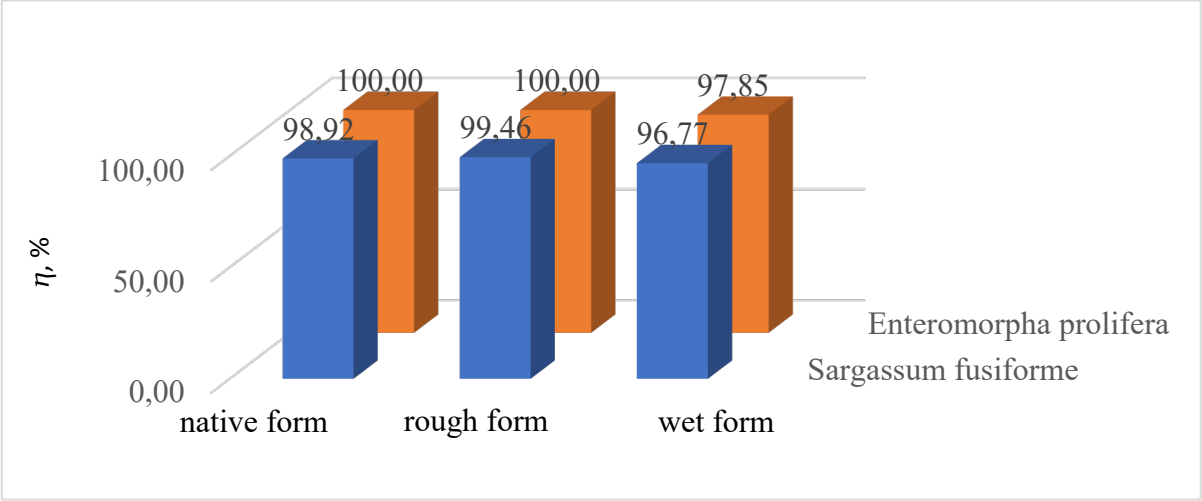

Figure 5.34. Comparison of lead ion water treatment yields testing the algae *Sargassum fusiforme* and *Enteromorpha prolifera.*

In the case of removal of lead ions from wastewater, comparing the results, the treatment yield was in all three cases higher when using *Enteromorpha prolifera* algae than when using *Sargassum fusiforme* algae.

CHAPTER. 6. FINAL CONCLUSIONS. ORIGINAL CONTRIBUTIONS. PERSPECTIVES

6.1. Final conclusions

The conclusions obtained as a result of the study of photocatalysis-based ecotechnology applied for the removal of detergents from wastewater using TiO_2 are as follows:

- The purification yield increased with decreasing number of carbon atoms in the long chain of compounds in the order C16-BAC, C-14-BAC, C12-BAC.
- For wastewater having an initial concentration of 5 mg/L for all three cationic surfactants, the photodegradation process for 12 hours resulted in the removal of 98% of C12-BAC, 97.2% of C14-BAC and 96.8% of C16-BAC.
- For wastewater with a surfactant concentration of 10 mg/L, the treatment efficiency was found to be 48.5% for C12-BAC, 43.5% for C14-BAC and 40.3% for C16-BAC.
- To improve the purification efficiency of the three cationic surfactants, a biological step was applied after the photocatalysis process. In the biological step, bacteria (*E. coli* in peptone water) were added per litre of wastewater. The use of pure *E. coli* strains was justified by the presence of this bacterial strain in the active sludge used in the surfactant biodegradation process. The efficiency of surfactant purification in the presence of active sludge containing a significant amount of *E. coli* bacteria showed a specificity of this strain in the biodegradation process. After 12 hours of biodegradation in the presence of *E. coli* bacteria for all three cationic surfactants, the purification efficiency increased significantly, reaching 98.1% for C12-BAC, 97.9% for C14-BAC and 97.3% for C16-BAC.

The conclusions obtained as a result of the study of activated carbon-based ecotechnology applied for the removal of detergents from wastewater are as follows:

- The correlation coefficients (R^2) and isotherm parameter values used show that all adsorption data for the activated carbon adsorbent material fit the Freundlich model better. These results support that the adsorption of C12-BAC on the activated carbon ecomaterial in wastewater occurs on heterogeneous sites.
- C12-BAC adsorption increases with increasing wastewater pH, and the maximum C12-BAC adsorption was obtained at pH 10.

- The adsorbent eco-material activated carbon had the highest adsorption capacity of 526 mg/g and the removal efficiency was 99.2% for 250 mg of adsorbent material for wastewater with a concentration of 50 mg C12-BAC/L and pH =10.

The conclusions obtained as a result of the study of adsorption-based ecotechnology applied for the removal of drugs from wastewater using activated carbon are as follows:

- Experiments found that the removal efficiency of drug residues from synthetic wastewater was maximum.

- In the case of pH 6 synthetic wastewater, using 1g of adsorbent material, the required treatment time was 120minutes for initial drug concentrations of 1mg/L.

- Two mathematical models were used to describe the adsorption processes. Based on the correlation factor (R^2), it can be concluded that the Langmuir model fits well the data for diclofenac and ketoprofen and the Freundlich model fits well the data for paracetamol and ibuprofen.

- Since organic pollutants in synthetic wastewater are relatively fixed, the accuracy of sample detection was ensured, with the TOC technique.

- Desorption studies of drugs retained on activated charcoal showed that ketoprofen residues (87.8%) were very well desorbed in the presence of 0.5M HCl solution, followed by diclofenac (80.2%), paracetamol (73.5%) and ibuprofen (69.7%) residues. All experiments were performed using 1g of adsorbent material and synthetic pollutant solutions of 1mg/L. Desorption time was 90 minutes for all pollutants tested in this study. All experiments showed that the adsorbent material used in this study can be reused in other adsorption studies. Activated carbon material is cheap and environmentally friendly

- The results obtained in this study also indicate the feasibility of using activated carbon as an adsorbent material for the removal of drug residues from wastewater.

The experimental research carried out in order to obtain a photocatalysis-based ecotechnology for the removal of drugs from wastewater concluded as follows:

- ZnO photocatalyst prepared by green synthesis precipitation method using grapefruit extract was tested for the purpose of removing acetaminophen from wastewater. The ZnO_2 photocatalyst had the highest degradation efficiency of 88% after 120 minutes of contact with 200 mg of material, for a solution with a concentration of 10 mg/L acetaminophen.

- Algae-based ecotechnology applied to remove lead ions from wastewater led to the following conclusions:

- At the end of the process, the highest treatment yield (i.e. 99.46%) was obtained using coarse-grained *Sargassum fusiform* algae. However, in all three cases (native, coarse, wet form), the purification yield was high, i.e. 99.46, 98.92 and 96.77 %.
- Maximum purification yields were obtained using *Enteromorpha prolifera* algae in native and coarse form in a time of 600 min (Figure 5.33.).
- Comparing the purification yields obtained for the removal of lead ions from wastewater using the two types of algae *Sargassum fusiforme* and *Enteromorpha prolifera* presented in the three forms studied, the values were higher when using *Enteromorpha prolifera* algae than when using *Sargassum fusiforme* algae.

The realization of the Photocatalysis-based Wastewater Organic Pollutants Removal Plant demonstrated the possibility of applying photocatalysis-based ecotechnology for the removal of detergents from wastewater on a larger scale for 12 L volumes.

6.2.Original contributions

- Original contributions, consolidated through research carried out during the doctoral program, include:
- The realization of an eco-technology that phases the use of the semiconducting nanomaterial TiO_2 with photocatalytic role through which the degradation of emerging organic pollutants such as detergents (dodecyl benzyldimethyl ammonium chloride (C12-BAC), $C_{21}H_{38}ClN$, dimethyl tetradecyl ammonium chloride (C14-BAC), $C_{23}H_{42}ClN$ and dimethyl hexadecyl ammonium chloride (C16-BAC), $C_{25}H_{46}ClN$ from water to CO_2 and H_2O is achieved;
- development of an eco-technology using the photocatalytic semiconductor nanomaterial ZnO to degrade emerging organic pollutants such as drugs (paracetamol) from wastewater to CO_2 and H_2O;
- development of an eco-technology based on the use of the environmentally friendly material activated charcoal for the removal of drugs (paracetamol, diclofenac, ketoprofen and ibuprofen) from waste water;
- development of an eco-technology based on the use of ecological activated carbon material for the removal of the detergent dodecyl benzyldimethyl ammonium chloride (C12-BAC), $C_{21}H_{38}ClN$ from waste water;
- development of an algae-based eco-technology for the removal of lead ions from wastewater, investigating the algae Sargassum fusiforme and Enteromorpha prolifera;

- development of a purification plant that removes organic pollutants such as detergents from wastewater by photocatalysis using nanomaterials TiO_2.

6.3.Perspectives

This PhD work represents a contribution to the advancement of research in the field of theory development and optimization of water treatment solutions using econanotechnologies.

To extend this research, the next step may be to test the durability of the materials used in ecotechnologies, including the number of operating cycles and the efficiency of the treatment process after regeneration.

The materials analysed in this PhD thesis can be studied in the context of removing other types of pollutants from wastewater.

LIST OF PUBLICATIONS

1. Cristina Ileana Covaliu-Mierlă, Ecaterina Matei, Oana Stoian, Leon Covaliu, Alexandra-Corina Constandache, Horia Iovu and Gigel Paraschiv, TiO_2–Based Nanofibrous Membranes for Environmental Protection, *Membranes* **12** (2022) 236, ***F.I. = 4,2***;

2. Leon Dumitru COVALIU, Oana STOIAN (PĂUNESCU), Ecaterina MATEI, Cristina Ileana COVALIU-MIERLĂ, Iulia Andreea GRIGORE, REDUCING THE TOXICITY OF WASTEWATER BY APPLYING THE PHOTOCATALYSIS PROCESS. A REVIEW, INTERNATIONAL SYMPOSIUM ISB-INMA TEH, VOL. 4, 2022, pp. 748-753.
3. Alexandra Corina CONSTANDACHE, Lidia FAVIER, Leon COVALIU, Anca Andreea ȘĂULEAN, Andra Mihaela PREDESCU, Cristian PREDESCU, Ecaterina MATEI, MORPHOLOGICAL AND STRUCTURAL INVESTIGATIONS OF ZnO RESULTED FROM GREEN SYNTHESIS, U.P.B. Sci. Bull., Series B, Vol. 85, Iss. 2, 2023, ***F.I.=0.5***;

4. Loredana Ioana Diaconu, Cristina Ileana Covaliu-Mierla, Oana Paunescu, Leon Dumitru Covaliu, Horia Iovu, Gigel Paraschiv, Phytoremediation of Wastewater Containing Lead and Manganese Ions Using Algae, *Biology* **12 (6),** (2023) 773. ***F.I. = 4,2***;

5. Leon COVALIU, Florinela PIRVU, Cristina Ileana COVALIU-MIERLĂ1, REMOVAL FROM WASTEWATER OF PHARMACEUTICAL RESIDUES BELONGING NON-STEROIDAL ANTI-INFLAMMATORY DRUGS CLASSES USING ACTIVATED CARBON MATERIAL, Buletin UPB, acceptat spre publicare, ***F.I.=0.5*** (ANEXA 1)

COVALIU

6. L. D. COVALIU, Iuliana PAUN, Vasile Ion IANCU, Ecaterina MATEI, Razvan TEODORESCU, Valerica TUDOR, Gigel PARASCHIV, Cristina Ileana COVALIU-MIERLA, ECOLOGICAL TREATMENT OF WATEWATER CONTAINING A CATIONIC SURFACTANT POLLUTANT, Scientific Papers. Series E. Land Reclamation, Earth Observation&Surveying, Environmental Engineering, acceptat spre publicare, **F.I.=0.4** (Anexa 2)

7. Alexandra Corina COSTANDACHE, Leon Dumitru COVALIU, Anca Andreea ȘĂULEAN, Cristina Ileana COVALIU-MIERLA, Ecaterina MATEI, Valerica TUDOR, Razvan TEODORESCU, Green-synthesized ZnO NPs as sustainable photocatalysts for the degradation of acetaminophen, Scientific Papers. Series E. Land Reclamation, Earth Observation&Surveying, Environmental Engineering, acceptat spre publicare, **F.I.=0.4** (Anexa 3)

PARTICIPATION IN INTERNATIONAL CONFERENCES

1) Autori: Oana Stoian (Păunescu), Leon Dumitru Covaliu, Cristina Ileana Covaliu-Mierlă;

Titlul lucrării: Reducing the toxicity of wastewater by applying the photocatalysis process. A review;

Titlul conferinței: ISB INMA-TEH 2022 International Symposium, Bucuresti

Perioada: 06-07 octombrie 2022.

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