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

APPLICATION OF NANOTECHNOLOGY IN INDUSTRIAL WASTEWATER TREATMENT

PhD coordinator: PhD student:

Prof. habil. dr. ing. Cristina-Ileana Covaliu-Mierlă   Oana Stoian (Păunescu)

Bucharest, 2023

CONTENT

PhD student: *Scientific coordinator:*
Oana Stoian (Păunescu) *Prof. habil. dr. ing. Cristina-Ileana Covaliu-Mierlă*

PhD student: *Scientific coordinator:*

Oana Stoian (Păunescu)   *Prof. habil. dr. ing. Cristina-Ileana Covaliu-Mierlă*

using TiO₂-based composite materials

PhD student: *Scientific coordinator:*

Oana Stoian (Păunescu)   *Prof. habil. dr. ing. Cristina-Ileana Covaliu-Mierlă*

FOREWORD

The PhD thesis entitled "***Application of nanotechnology in industrial wastewater treatment***" aims to remove pollutants from wastewater using nanomaterials through adsorption and photocatalysis processes.

The PhD thesis is structured in five chapters, developed in 267 pages, contains 126 figures and graphics, 45 tables, as well as a bibliography of 377 references.

The PhD thesis presents a synthesis of the theoretical and experimental research carried out by the author on the application of nanotechnology in the field of industrial wastewater treatment.

Chapter I of the PhD thesis entitled "Importance of the topic. Objectives of the PhD thesis" highlights the importance of the topic chosen to develop it in the PhD thesis and the objectives proposed and achieved with regard to the experimental research during the PhD internship.

Chapter II of the PhD thesis entitled "Literature review on the application of nanotechnology in industrial wastewater treatment" comprises 3 subchapters and highlights the current state of research in wastewater treatment domain. It is based on a comprehensive literature review of methods for the removal of heavy metal ions from wastewater and the application of nanotechnology in wastewater treatment. The first subchapter entitled "Industrial wastewater" presents heavy metals contained in industrial waters, the sources of pollution and how they affect the human body. The second subchapter entitled "Conventional techniques for industrial wastewater treatment" includes the conventional treatment techniques used by researchers for wastewater treatment. The techniques presented in this subchapter are: chemical precipitation, ion exchange, adsorption, membrane filtration, coagulation and flocculation, flotation and electrochemical treatment. These are presented in detail showing the results of the studies carried out so far and highlighting the treatment yields obtained. Subchapter 2.3. entitled "Unconventional techniques for industrial wastewater treatment" provides information on nanotechnology and photocatalysis as unconventional techniques applied to remove pollutants from wastewater. Also presented in these sub-chapters are the results of studies carried out to date identifying adsorption capacities. The chapter concludes with the conclusion part which presents the disadvantages of applying conventional techniques for water treatment and the advantages of replacing them with unconventional techniques.

Chapter III of the PhD thesis entitled "Experimental research methodology" presents how the research was carried out in the environmental quality analysis laboratory of the Faculty of Biotechnical Systems Engineering, Polytechnic University of Bucharest.

Chapter IV "Experimental Research" presents the results of experimental research on the removal of copper, lead and manganese ions from wastewater using different adsorbent nanomaterials, namely magnetite, a composite nanomaterial (Fe3O4-PVP) and composite materials based on haloisite nanotubes, as well as the removal of methylene blue using titanium dioxide-based materials by photocatalysis.

Chapter V entitled "Original contributions. Final conclusions. Perspectives." presents the general conclusions that emerge from the experimental research in the PhD thesis on the application of nanotechnology in the field of industrial water treatment. It also highlights the original aspects of the experimental studies carried out in the PhD thesis that can be addressed by researchers in the field in the future.

At the end of the thesis, publications, presentations at international conferences and literature consulted are presented.

The experimental data obtained in the PhD thesis made it possible to publish 11 articles in national and international journals, 6 of them are published in journals with an

PhD student: *Scientific coordinator:*
Oana Stoian (Păunescu)   *Prof. habil. dr. ing. Cristina-Ileana Covaliu-Mierlă*

impact factor between 0.5 and 4.2, and 7 of them appear in the ISI Web of Knowledge database.

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

1.1. Importance of the topic

The environmental pollution endangering human health requires new and efficient wastewater treatment techniques.

It is known that the most important pollutants are present in industrial wastewater, which is currently treated by techniques that have several disadvantages: low treatment yields; high cost; consumption of chemical reagents; toxic waste formed at the end of treatment.

For these reasons, for the study it was chosen to discover and develop new wastewater treatment techniques based on the latest research in nanotechnology. The arguments supporting the importance of the PhD topic are the advantages offered by the use of nanomaterials in the treatment processes such as: high specific surface area; high treatment efficiency; ability to remove low concentrations of pollutants from wastewater; possibility of regeneration, recovery and reuse of nanomaterials used for treatment; low price; lack of toxicity; use of small quantities of nanomaterials to obtain high treatment efficiencies (economic efficiency).

The importance of studying the application of nanotechnology for the removal of heavy metals from wastewater is due to the highly toxic effects that they produce to humans when they enter the body, such as: cancer, lung disease, kidney and liver damage, internal bleeding, neurological disorders, sterility, abortion, nausea, skin irritations.

The application of nanotechnology for the removal of dyes from wastewater by the photocatalysis process in this PhD thesis is justified due to the prevention of their negative impact on the environment and due to the advantages compared to conventional techniques (green, economical, and efficient technology).

1.2. Objectives of the PhD thesis

The objective of this thesis is to use nanomaterials to remove heavy metal ions and methylene blue dye from wastewater by adsorption and photocatalysis processes. The materials used in the experimental research presented in this PhD thesis have properties such as: easy to use, simple extraction from the system and possibility of regeneration and reuse, high specific surface area or resistance to heat treatment. In the experimental research, the removal of copper, lead and manganese ions and methylene blue from wastewater was demonstrated using different nanomaterials and composite materials (Fe_3O_4, Fe_3O_4-PVP, HNTs:PANI, PRGO HNTs $CoCl_2$, HNTs-Prussian Blue, HNTs:$CoFe_2O_4$, HNTs:CaNaAlg, TiO_2/AgPd Ca(Na)Alg gel spheres and microgel).

The PhD thesis is based on a comprehensive literature review of methods for the removal of heavy metal ions (chromium, cobalt, selenium, cadmium, lead, zinc, copper, nickel, mercury, aluminium, arsenic, manganese) from wastewater and the application of nanotechnology in the field of wastewater treatment.

The topic of this PhD thesis contributes on the scientific side by:
- Wastewater treatment aiming the pollutants removal by adsorption and photocatalysis processes;
- Testing nanomaterials and new composite materials;
- Possibility to apply experimental research on an industrial scale.

PhD student: *Scientific coordinator:*
Oana Stoian (Păunescu)   *Prof. habil. dr. ing. Cristina-Ileana Covaliu-Mierlă*

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

2.1. Industrial wastewater

Water is the essential substance for life on earth and is a precious resource for human civilisation. Access to clean water is considered one of the most basic humanitarian goals and remains a major global challenge for the 21st century [1].

2.1.1. Sources of water pollution

Water pollution affects both the environment and human health. There are various commercial and non-commercial ways to combat this problem, which is advancing every day due to technological progress [2, 3].

Sources of heavy metal pollution

The main sources of heavy metal wastewater pollution, also shown in Figure 2.1., include: mining waste; tailings from landfills; municipal wastewater; urban wastewater; industrial wastewater, especially from the galvanic, electronics and metal finishing industries.
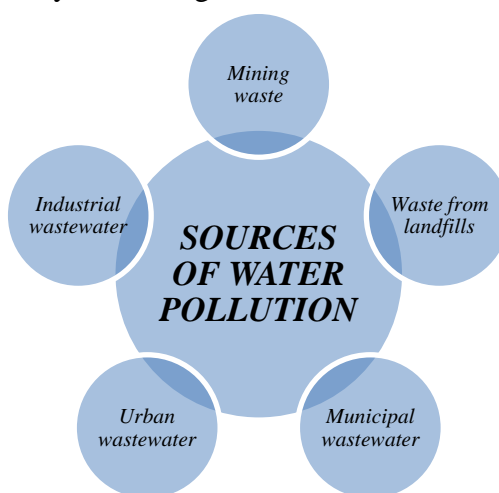
Figure 2.1. Scheme of the main sources of water pollution [4].

With the increasing generation of metals from technological activities, the issue of their removal from wastewater has become of paramount importance. Aquatic environments are experiencing concentrations of metals that exceed water quality criteria designed to protect the environment, animals and humans [3].

Figure 2.2. shows examples of sources of wastewater pollution with lead ions through the dumping of waste from different industries into water.

PhD student:
Oana Stoian (Păunescu)

Scientific coordinator:
Prof. habil. dr. ing. Cristina-Ileana Covaliu-Mierlă

Figure 2.2. Sources of wastewater pollution with Pb^{2+} ions (a) battery processing, (b) oil industry, (c) paint industry, (d) automotive industry, (e) aircraft industry, (f) explosives manufacturing, (g) steel industry [5].

Sources of wastewater pollution with copper ions can be represented by the following industries, also shown in Figure 2.3: mining industry, textile industry, metallurgical industry, steel industry, paint industry.

Figure 2.3. Sources of wastewater pollution with Cu^{2+} ions (a) mining industry, (b) textile industry, (c) metallurgical industry, (d) steel industry, (e) paint industry [5].

Sources of manganese pollution are represented by: mining, alloy production, commodity processing, iron-manganese operations, welding, agrochemical production, other anthropogenic activities [4]. Figure 2.4. shows pictures illustrating wastewater polluted with heavy metal ions.
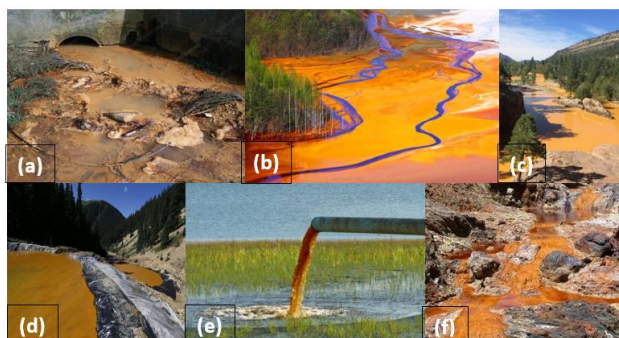
Figure 2.4. Wastewater polluted with heavy metals: (a) Thame River in Walsall, England, polluted with nickel, zinc and copper ions; (b) water pollution with copper ions; (c) and (d) Animas River in the USA, polluted with lead, cadmium, mercury and arsenic; (e) heavy metal pollution from various industries; (f) Rio Tinto in Spain polluted with copper ions [5].

Following accidental consumption of water containing heavy metals, human health is severely affected, and the effects can be seen in Figure 2.5. as follows: (1) the appearance of

non-healing skin wounds from arsenic poisoning; (2) villagers' bodies are slowly mutating and deforming as a result of lead pollution diseases in China; (3) and (4) skin and lung damage respectively from mercury poisoning; (5) "ITAI - ITAI" bone disease caused by cadmium (Cd) poisoning is characterised by multiple fractures, combined changes of osteoporosis and osteomalacia, kidney damage, emphysema and anaemia. In Japanese it means "ay - ay" and is so named because of the cries of pain emitted by those affected in the Jitzu River area of Japan, where massive cadmium poisoning first manifested itself in rice fields in 1912 in Japan's Toyama prefecture; (6) Wilson's disease whereby, if the copper storage capacity of the liver is exceeded, copper is released into the blood and travels to other organs including the brain, kidneys and, in this case, the eyes.

Figure 2.5. Arsenic (1), lead (2), mercury (3,4), cadmium (5), copper (6), silver (7) poisoning [5].

Sources of dye pollution

Waste dyes from different sources, such as the textile industry, the cellulose industry, the paper industry, the pharmaceutical industry, the tannery industry, are a wide variety of organic pollutants introduced into our natural water resources or wastewater treatment plants. One of the main sources of serious pollution problems worldwide is the textile industry and wastewater from this industry contains dyes, 10-25% of dyes in the textile industry are lost. During the dyeing process, between 2-20% of dyes are discharged directly as aqueous effluents into various components of the environment [13]. The discharge of effluents containing dyes into water is undesirable because of the colouring and because they are highly toxic and carcinogenic, mainly due to the presence of carcinogens such as naphthalene, benzamine and other aromatic compounds. If not removed, these dyes remain in the environment for a long time [14, 15].

In Dhaka, Bangladesh's booming textile industry hub, some 22,000 cubic metres of liquid waste is discharged into the city's main river, the Buriganga (Figure 2.6.). As a result, the groundwater used to grow crops is polluted with chemicals and the produce from the crops becomes infested with toxic additives [19].

PhD student: *Scientific coordinator:*
Oana Stoian (Păunescu)   *Prof. habil. dr. ing. Cristina-Ileana Covaliu-Mierlă*

Figure 2.6. Pollution of the Buriganga River with dyes from the textile industry [19].

2.1.2. Heavy metals, toxic pollutants

Toxic pollutants include heavy metals, petroleum compounds, synthetic surface active agents, etc. Heavy metal pollution of water is a frequent and serious environmental problem because, unlike many organic wastes, they do not degrade into harmless products and are toxic to the human body [20, 21]. Heavy metals, unlike organic pollutants, are not biodegradable and tend to accumulate in living organisms and many heavy metal ions are known to be toxic or carcinogenic [23].

2.1.3. Dyes

Many dyes and pigments are hazardous and toxic to humans and aquatic life at the concentration at which they are discharged into receiving waters. It is known that high concentration of dyes can cause skin and mucous membrane ulceration, dermatitis, perforation of the nasal septum, severe irritation of the respiratory tract, and when ingested can cause vomiting, pain, bleeding and acute diarrhoea [69]. In recent decades, the increasing demand for dyes by the textile industry has shown a high polluting potential. It is estimated that about 10-15% of dyes are lost in wastewater during dyeing processes. There are different types of dyes, namely: azo, anthraquinone, disperse.

2.2. Conventional techniques for industrial wastewater treatment

2.2.1. Chemical precipitation

Chemical precipitation is efficient and by far widely used in industry because it is relatively simple and cheap to operate. In precipitation processes, chemicals react with heavy metal ions to form insoluble precipitates. The precipitates formed can be separated from water by sedimentation or filtration. The treated water is then decanted and discharged or reused appropriately. Conventional chemical precipitation processes include hydroxide precipitation and sulphide precipitation [23].

2.2.2. Ion exchange

Ion exchange processes have been widely used to remove heavy metals from wastewater due to their numerous advantages such as high removal efficiency, high treatment

PhD student: *Scientific coordinator:*
Oana Stoian (Păunescu)   *Prof. habil. dr. ing. Cristina-Ileana Covaliu-Mierlă*

capacity, and fast kinetics [78]. Ion exchange resins have the ability to exchange their cations with metals present in wastewater. Among the materials used in ion exchange processes, synthetic resins are the most preferred because they are effective in removing heavy metals from wastewater [79].

2.2.3. Adsorption

Adsorption is recognised as an efficient and economical method for treating water containing heavy metals. The adsorption process offers flexibility in design and operation and in many cases will produce high quality treated effluent. In addition, because adsorption is sometimes reversible, adsorbents can be regenerated by a suitable desorption process [23].

2.2.4. Membrane filtration

Filtration technologies using various types of membranes are used to remove heavy metals from wastewater due to their high efficiency, space saving and easy operation. Membrane processes used to remove heavy metals from wastewater are ultrafiltration, reverse osmosis, nanofiltration and electrodialysis [23].

2.2.5. Coagulation and flocculation

Coagulation and flocculation followed by sedimentation and filtration are also used to remove heavy metals from wastewater. Coagulation is the destabilisation of colloids by neutralising the forces that separate them. Many coagulants are widely used in conventional wastewater treatment processes, such as aluminium, ferrous sulphate and ferric chloride, resulting in the effective removal of wastewater particles and impurities by neutralising the particle loading and impregnating the impurities onto the precipitates formed by amorphous metal hydroxide [187].

2.2.6. Flotation

Flotation is now widely used in wastewater treatment. Flotation has been used to separate heavy metals from a liquid phase. Dissolved air flotation, ionic flotation and precipitation flotation are the main flotation processes for the removal of metal ions from wastewater [23].

2.2.7. Electrochemical treatment

Electrochemical methods involve coating the cathode surface with metal ions and can recover metals in an elemental metallic state. Electrochemical wastewater technologies involve relatively large capital investments and expensive electricity supplies, so they have not been widely applied. However, with strict environmental regulations on wastewater discharge, electrochemical technologies have regained importance worldwide in the last two decades. [195].

2.3. Unconventional techniques for industrial wastewater treatment

2.3.1. Nanotechnology applied for wastewater treatment by adsorption

Nanotechnology is the manipulation of matter at the molecular and atomic level to create a new structure, device and system with superior electronic, optical, magnetic, conductive and mechanical properties. Nanotechnology is being explored as a promising technology and has demonstrated remarkable achievements in various fields, including wastewater treatment. Nanostructures offer unparalleled opportunities to realize more efficient catalysts and redox active media for wastewater treatment due to their small size, large surface area and ease of functionalization. Nanomaterials have been shown to be effective in removing several pollutants from wastewater, such as heavy metals, organic and inorganic solvents, dyes, as well as biological toxins and pathogens that cause diseases such as cholera and typhus [2].

There are recent advances using various nanomaterials (nanostructured catalytic membranes, nanosorbates, nanocatalysts, bioactive nanoparticles, biomimetic membranes and molecularly imprinted polymers (MIPs)) for the removal of toxic metal ions, microbes, organic and inorganic pollutants from water [2].

2.3.2. Nanotechnology applied for wastewater treatment by photocatalysis

Advanced photochemical oxidation technologies are most preferred because they offer the possibility of using naturally available and renewable solar energy as a light source for photochemical waste remediation, thus making the process green and sustainable.

The mechanism of the heterogeneous photocatalysis process is shown schematically in Figure 2.30.
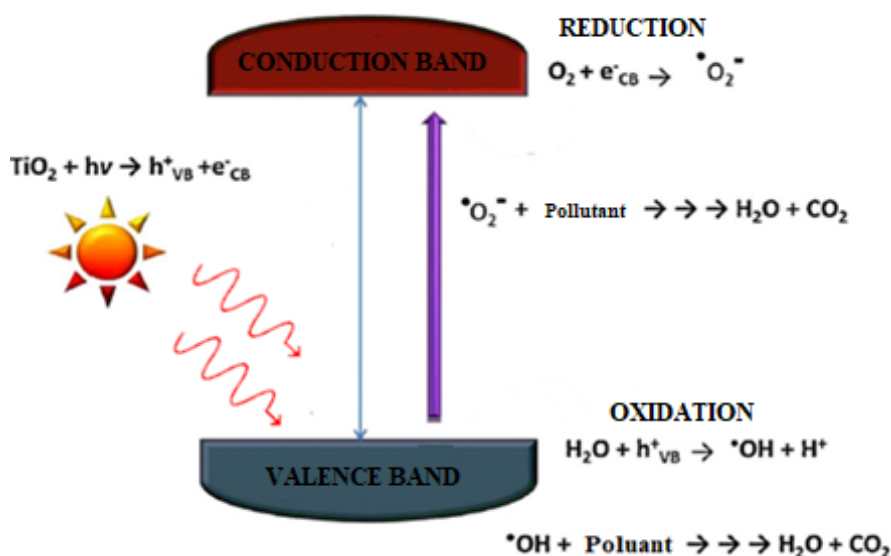

Figure 2.30. Mechanism of the photodegradation process.

The excited electrons that are now in the conduction band (e^-_{CB}) will react with oxygen (O_2), which produces superoxide radicals (O_2-) or hydroperoxide radicals (HO_2). These reactive oxygen species are then used to degrade pollutants into water (H_2O) and carbon dioxide (CO_2). Superoxide radicals can also be used for secondary degradation steps. While this reaction is going on, oxidation of water takes place at the positive hole in the valence band (h^+_{VB}). This reaction generates hydroxyl radicals (OH) and hydrogen ions (H^+). OH reacts with the pollutants present to form H_2O and CO_2 [271].

PhD student: *Scientific coordinator:*
Oana Stoian (Păunescu)   *Prof. habil. dr. ing. Cristina-Ileana Covaliu-Mierlă*

CONCLUSIONS

The removal of heavy metals from wastewater by chemical precipitation is carried out due to its simplicity and low capital cost. However, chemical precipitation is usually suited for treatment of high concentration waters containing heavy metal ions and is ineffective when the metal ion concentration is low. Chemical precipitation is not economical and can produce a large amount of sludge which is treated with great difficulty.

Ion exchange has been widely applied to remove heavy metals from wastewater. However, ion exchange resins must be regenerated with chemical reagents, and regeneration can cause serious secondary pollution. It is a costly process, especially when a large amount of wastewater containing heavy metals in low concentration is depleted, so it cannot be used on a large scale.

Adsorption is a recognised method for the removal of heavy metals from low concentration waters containing heavy metals. The high cost of activated carbon limits its use in the adsorption process. Many varieties of low-cost adsorbents have been developed and tested to remove heavy metal ions. However, adsorption efficiency depends on the type of adsorbent. Bioadsorption of heavy metals from wastewater is a relatively new process that has shown great promise for the removal of heavy metals from wastewater.

Membrane filtration technology can remove heavy metal ions with high efficiency, but its problems such as high cost, process complexity, membrane fouling and low permeate flux have limited its use in heavy metal removal.

Using the coagulation-flocculation technique for the treatment of water polluted with heavy metals, the sludge produced has good sedimentation and dewatering characteristics. This method involves the consumption of chemicals and the increase of sludge volume.

Flotation offers several advantages over other conventional methods, such as high metal selectivity, high removal efficiency, high spillage rate, low detention times, low operating cost and more concentrated sludge production. Disadvantages include high initial capital cost, high maintenance, and operating costs.

Electrochemical techniques for treating heavy metal-polluted water are considered to be fast and well-controlled, requiring fewer chemicals, offering good reduction efficiencies, and producing less sludge. However, electrochemical technologies, which involve high initial capital investment and expensive electricity supply, limit its development.

Although all of the above techniques can be used for the treatment of water containing heavy metals, it is important to note that the choice of the most suitable treatment techniques depends on the initial metal concentration, wastewater component, capital investment and operational cost, as well as reliability and environmental impact.

PhD student: *Scientific coordinator:*
Oana Stoian (Păunescu)   *Prof. habil. dr. ing. Cristina-Ileana Covaliu-Mierlă*

CHAPTER 3. EXPERIMENTAL RESEARCH METHODOLOGY

Experimental research has been developed through:

- application of the oxide nanomaterial magnetite (Fe_3O_4) for the removal of copper, lead, and manganese ions from wastewater by the adsorption process;
- application of composite nanomaterial (Fe_3O_4-PVP) to remove copper ions from wastewater by adsorption process;
- the use of composite adsorbent nanomaterials based on halloysite nanotubes (HNTs:PANI, PRGO HNT $CoCl_2$, HNTs-Prussian Blue, HNTs:$CoFe_2O_4$, HNTs:CaNaAlg) to treat wastewater containing copper and lead ions;
- application of titanium dioxide based composite nanomaterials (TiO_2/AgPd Ca(Na)Alg gel spheres and microgel) for the degradation of methylene blue in wastewater by photocatalysis process.

The scientific literature has provided the background information for the application of nanomaterials in experimental research.

In these experimental investigations, the influence of nanomaterial quantities, the influence of heavy metal ion concentrations, the influence of wastewater pH and treatment time on the removal of pollutants from wastewater were considered.

The methodology, the work plan, as well as the scientific experiments were designed and carried out within the framework of the Doctoral School of Biotechnical Systems Engineering at University POLITEHNICA of Bucharest.

CHAPTER 4. EXPERIMENTAL RESEARCH

4.1. Adsorption of Cu^{2+}, Pb^{2+} and Mn^{2+} ions from wastewater using magnetite (Fe_3O_4)

4.1.1. General considerations

Nanotechnology is being used for environmental remediation because it can provide a potentially cheap and efficient way of treating water [277]. Magnetic nanoadsorbents, such as spinel ferrites, maghemite and hematite, are powerful adsorbents for removing pollutants from wastewater. The application of an external magnetic field will easily isolate them from the reaction medium due to their magnetic properties. In addition, the application of magnetic separation to separate nanoadsorbents offers the invaluable advantage of rapid recovery of toxic metals from wastewater [278]. Due to their easy separation from wastewater and low toxicity, iron oxide nanoparticles are commonly used for the removal of heavy metals from water [279]; in addition, if the nanoparticles are composed of magnetite, they can be easily separated from associated pollutants [280].

4.1.2. Experimental research

4.1.2.1. Copper (Cu^{2+}) ions adsorption experiments

Adsorption experiments were carried out to remove copper ions from wastewater at different pH values and pollutant concentrations using magnetite (Fe_3O_4) as adsorbent nanomaterial. The specific surface area of magnetite is 300 m^3/g. Thus, samples (with concentrations of 0.70; 1.00 and 1.20 mg/L) were prepared from a standard copper solution of

PhD student: *Scientific coordinator:*
Oana Stoian (Păunescu)   *Prof. habil. dr. ing. Cristina-Ileana Covaliu-Mierlă*

1000 mg/L. For these samples, 0.01; 0.02 and 0.20g magnetite were used (Figure 4.9.). The pH was set to values of 8 and 11.5. After the wastewater was prepared, it was homogenized using an ultrasonic bath and a mechanical stirrer (Figure 4.10.). Samples taken were prepared (Figure 4.11.) for the determination of copper ion concentrations using the PhotoLab S12 photometer. Yields were calculated with the formula:

$$\eta(\%) = \frac{c_i - c_f}{c_i} * 100 \qquad (25)$$

where: η represents the treatment yield [%];
      c_i represents the initial concentration [mg/L];
      c_f represents the final concentration [mg/L].

Figure 4.9. Weighing oxide nanomaterial Fe_3O_4.

Figure 4.10. Wastewater treatment using the oxide nanomaterial Fe_3O_4.
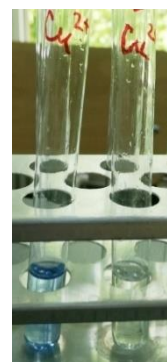
Figure 4.11. Preparation of solutions for measuring copper ions concentrations during treatment processes.

The results obtained with the PhotoLab S12 photometer were determined according to ISO 8466-1 and DIN 38402 A51 (10 mm cell) with a measuring range of 0.10 - 6.00 mg/L Cu^{2+}.

Figures 4.12. and 4.13. plot the variation of copper ion concentrations and treatment efficiencies, respectively, for the removal of copper ions from wastewater at a concentration of 0.70 mg/L using 0.01 g Fe_3O_4 oxide nanomaterial at pH 8.
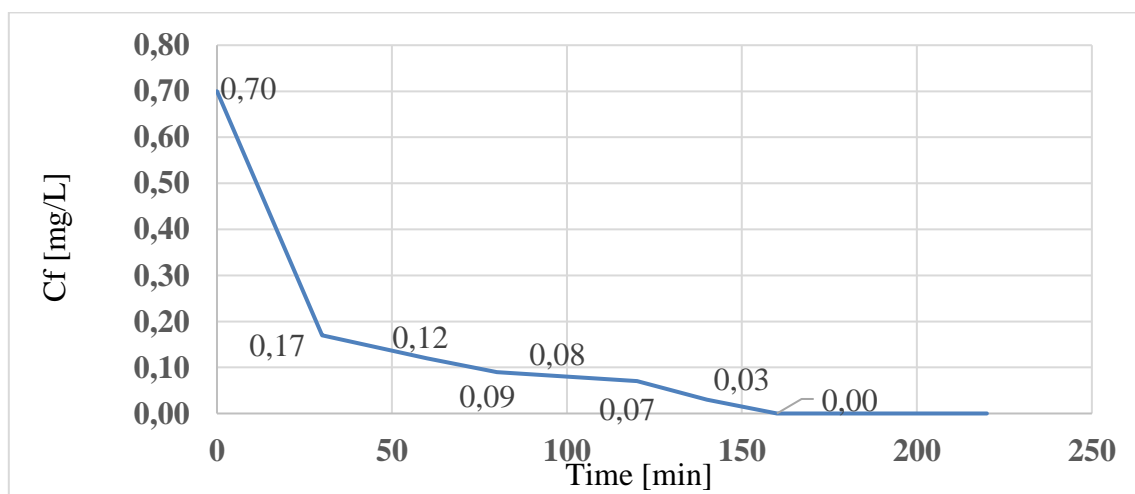

Figure 4.12. Cu^{2+} ion concentrations variation over time for wastewater system containing 0.70 mg/L Cu^{2+} and 0.01 g Fe_3O_4 at pH 8.

PhD student: *Scientific coordinator:*
Oana Stoian (Păunescu)   *Prof. habil. dr. ing. Cristina-Ileana Covaliu-Mierlă*

Figure 4.12. shows the variation of copper ion concentrations over time. A sharp decrease to a concentration of 0.17 mg/L Cu(II) was observed within 30 minutes. In the following treatment time period, a steady decrease of copper ions in the wastewater was observed until total removal, finding that the required treatment time is 160 minutes.
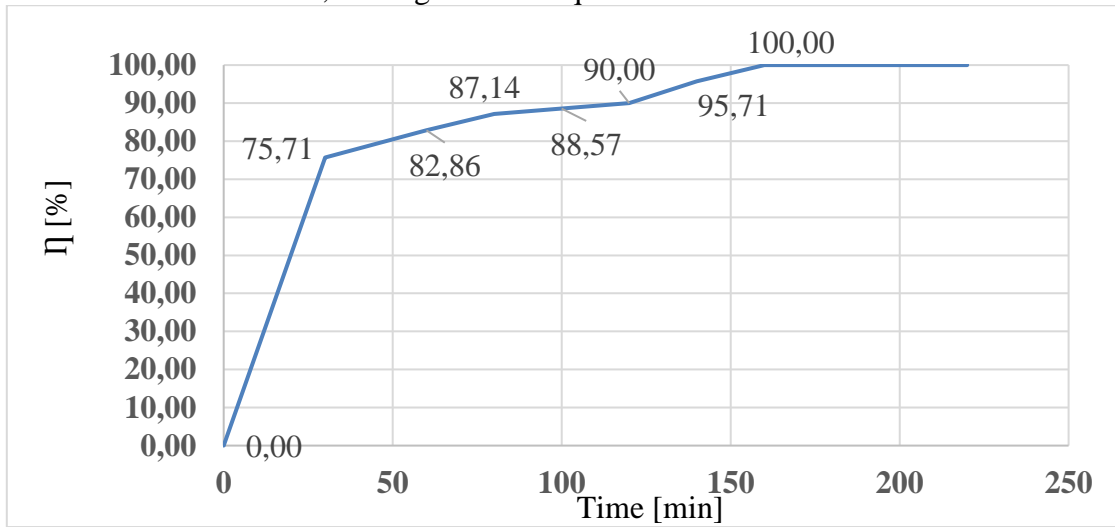

Figure 4.13. Treatment efficiencies variation over time for wastewater system containing 0.70 mg/L Cu^{2+} and 0.01 g Fe_3O_4 at pH 8.

In Figure 4.13. we can see that the treatment efficiency reached 75.71% after a time period of only 30 minutes, steadily increasing to the maximum treatment efficiency in 160 minutes.

Figure 4.14. plots the decrease in copper ion concentrations over the 270 minute time interval and Figure 4.15. plots the increase in treatment efficiencies from an initial concentration of 1.00 mg/L Cu(II) using 0.01 g Fe_3O_4 at pH 8 of wastewater.
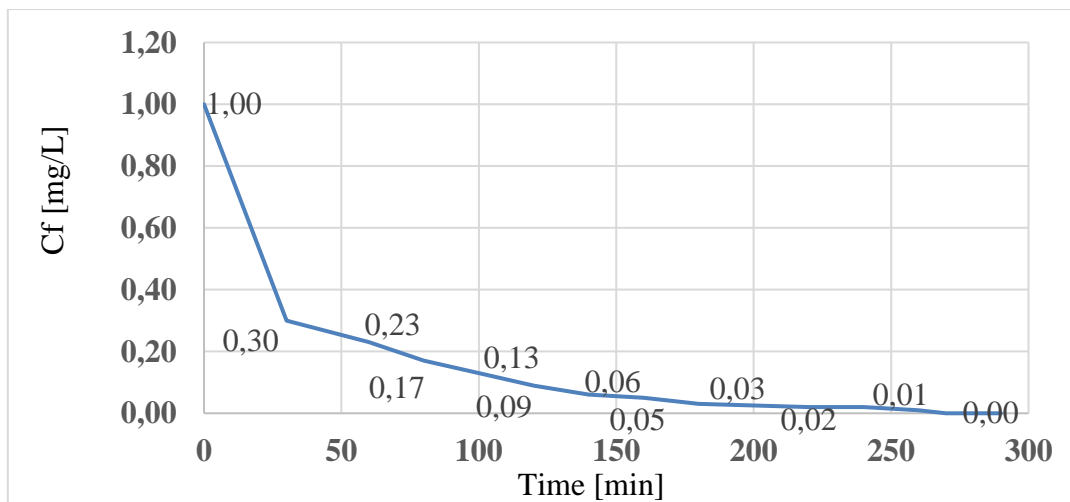

Figure 4.14. Cu^{2+} ion concentrations variation over time for wastewater system containing 1.00 mg/L Cu^{2+} and 0.01 g Fe_3O_4 at pH 8.

Figure 4.14. shows a sharp drop in the concentration of copper ions in the wastewater to a concentration of 0.30 mg/L in a time period of 30 minutes. In the following time period, up to 270 minutes the decrease of copper ions concentration is constant until the complete removal of copper ions from the wastewater.
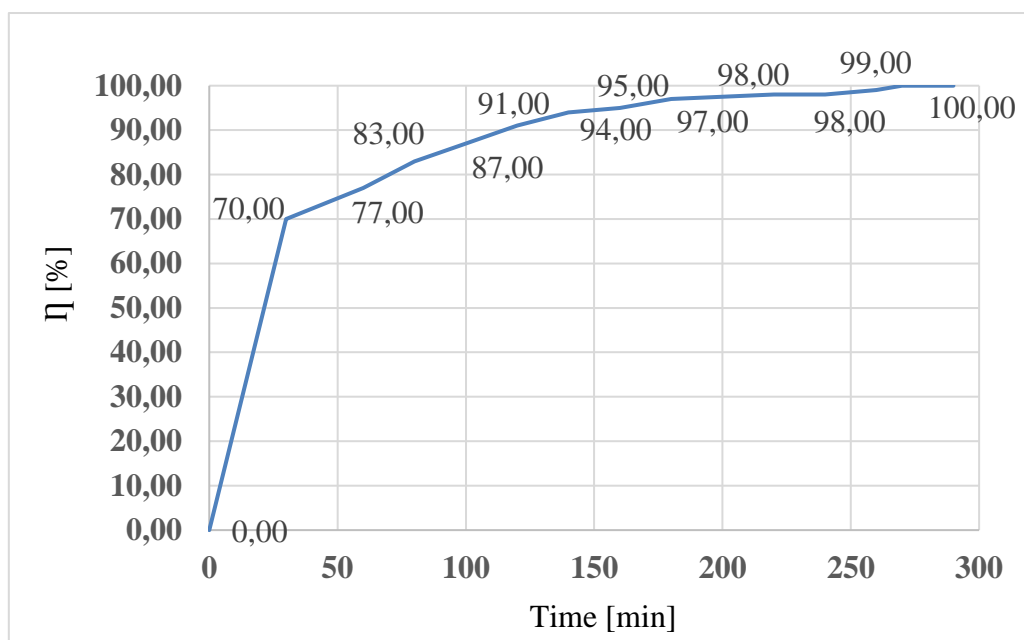
PhD student: *Scientific coordinator:*
Oana Stoian (Păunescu)   *Prof. habil. dr. ing. Cristina-Ileana Covaliu-Mierlă*

Figure 4.15. Treatment efficiencies variation over time for wastewater system containing 1.00 mg/L Cu^{2+} and 0.01 g Fe_3O_4 at pH 8.

Figure 4.15. shows the high increase in treatment efficiency of up to 70.00% in a short period of time. It can be seen that the treatment efficiency increases steadily until the maximum efficiency is reached.

Figures 4.16. and 4.17. plot the variations of copper ion concentrations and treatment efficiencies over time for the removal of 1.20 mg/L from wastewater using 0.01 g magnetite at wastewater pH 8.
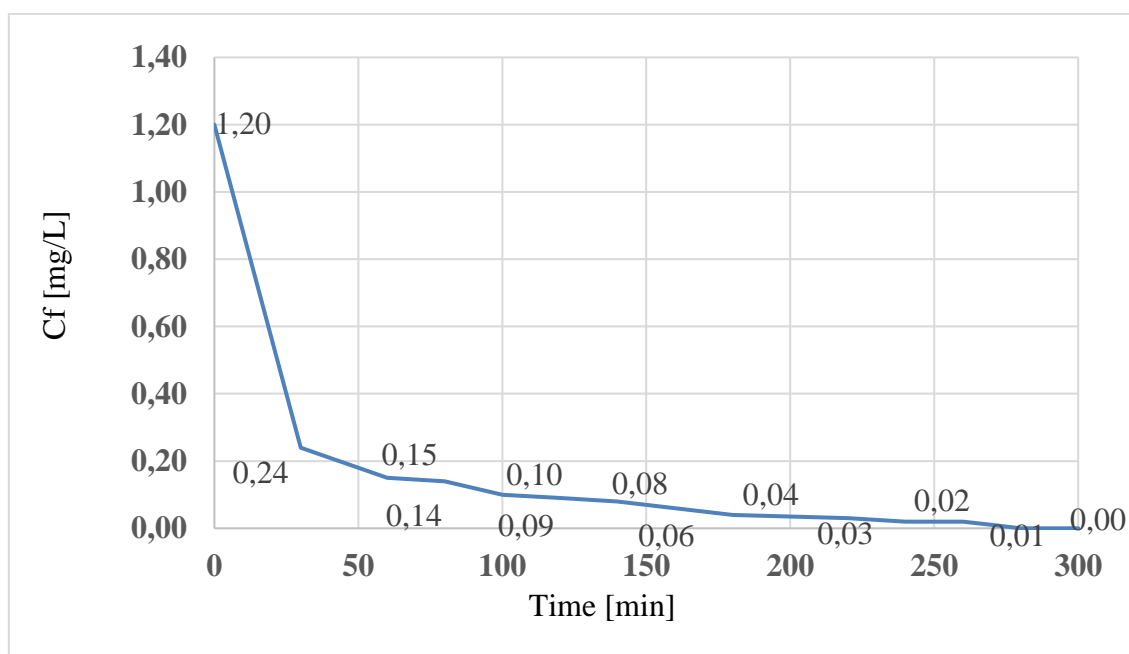

Figure 4.16. Cu^{2+} ion concentrations variation over time for wastewater system containing 1.20 mg/L Cu^{2+} and 0.01 g Fe_3O_4 at pH 8.

PhD student: *Scientific coordinator:*
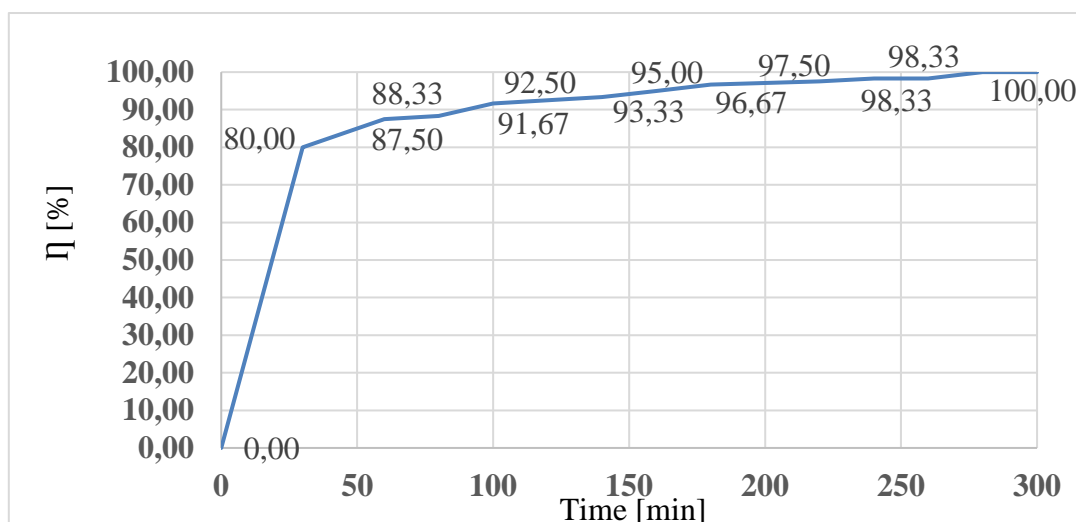*Oana Stoian (Păunescu)*   *Prof. habil. dr. ing. Cristina-Ileana Covaliu-Mierlă*

Figure 4.17. Treatment efficiencies variation over time for wastewater system containing 1.20 mg/L Cu^{2+} and 0.01 g Fe_3O_4 at pH 8.

In the first 30 minutes of treatment time the concentration of copper ions decreases to 0.24 mg/L, and until the complete removal of copper ions from the wastewater, it decreases steadily until the treatment time of 280 minutes (Figure 4.16.). Also, in the first 30 minutes the treatment efficiency increases rapidly to 80.00%, reaching maximum efficiency in 280 minutes (Figure 4.17.).

Figures 4.18. and 4.19. plot the variations of concentrations and treatment efficiencies over time respectively for the removal of 0.70 mg/L Cu(II) using 0.02 g of Fe_3O_4 oxide nanomaterial at pH 8 of wastewater.
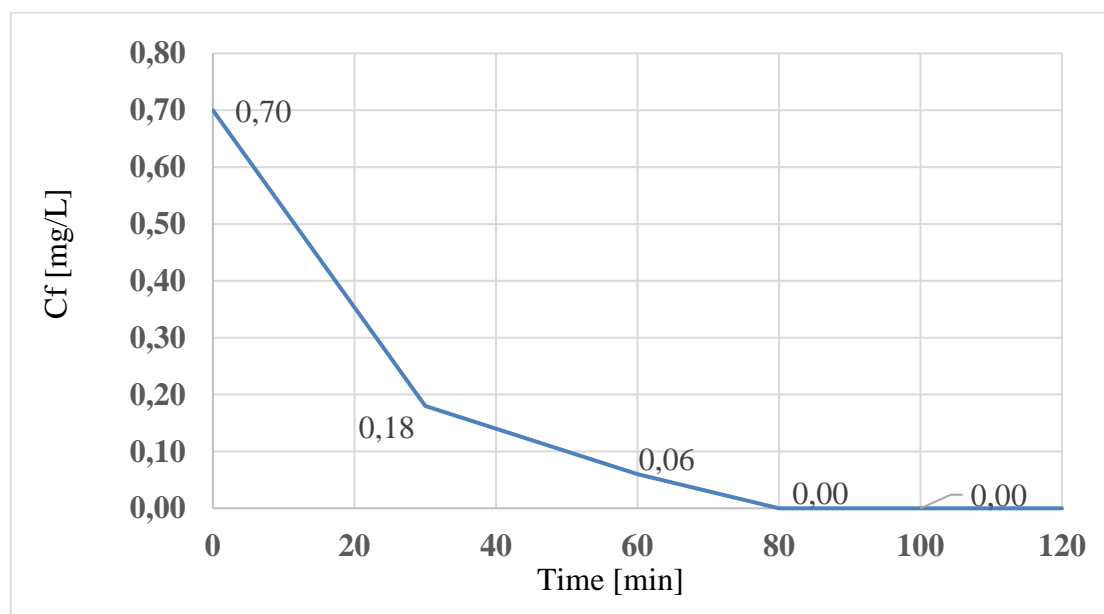

Figure 4.18. Cu^{2+} ion concentrations variation over time for wastewater system containing 0.70 mg/L Cu^{2+} and 0.02 g Fe_3O_4 at pH 8.

From Figure 4.18. it can be seen that the concentration of copper ions in the wastewater is decreasing rapidly. It can be seen that the complete removal of copper ions was achieved in only 80 minutes.
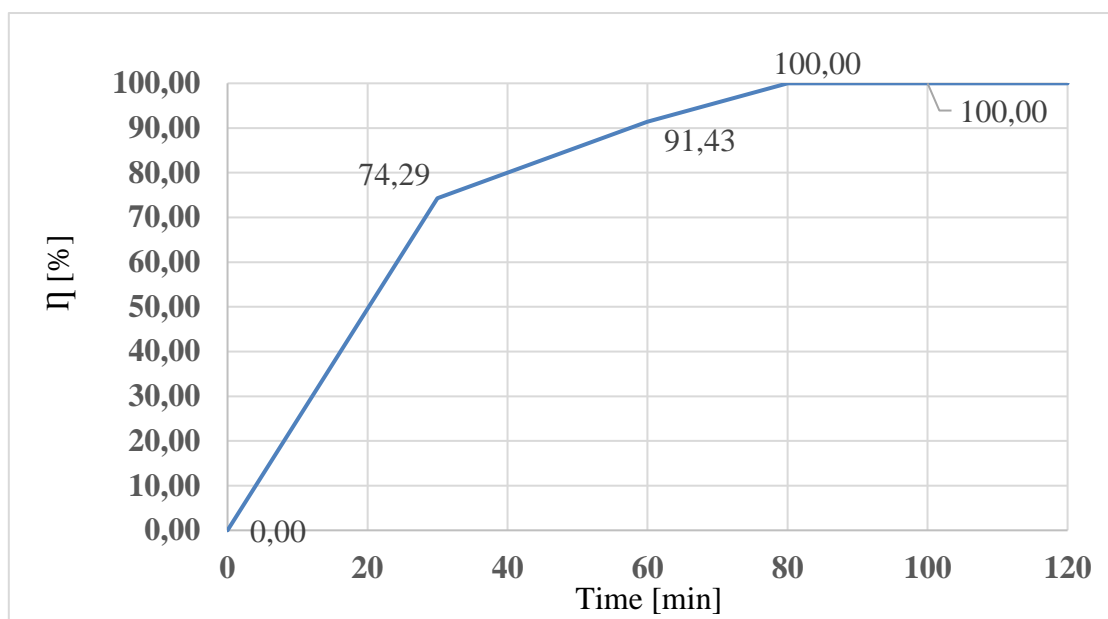
18

PhD student:
Oana Stoian (Păunescu)

Scientific coordinator:
Prof. habil. dr. ing. Cristina-Ileana Covaliu-Mierlă

Figure 4.19. Treatment efficiencies variation over time for wastewater system containing 0.70 mg/L Cu^{2+} and 0.02 g Fe_3O_4 at pH 8.

Figure 4.19. shows the rapid increase in wastewater treatment efficiencies and shows that the complete removal of copper ions was achieved in a time period of only 80 minutes, reaching a treatment efficiency of 100.00%.

Figures 4.20. and 4.21. plot the variations of concentrations and treatment efficiencies over time respectively for the removal of 1.00 mg/L Cu(II) using 0.02 g of Fe_3O_4 oxide nanomaterial at pH 8 of wastewater.
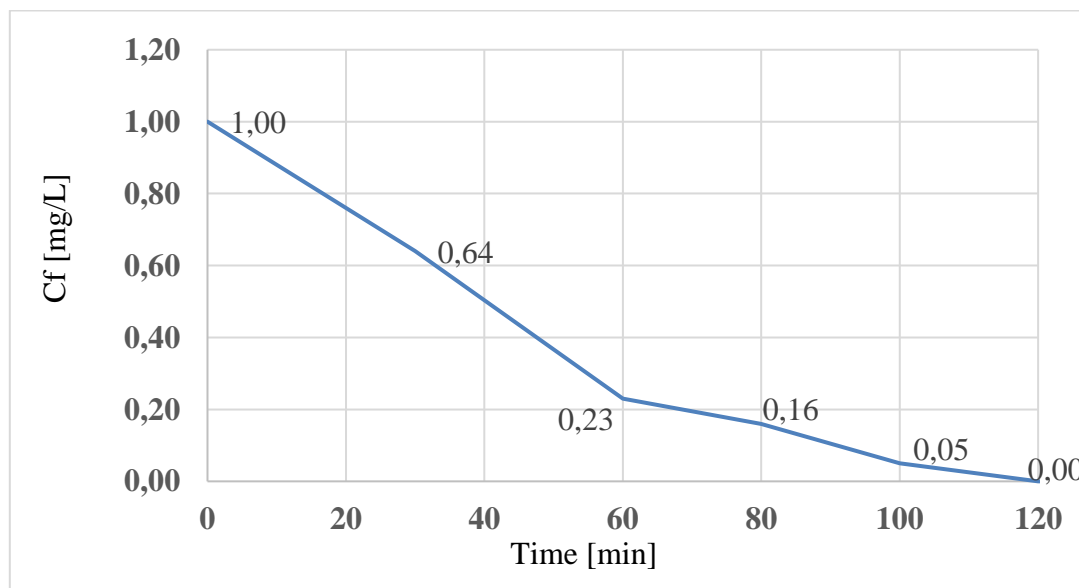

Figure 4.20. Cu^{2+} ion concentrations variation over time for wastewater system containing 1.00 mg/L Cu^{2+} and 0.02 g Fe_3O_4 at pH 8.

Figure 4.20. shows the rapid decrease of copper ion concentration in wastewater. The concentration of copper ions reached 0.64 mg/L after 30 minutes, 0.23 mg/L after 60 minutes, 0.16 mg/L after 80 minutes, 0.05 mg/L after 100 minutes of treatment time. It is found that complete removal of copper ions was achieved in a time period of 120 minutes.
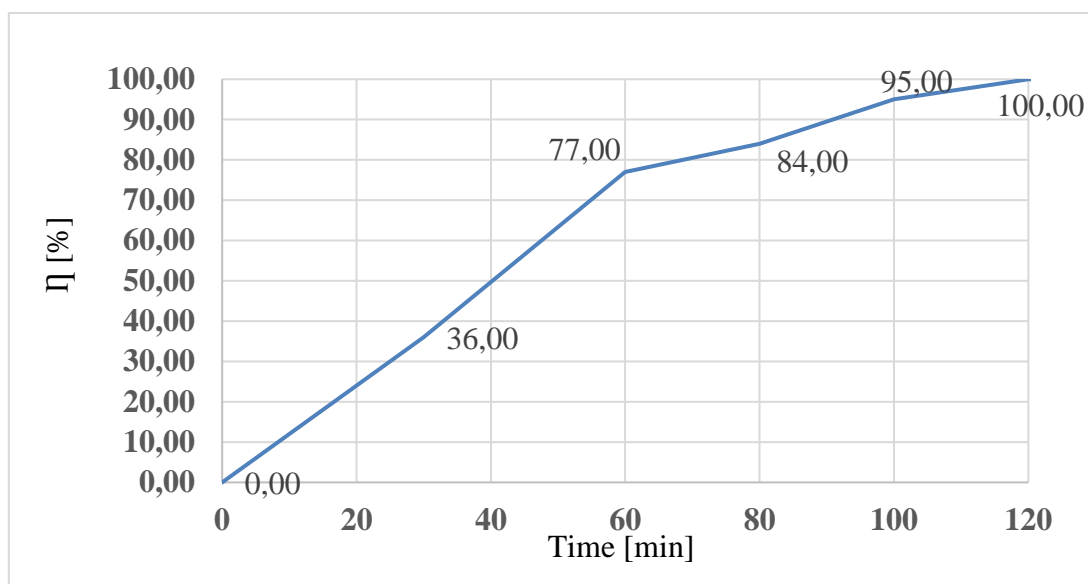
PhD student: *Scientific coordinator:*
Oana Stoian (Păunescu)   *Prof. habil. dr. ing. Cristina-Ileana Covaliu-Mierlă*

Figure 4.21. Treatment efficiencies variation over time for wastewater system containing 1.00 mg/L Cu^{2+} and 0.02 g Fe_3O_4 at pH 8.

Figure 4.21. shows the rapid increase in wastewater treatment efficiencies. It can be seen that after only 60 minutes of treatment time, the efficiency has reached 77.00%. It can be seen that the complete removal of copper ions was achieved in a time period of 120 minutes, reaching the treatment efficiency of 100.00 %.

Figures 4.22. and 4.23. plot the variations of concentrations and treatment yields over time for the removal of 1.20 mg/L Cu(II) using 0.02 g of Fe_3O_4 oxide nanomaterial at pH 8 of wastewater.
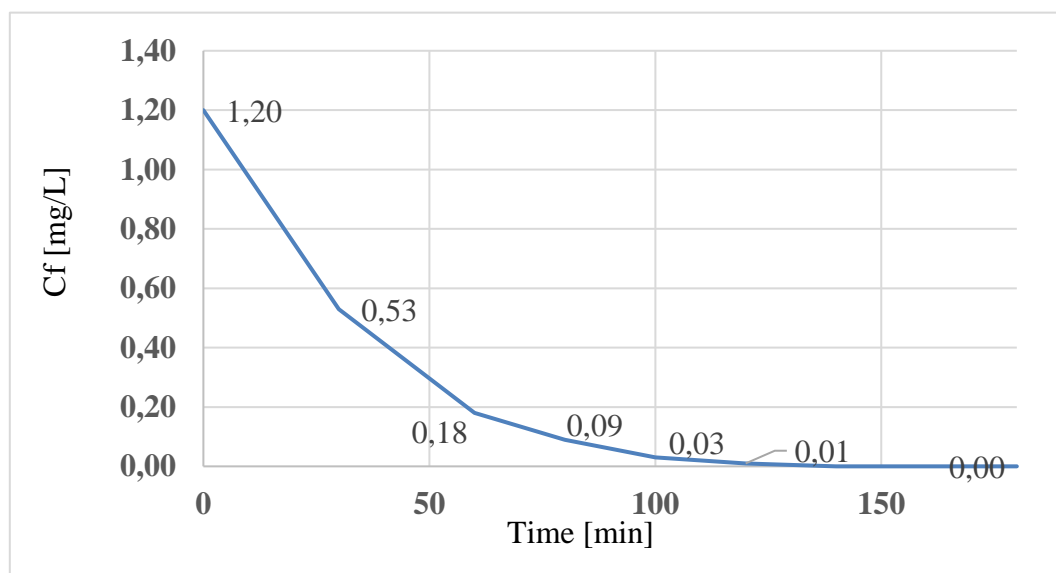

Figure 4.22. Cu^{2+} ion concentrations variation over time for wastewater system containing 1.20 mg/L Cu^{2+} and 0.02 g Fe_3O_4 at pH 8.

Figure 4.22. shows the rapid decrease in the concentration of copper ions in the wastewater until they are completely removed in a time period of 140 minutes, a longer treatment time than for the removal of concentrations of 0.70 and 1.00 mg/L.
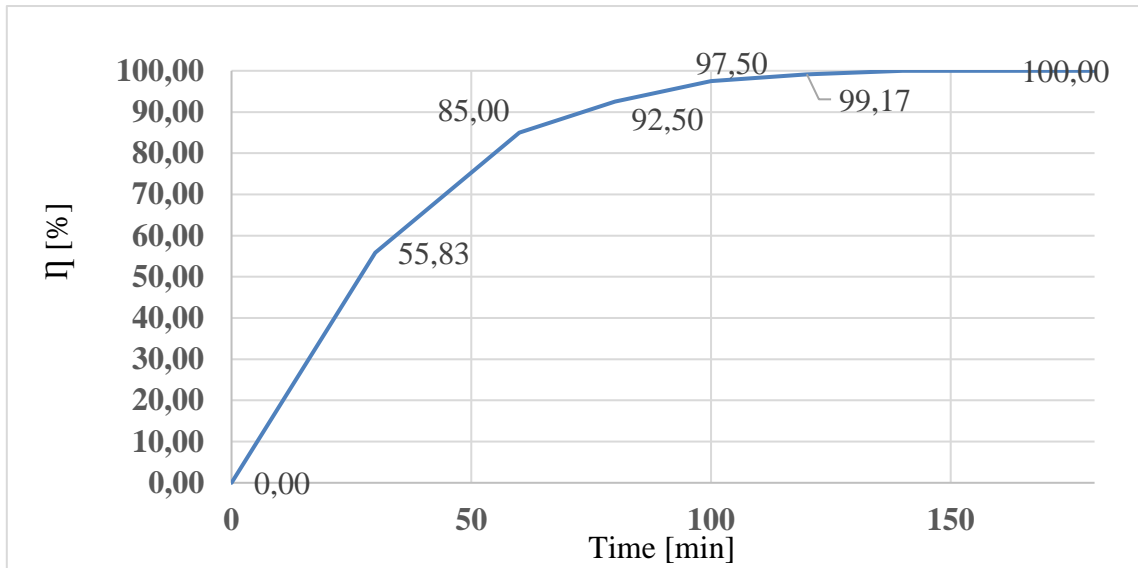
PhD student: *Scientific coordinator:*
Oana Stoian (Păunescu)   *Prof. habil. dr. ing. Cristina-Ileana Covaliu-Mierlă*

Figure 4.23. Treatment efficiencies variation over time for wastewater system containing 1.20 mg/L Cu^{2+} and 0.02 g Fe_3O_4 at pH 8.

The increase in treatment efficiency proved to be rapid, as depicted in Figure 4.23., with treatment efficiency reaching 55.83% after 30 minutes, 85.00% after 60 minutes, 92.50% after 80 minutes, 97.50% after 100 minutes and reaching the maximum efficiency of 100.00% after 140 minutes of contact time.

Figure 4.24. plots the decrease in copper ion concentrations over 270 minutes and Figure 4.25. plots the increase in treatment efficiencies from an initial concentration of 0.70 mg/L Cu(II) using 0.20 g Fe_3O_4 at pH 8 of the wastewater.
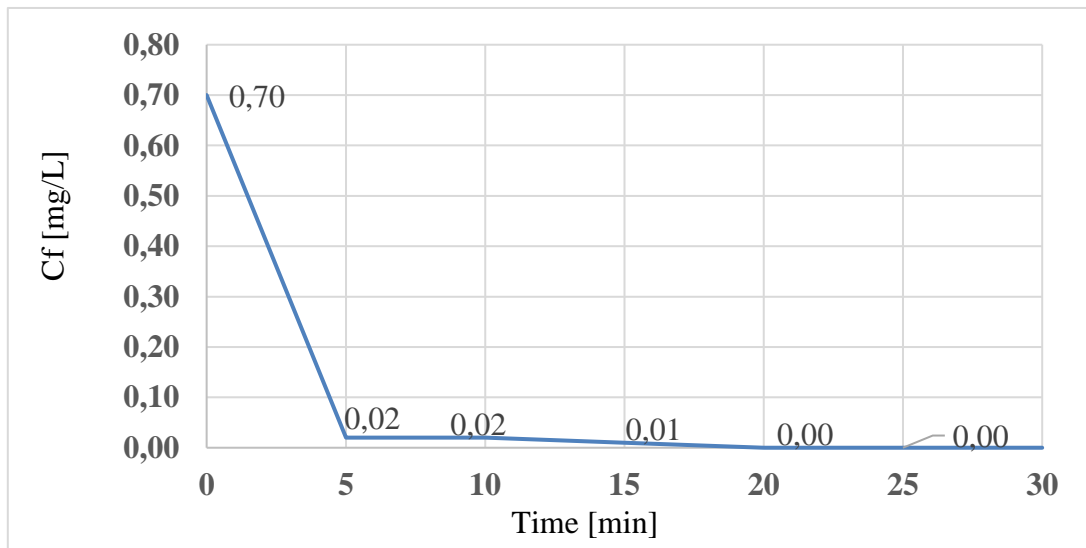

Figure 4.24. Cu^{2+} ion concentrations variation over time for wastewater system containing 0.70 mg/L Cu^{2+} and 0.20 g Fe_3O_4 at pH 8.

Figure 4.24. shows a sudden drop in the concentration of copper ions in the wastewater to a concentration of 0.02 mg/L in a time period of only 5 minutes. In the following time period up to 20 minutes the decrease of copper ions concentration is constant until the complete removal of copper ions from the wastewater.
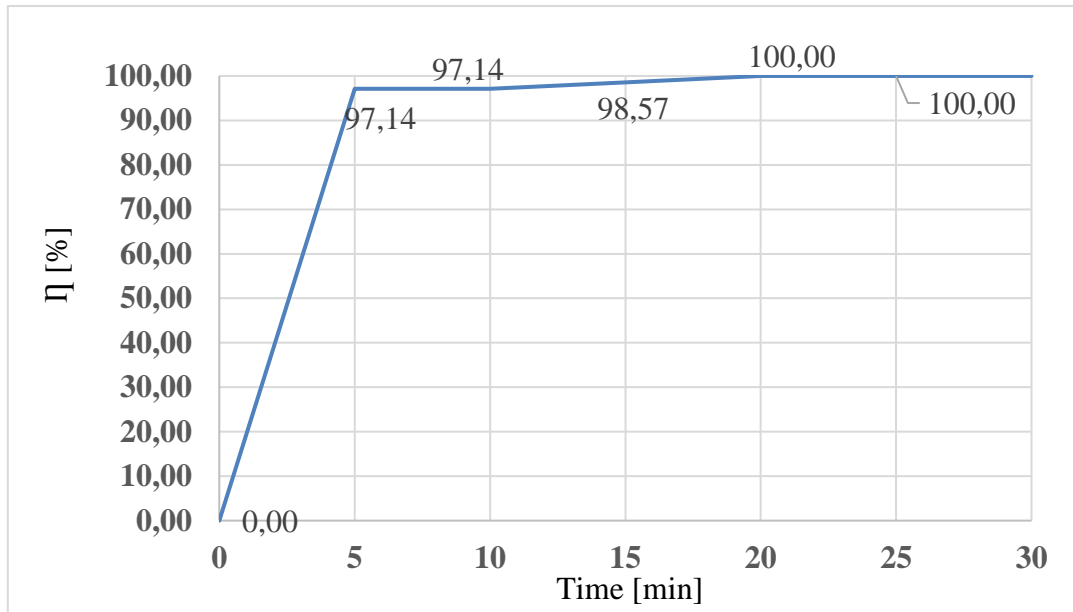
PhD student: *Scientific coordinator:*
Oana Stoian (Păunescu)   *Prof. habil. dr. ing. Cristina-Ileana Covaliu-Mierlă*

Figure 4.25. Treatment efficiencies variation over time for wastewater system containing 0.70 mg/L Cu^{2+} and 0.20 g Fe_3O_4 at pH 8.

Figure 4.25. shows the high increase in treatment efficiency, up to 97.14 % in a short time (5 minutes). It can be seen that the treatment efficiency increases steadily until the maximum efficiency is reached (100.00%).

Figures 4.26. and 4.27. plot the variations of copper ion concentrations and treatment efficiencies over time for the removal of 1.00 mg/L from wastewater using 0.20 g magnetite at wastewater pH 8.
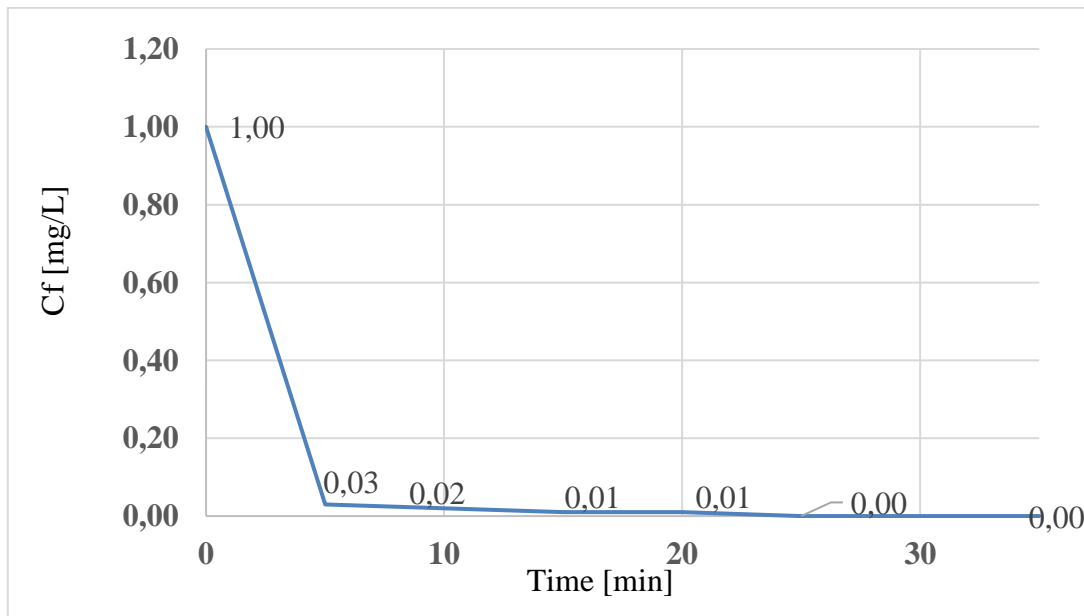

Figure 4.26. Cu^{2+} ion concentrations variation over time for wastewater system containing 1.00 mg/L Cu^{2+} and 0.20 g Fe_3O_4 at pH 8.

PhD student:
Oana Stoian (Păunescu)

Scientific coordinator:
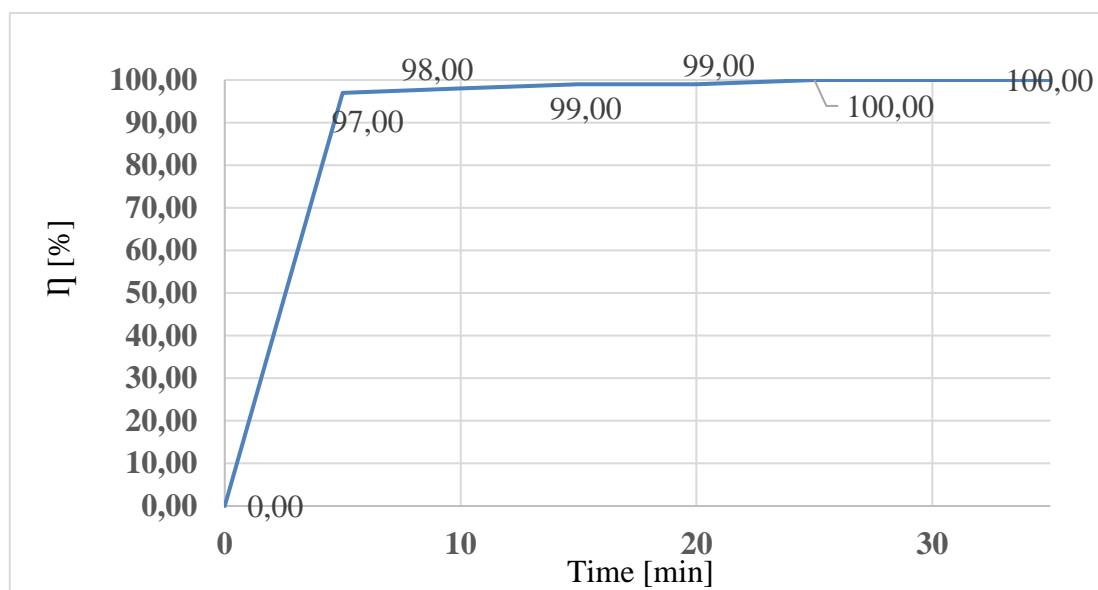*Prof. habil. dr. ing. Cristina-Ileana Covaliu-Mierlă*

Figure 4.27. Treatment efficiencies variation over time for wastewater system containing 1.00 mg/L Cu^{2+} and 0.20 g Fe_3O_4 at pH 8.

In the first 5 minutes of treatment time the concentration of copper ions decreases to 0.03 mg/L, and until the complete removal of copper ions from the wastewater, it decreases steadily in 25 minutes (Figure 4.26.). Also, in the first 5 minutes the treatment efficiency increases rapidly to 97.00%, reaching maximum efficiency in 25 minutes (Figure 4.27.).

Figures 4.28. and 4.29. plot the variations of concentrations and treatment efficiencies over time respectively for the removal of 1.20 mg/L Cu(II) using 0.20 g of Fe_3O_4 oxide nanomaterial at pH 8 of wastewater.
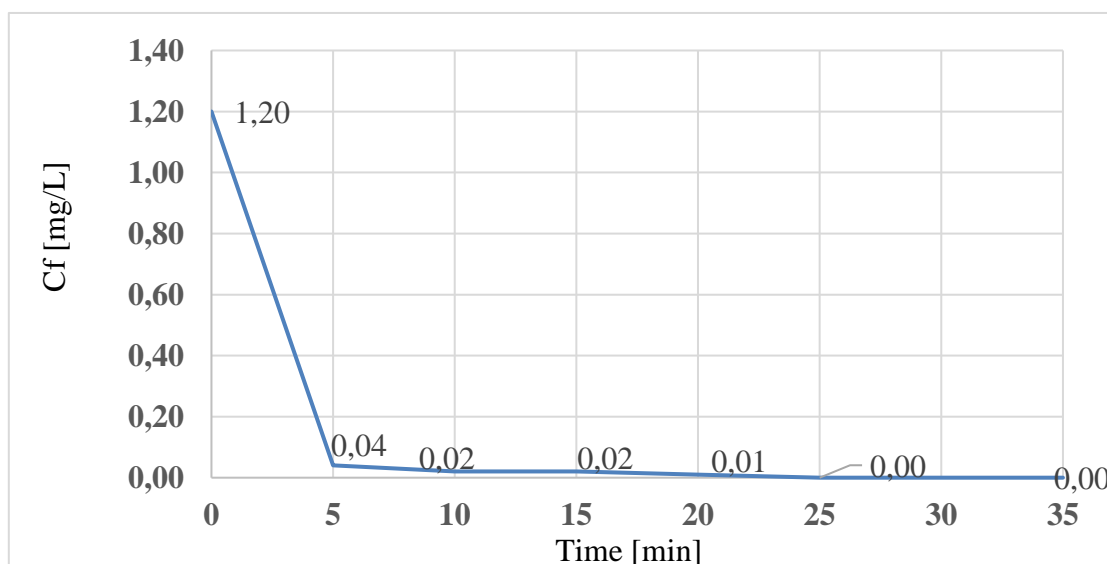

Figure 4.28. Cu^{2+} ion concentrations variation over time for wastewater system containing 1.20 mg/L Cu^{2+} and 0.20 g Fe_3O_4 at pH 8.

Figure 4.28. shows the rapid decrease in the concentration of copper ions in wastewater. It can be seen that the complete removal of copper ions was achieved in only 25 minutes.
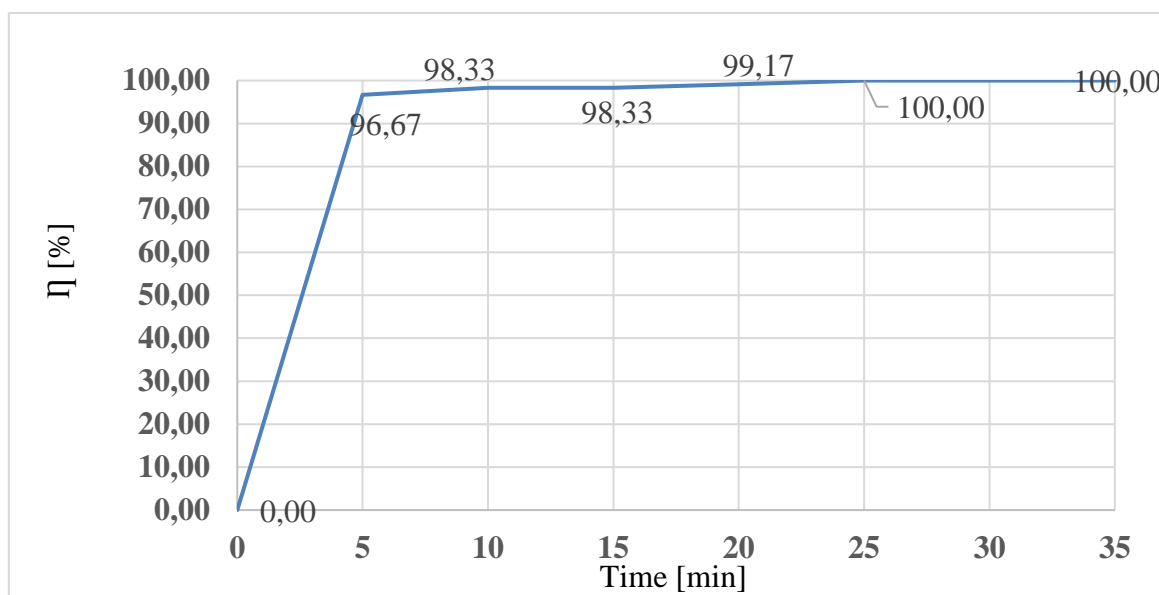
PhD student: *Scientific coordinator:*
Oana Stoian (Păunescu)   *Prof. habil. dr. ing. Cristina-Ileana Covaliu-Mierlă*

Figure 4.29. Treatment efficiencies variation over time for wastewater system containing 1.20 mg/L Cu^{2+} and 0.20 g Fe_3O_4 at pH 8.

Figure 4.29. shows the rapid increase in wastewater treatment efficiencies and shows that the complete removal of copper ions was achieved in a time period of only 25 minutes, reaching a treatment efficiency of 100.00%.

In the following figures (Figures 4.30, 4.31 and 4.32) the required treatment time for each experiment is plotted as a function of the concentration of copper ions in the wastewater and the quantities of magnetite used in the experimental investigations.
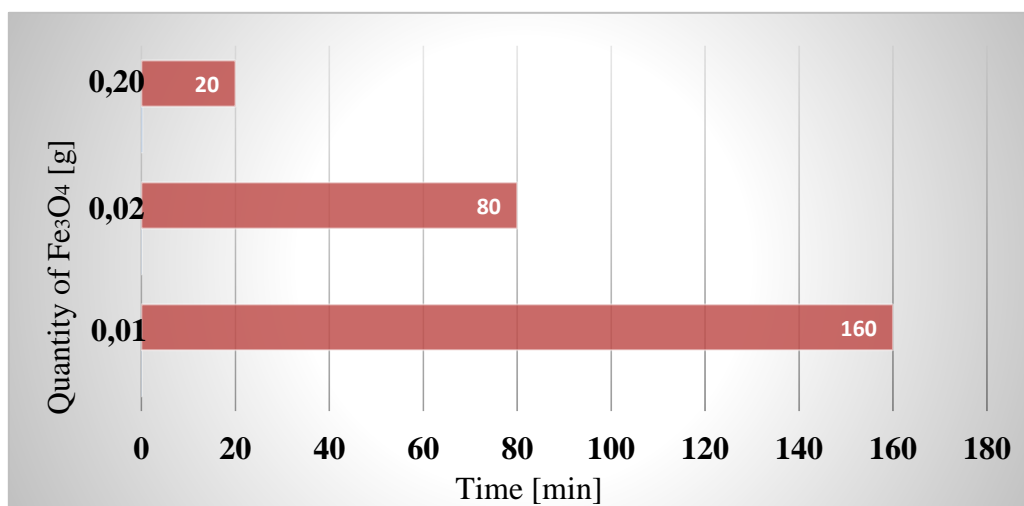

Figure 4.30. Treatment time required for 0.70 mg/L Cu^{2+} concentration using 0.20; 0.02 and 0.01 g Fe_3O_4, pH 8.

Figure 4.30. shows that the time required to remove a copper ion concentration of 0.70 mg/L was a maximum of 20 minutes using 0.20 g of Fe_3O_4 oxide nanomaterial, a maximum of 80 minutes using 0.02 g of Fe_3O_4 oxide nanomaterial and a maximum of 160 minutes using 0.01 g of Fe_3O_4 oxide nanomaterial.

PhD student: *Scientific coordinator:*
Oana Stoian (Păunescu)   *Prof. habil. dr. ing. Cristina-Ileana Covaliu-Mierlă*

Figure 4.31. Treatment time required for 1.00 mg/L Cu^{2+} concentration using 0.20; 0.02 and 0.01 g Fe_3O_4, pH 8.

From Figure 4.31. it can be seen that the time required to remove a copper ion concentration of 1.00 mg/L was a maximum of 25 minutes when using 0.20 g of Fe_3O_4 oxide nanomaterial, a maximum of 120 minutes using 0.02 g of Fe_3O_4 oxide nanomaterial and a maximum of 270 minutes u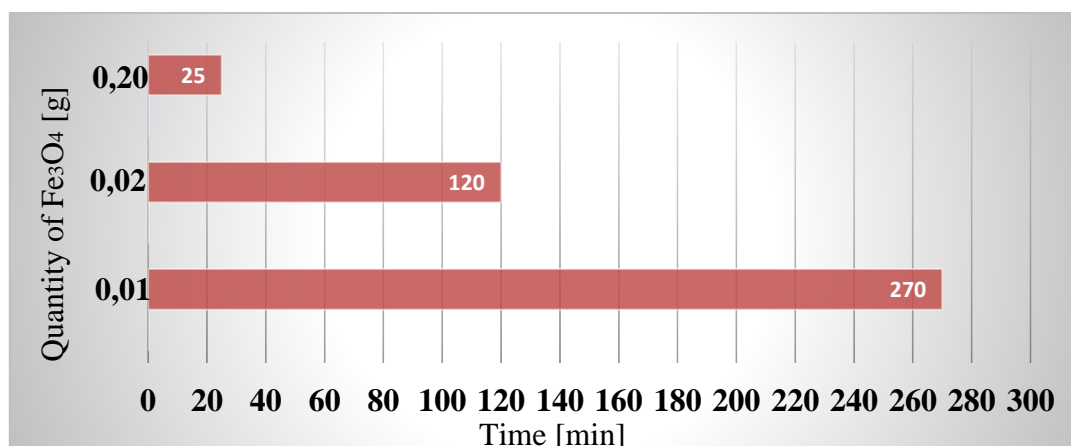sing 0.01 g of Fe_3O_4 oxide nanomaterial. It can be seen that, compared to the results shown in Figure 4.30., the treatment time using an amount of 0.20 g of Fe_3O_4 oxide nanomaterial is close, while in the other two cases the required treatment time increased considerably.
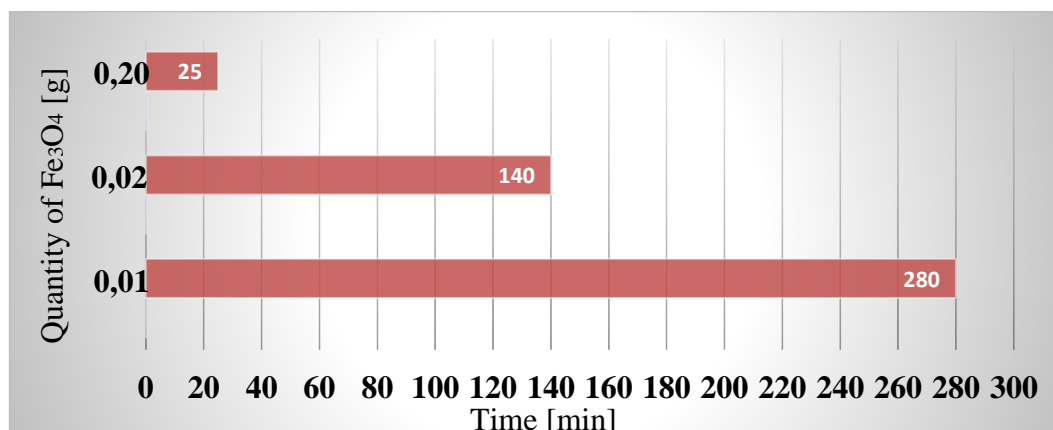

Figure 4.32. Treatment time required for 1.20 mg/L Cu^{2+} concentration using 0.20; 0.02 and 0.01 g Fe_3O_4, pH 8.

From Figure 4.32. it can be seen that the time required to remove a copper ion concentration of 1.20 mg/L was a maximum of 25 minutes using 0.20 g of Fe_3O_4 oxide nanomaterial, a maximum of 140 minutes using 0.02 g of Fe_3O_4 oxide nanomaterial and a maximum of 280 minutes using 0.01 g of Fe_3O_4 oxide nanomaterial. It can be seen that, compared to the results shown in Figure 4.30., the treatment time using an amount of 0.20 g of Fe_3O_4 oxide nanomaterial is close, while in the other two cases the required treatment time is almost double. However, these results are close to those shown in Figure 4.31.

In Figures 4.33. and 4.34. are plotted the variation of copper ion concentrations and treatment efficiencies, respectively, for the removal of copper ions from wastewater at a concentration of 0.70 mg/L using 0.01 g Fe_3O_4 oxide nanomaterial at pH 11.5.

PhD student: *Scientific coordinator:*
Oana Stoian (Păunescu)   *Prof. habil. dr. ing. Cristina-Ileana Covaliu-Mierlă*
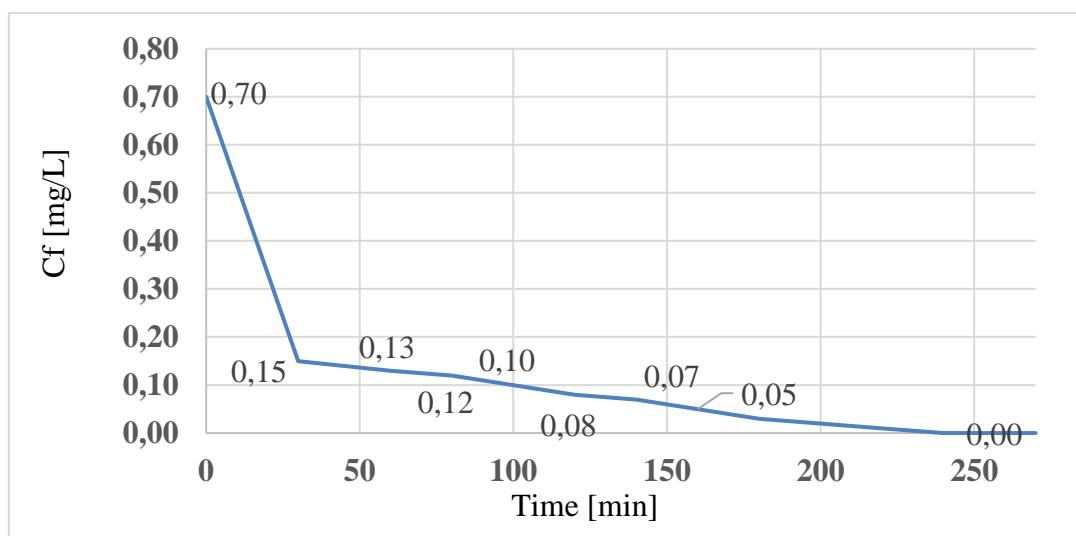
Figure 4.33. Concentration variation over time for the removal of 0.70 mg/L Cu^{2+} using 0.01 g Fe_3O_4, pH 11.5.

Figure 4.33. shows the variation of copper ion concentrations over time. A sharp decrease to a concentration of 0.15 mg/L Cu(II) was observed within a period of 30 minutes. In the following treatment time period, a steady decrease of copper ions in the wastewater was observed until total removal, finding that the required treatment time is 240 minutes.
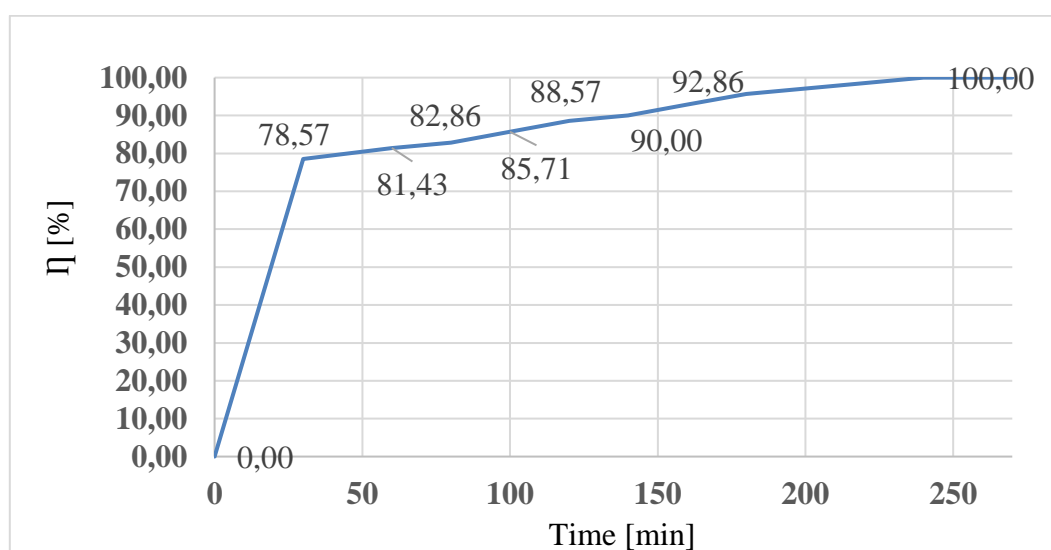

Figure 4.34. Variation of treatment efficiencies over time for the removal of 0.70 mg/L Cu^{2+} using 0.01 g Fe_3O_4, pH 11.5.

In Figure 4.34. we can see that the treatment efficiency reached 78.57% after a time period of only 30 minutes, steadily increasing to the maximum treatment efficiency in 240 minutes.

Figure 4.35. plots the decrease in copper ion concentrations over the time interval of 290 minutes and Figure 4.36. plots the increase in treatment efficiencies from an initial concentration of 1.00 mg/L Cu(II) using 0.01 g Fe_3O_4 at pH 11.5 of wastewater.
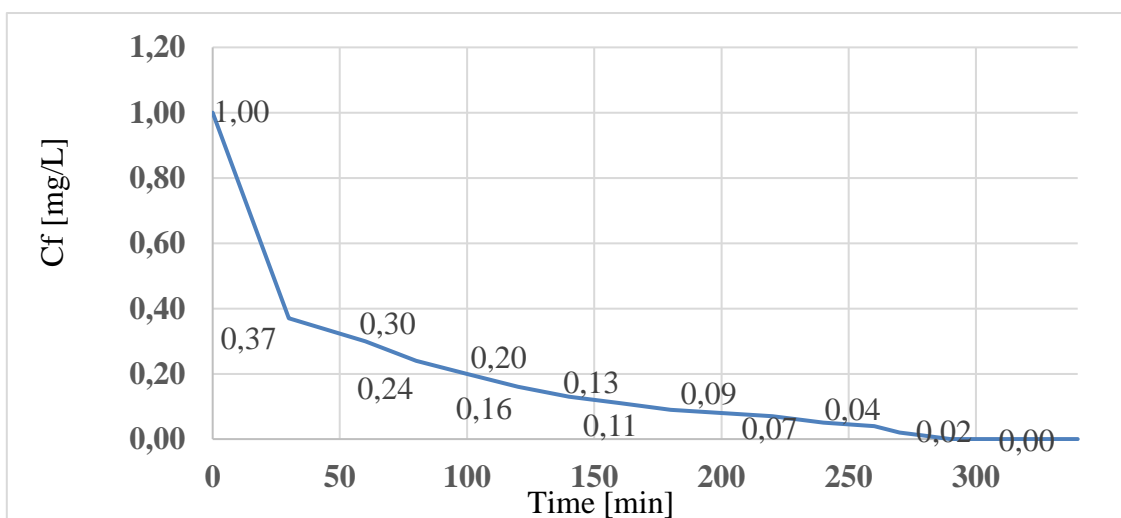
PhD student:
Oana Stoian (Păunescu)

Scientific coordinator:
Prof. habil. dr. ing. Cristina-Ileana Covaliu-Mierlă

Figure 4.35. Concentration variation over time for removal of 1.00 mg/L Cu^{2+} using 0.01 g Fe_3O_4, pH 11.5.

Figure 4.35. shows a sharp drop in the concentration of copper ions in the wastewater to a concentration of 0.37 mg/L in a time period of 30 minutes. In the next time period, up to 290 minutes the decrease of copper ions concentration is constant until the complete removal of copper ions from wastewater.
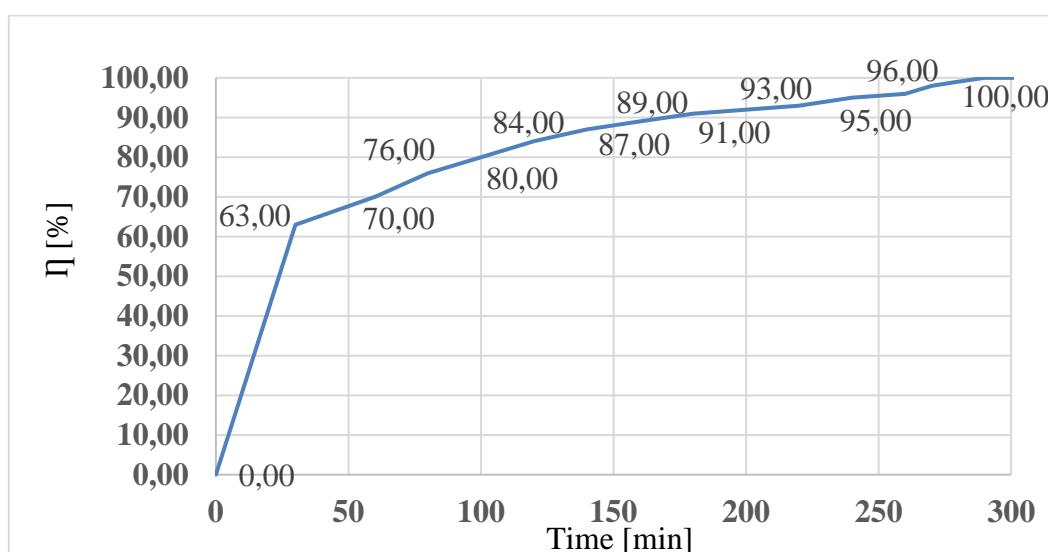

Figure 4.36. Variation of treatment efficiencies over time for the removal of 1.00 mg/L Cu^{2+} using 0.01 g Fe_3O_4, pH 11.5.

Figure 4.36. shows the increase in treatment efficiency, up to 63.00 % in a short period of time. It can be seen that the treatment efficiency increases steadily until the maximum efficiency is reached.

In Figures 4.37. and 4.38. plot the variations of copper ion concentrations and treatment efficiencies over time for the removal of 1.20 mg/L from wastewater using 0.01 g magnetite at pH 11.5 of wastewater.
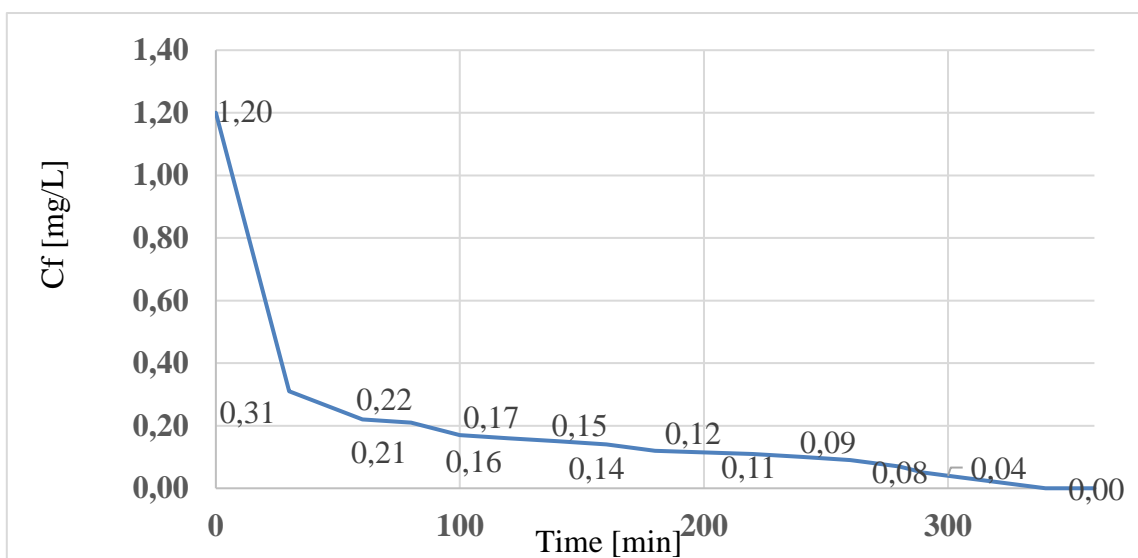
27

PhD student: *Scientific coordinator:*
Oana Stoian (Păunescu)   *Prof. habil. dr. ing. Cristina-Ileana Covaliu-Mierlă*

Figure 4.37. Concentration variation over time for removal of 1.20 mg/L Cu^{2+} using 0.01 g Fe_3O_4, pH 11.5.
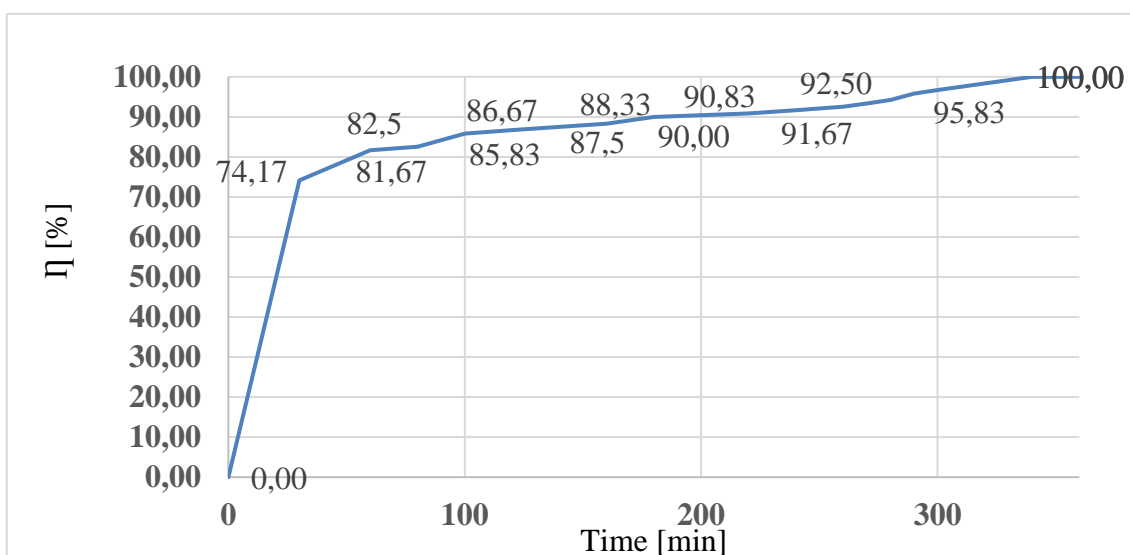

Figure 4.38. Variation of treatment efficiencies over time to remove 1.20 mg/L Cu^{2+} using 0.01 g Fe_3O_4, pH 11.5.

In the first 30 minutes of treatment time the concentration of copper ions decreases to 0.31 mg/L, and until the complete removal of copper ions from the wastewater, it decreases steadily until the treatment time of 340 minutes (Figure 4.37.). Also, in the first 30 minutes the treatment efficiency increases rapidly to 74.17%, reaching the maximum efficiency in 340 minutes (Figure 4.38.).

In Figures 4.39. and 4.40. are plotted the variations of concentrations and treatment efficiencies over time respectively for the removal of 0.70 mg/L Cu(II) using 0.02 g of Fe_3O_4 oxide nanomaterial at pH 11.5 of wastewater.

PhD student: *Scientific coordinator:*
Oana Stoian (Păunescu)   *Prof. habil. dr. ing. Cristina-Ileana Covaliu-Mierlă*
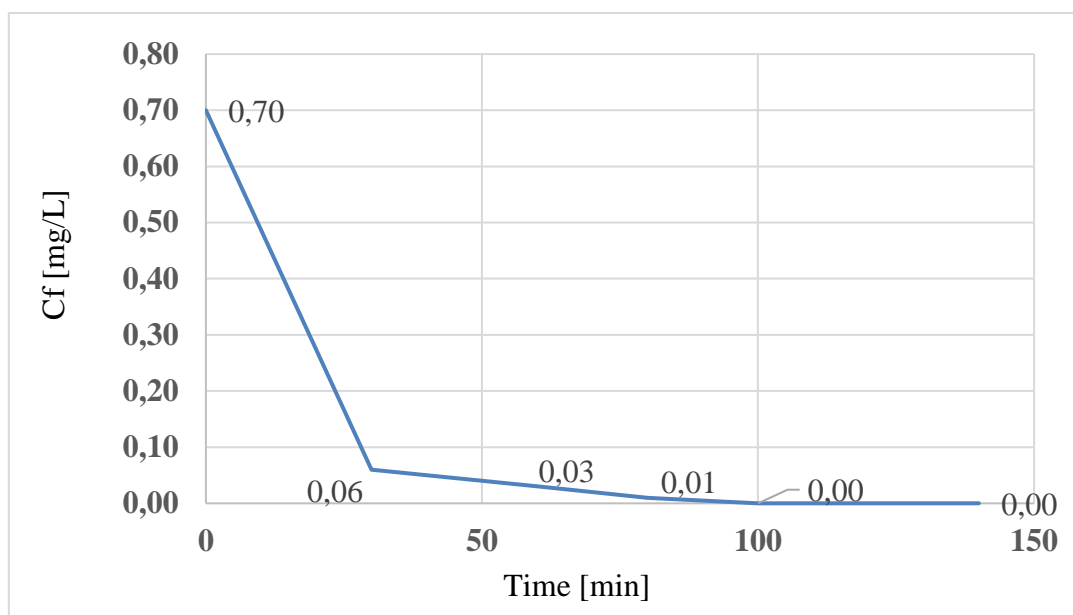
Figure 4.39. Concentration variation over time for the removal of 0.70 mg/L Cu^{2+} using 0.02 g Fe_3O_4, pH 11.5.

From Figure 4.39. it can be seen that the concentration of copper ions in the wastewater is decreasing rapidly. It can be seen that the complete removal of copper ions was achieved in only 100 minutes.
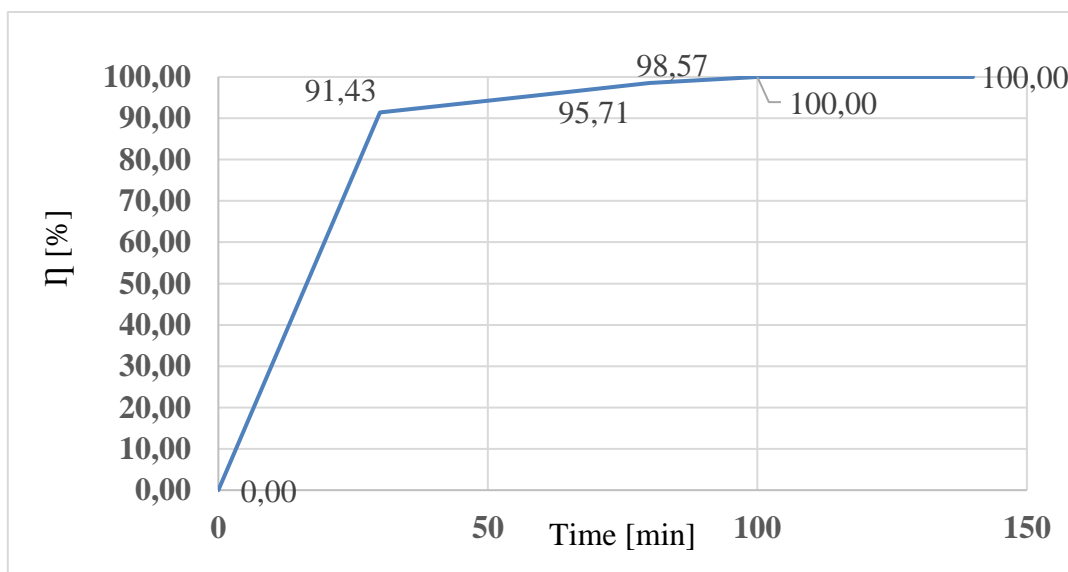

Figure 4.40. Variation of treatment efficiencies over time for the removal of 0.70 mg/L Cu^{2+} using 0.02 g Fe_3O_4, pH 11.5.

Figure 4.40. shows the rapid increase in wastewater treatment efficiencies and shows that the complete removal of copper ions was achieved in a time period of only 100 minutes, reaching a treatment efficiency of 100.00%.

In Figures 4.41. and 4.42. are plotted the variations of concentrations and treatment efficiencies over time respectively for the removal of 1.00 mg/L Cu(II) using 0.02 g of Fe_3O_4 oxide nanomaterial at pH 11.5 of wastewater.
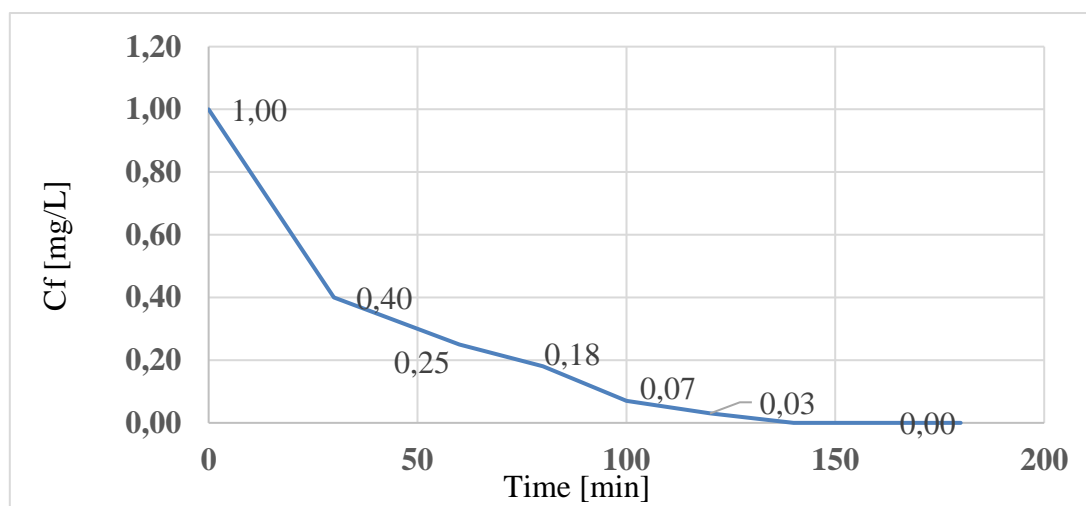
PhD student: *Scientific coordinator:*
Oana Stoian (Păunescu)   *Prof. habil. dr. ing. Cristina-Ileana Covaliu-Mierlă*

Figure 4.41. Concentration variation over time for removal of 1.00 mg/L Cu^{2+} using 0.02 g Fe_3O_4, pH 11.5.

Figure 4.41. shows the rapid decrease in the concentration of copper ions in wastewater. The concentration of copper ions reached 0.40 mg/L after 30 minutes, 0.25 mg/L after 60 minutes, 0.18 mg/L after 80 minutes, 0.07 mg/L after 100 minutes, 0.03 mg/L after 120 minutes of treatment time. It is found that complete removal of copper ions was achieved in a time period of 140 minutes.
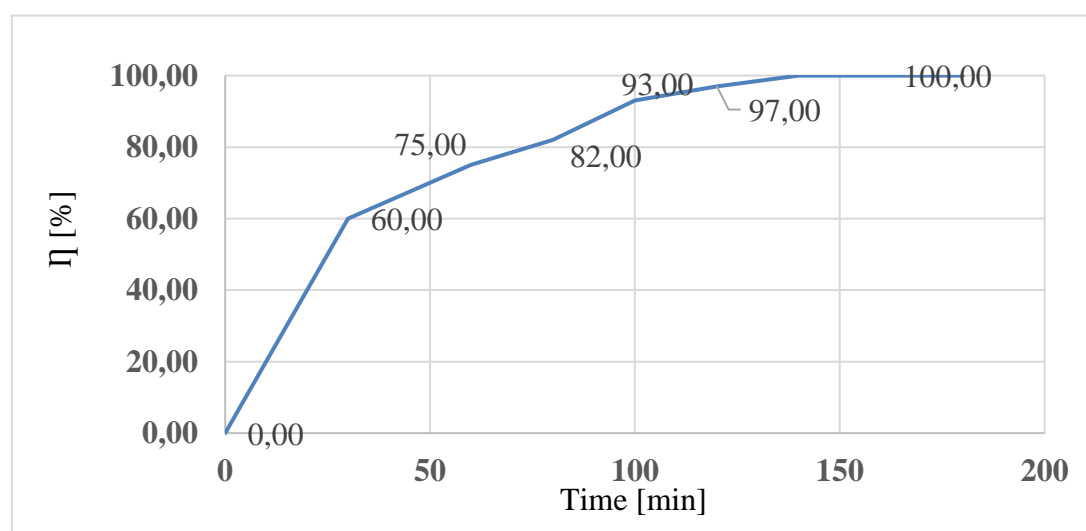

Figure 4.42. Variation of treatment efficiencies over time to remove 1.00 mg/L Cu^{2+} using 0.02 g Fe_3O_4, pH 11.5.

Figure 4.42. shows the rapid increase in wastewater treatment efficiencies. It can be seen that after only 30 minutes of treatment time, the efficiency reached 60.00%. It can be seen that the complete removal of copper ions was achieved in a time period of 140 minutes, reaching the treatment efficiency of 100.00 %.

In Figures 4.43. and 4.44. plot the variations of concentrations and treatment yields over time for the removal of 1.20 mg/L Cu(II) using 0.02 g of Fe_3O_4 oxide nanomaterial at pH 11.5 of wastewater.

30

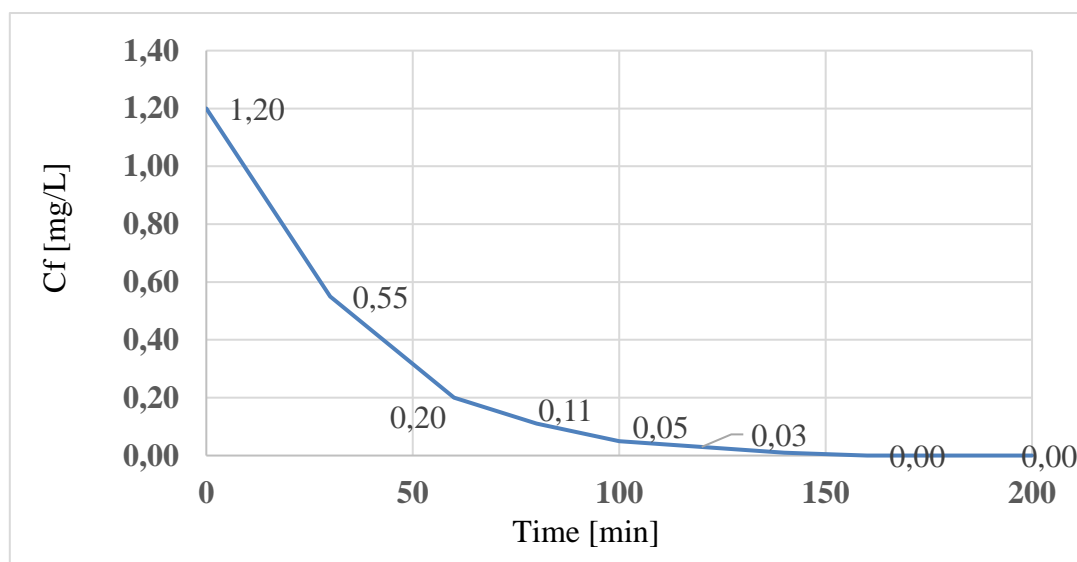*PhD student:*   *Scientific coordinator:*

Oana Stoian (Păunescu)   *Prof. habil. dr. ing. Cristina-Ileana Covaliu-Mierlă*

Figure 4.43. Concentration variation over time for removal of 1.20 mg/L Cu^{2+} using 0.02 g Fe_3O_4, pH 11.5.

Figure 4.43. shows the rapid decrease in the concentration of copper ions in the wastewater until they are completely removed in a time period of 160 minutes, a longer treatment time than for the removal of concentrations of 0.70 and 1.00 mg/L.
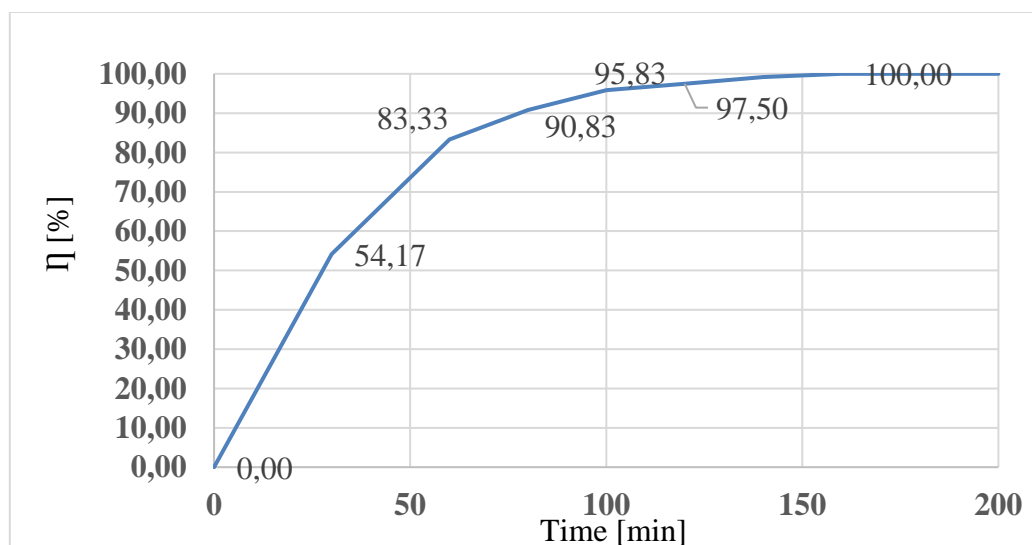

Figure 4.44. Variation of treatment efficiencies over time to remove 1.20 mg/L Cu^{2+} using 0.02 g Fe_3O_4, pH 11.5.

The increase in treatment efficiency proved to be rapid, as shown in Figure 4.44., with treatment efficiency reaching 54.17% after 30 minutes, 83.33% after 60 minutes, 90.83% after 80 minutes, 95.83% after 100 minutes, 97.50% after 120 minutes and reaching the maximum efficiency of 100.00% after 160 minutes of contact time.

Figure 4.45. plots the decrease in copper ion concentrations over the 270 minute time interval and Figure 4.46. plots the increase in treatment efficiencies from an initial concentration of 0.70 mg/L Cu(II) using 0.20 g Fe_3O_4 at pH 11.5 of the wastewater.

PhD student: *Scientific coordinator:*
Oana Stoian (Păunescu)   *Prof. habil. dr. ing. Cristina-Ileana Covaliu-Mierlă*
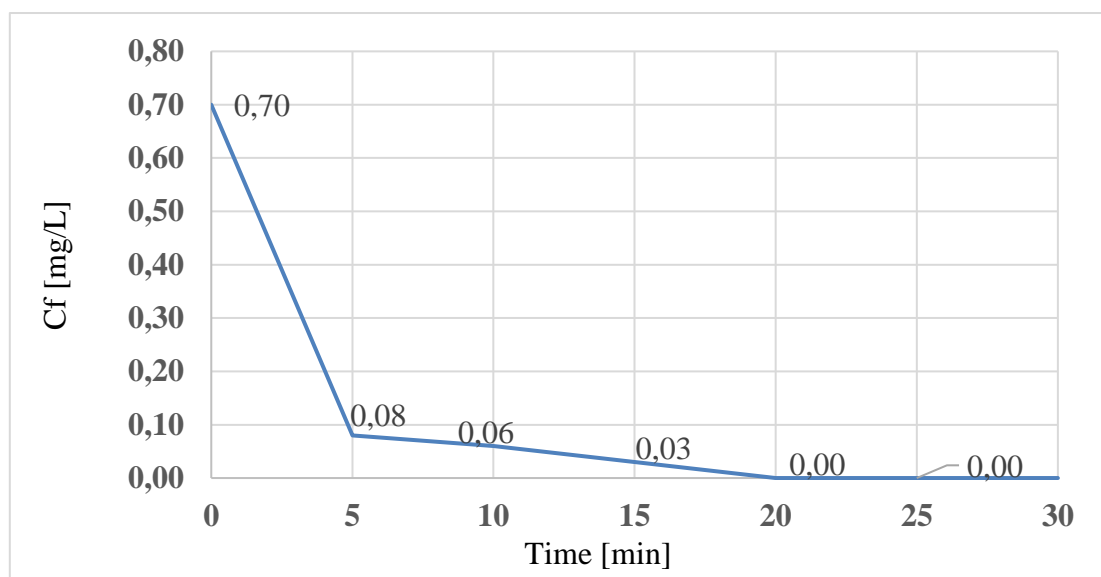
Figure 4.45. Concentration variation over time for the removal of 0.70 mg/L Cu^{2+} using 0.20 g Fe_3O_4, pH 11.5.

In Figure 4.45. shows a sharp drop in the concentration of copper ions in the wastewater to a concentration of 0.08 mg/L in a period of only 5 minutes. In the following time period, up to 20 minutes the decrease of copper ion concentrations is constant until they are completely removed from the wastewater.
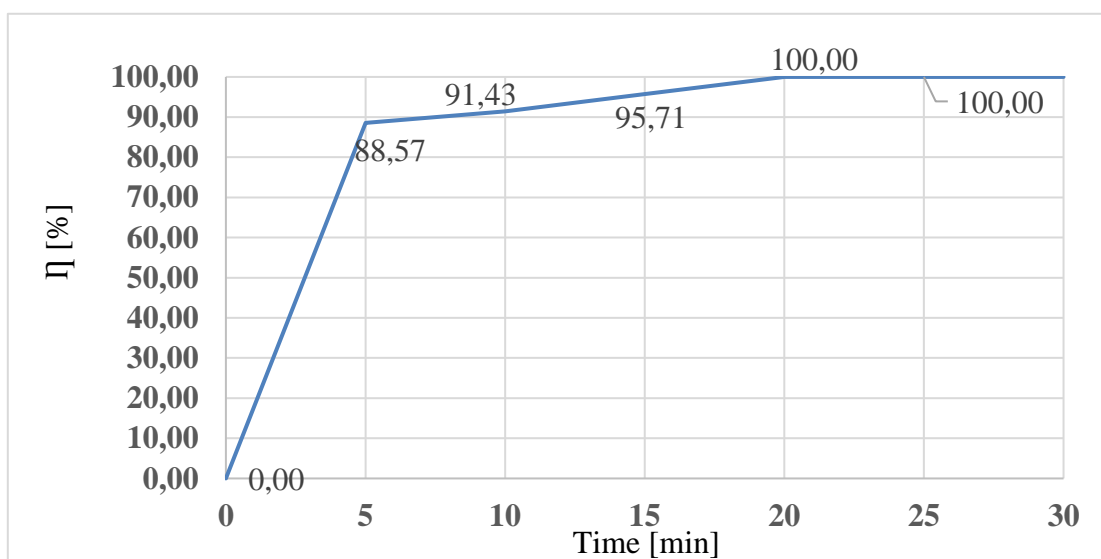
Figure 4.46. Variation of treatment efficiencies over time to remove 0.70 mg/L Cu^{2+} using 0.20 g Fe_3O_4, pH 11.5.

Figure 4.46. shows the high increase in treatment efficiency, up to 88.57 % in a short time (5 minutes). It can be seen that the treatment efficiency increases steadily until the maximum efficiency is reached (100.00 %).

In Figures 4.47. and 4.48. are plotted the variations of copper ion concentrations and treatment efficiencies over time for the removal of 1.00 mg/L from wastewater using 0.20 g magnetite at pH 11.5 of wastewater.

PhD student:
Oana Stoian (Păunescu)

Scientific coordinator:
Prof. habil. dr. ing. Cristina-Ileana Covaliu-Mierlă

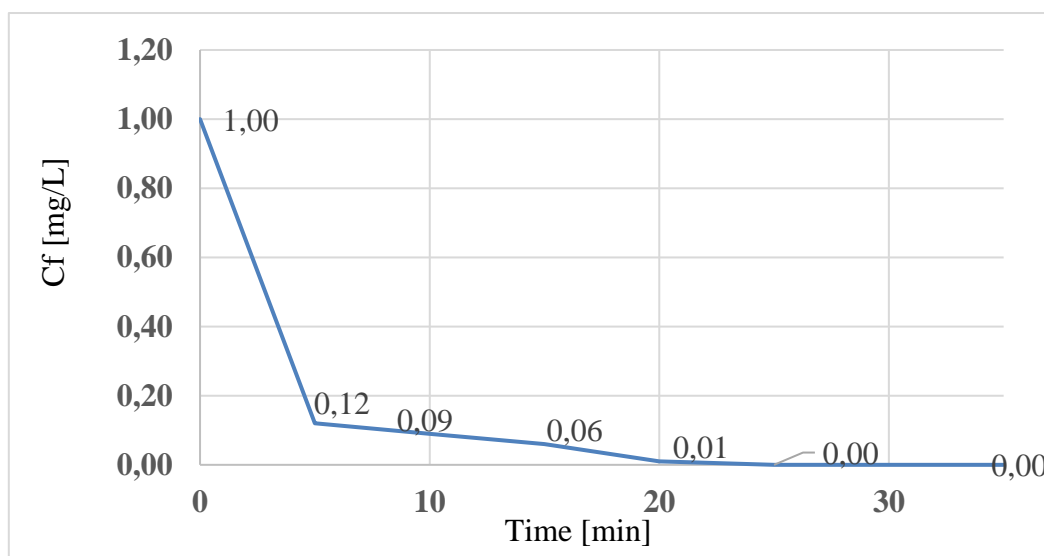**Figure 4.47.** Concentration variation over time for removal of 1.00 mg/L Cu^{2+} using 0.20 g Fe_3O_4, pH 11.5.

Figure 4.48. Variation of treatment efficiencies over time for the removal of 1.00 mg/L Cu^{2+} using 0.20 g Fe_3O_4, pH 11.5.

In the first 5 minutes of treatment time the concentration of copper ions decreases to 0.12 mg/L, and until the complete removal of copper ions from the wastewater, it decreases steadily until the treatment time of 25 minutes (Figure 4.47.). Also, in the first 5 minutes the treatment efficiency increases rapidly to 88.00%, reaching the maximum efficiency in 25 minutes (Figure 4.48.).

In Figures 4.49. and 4.50. are plotted the variations of concentrations and treatment efficiencies over time respectively for the removal of 1.20 mg/L Cu(II) using 0.20 g of Fe_3O_4 oxide nanomaterial at pH 11.5 of wastewater.

PhD student: *Scientific coordinator:*
Oana Stoian (Păunescu)   *Prof. habil. dr. ing. Cristina-Ileana Covaliu-Mierlă*

Figure 4.49. Concentration variation over time for removal of 1.20 mg/L Cu^{2+} using 0.20 g Fe_3O_4, pH 11.5.

Figure 4.49. shows the rapid decrease in the concentration of copper ions in wastewater. It can be seen that the complete removal of copper ions was achieved in only 25 minutes.
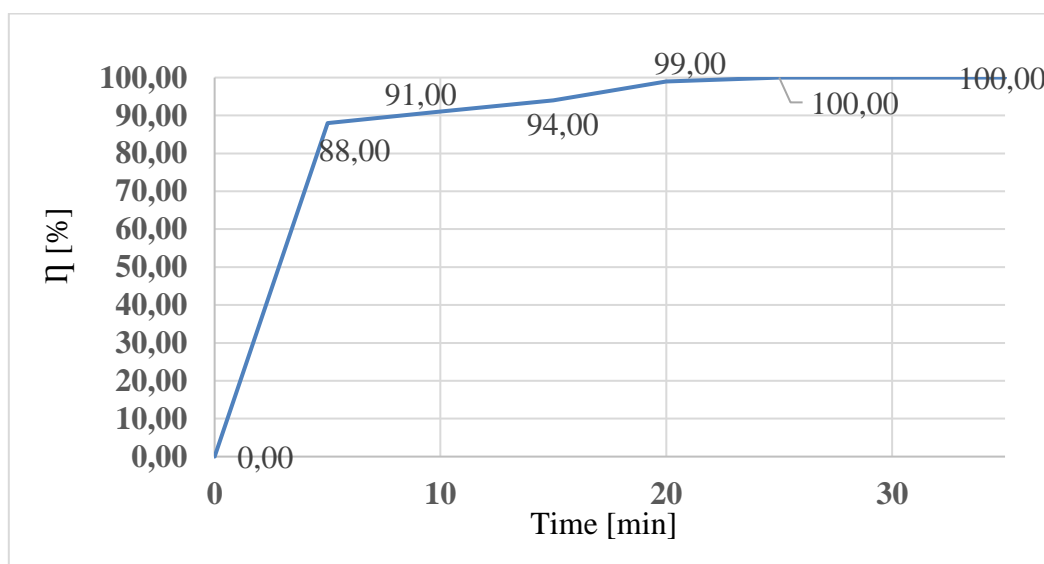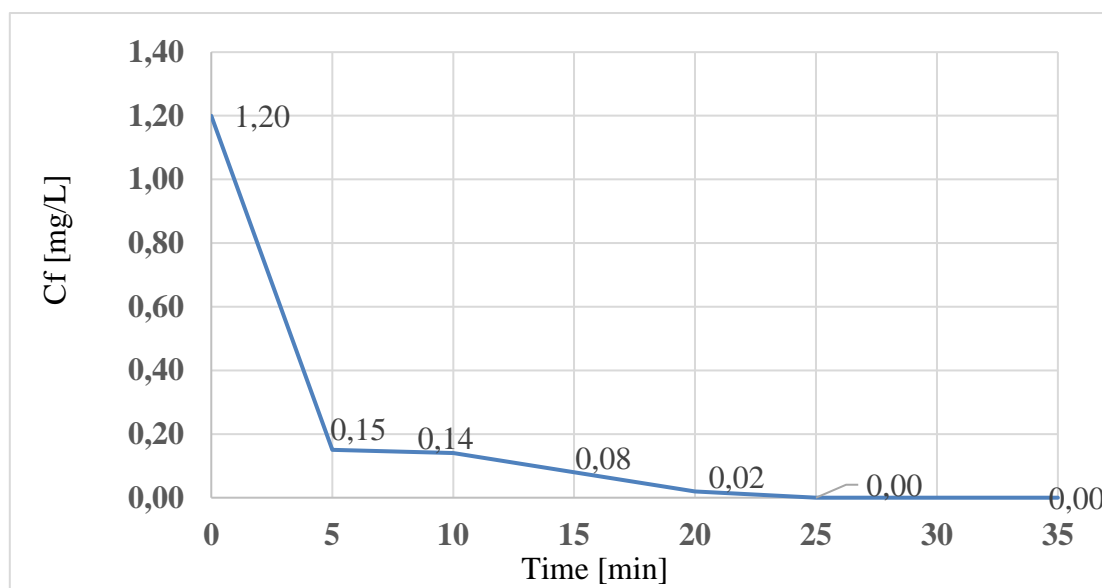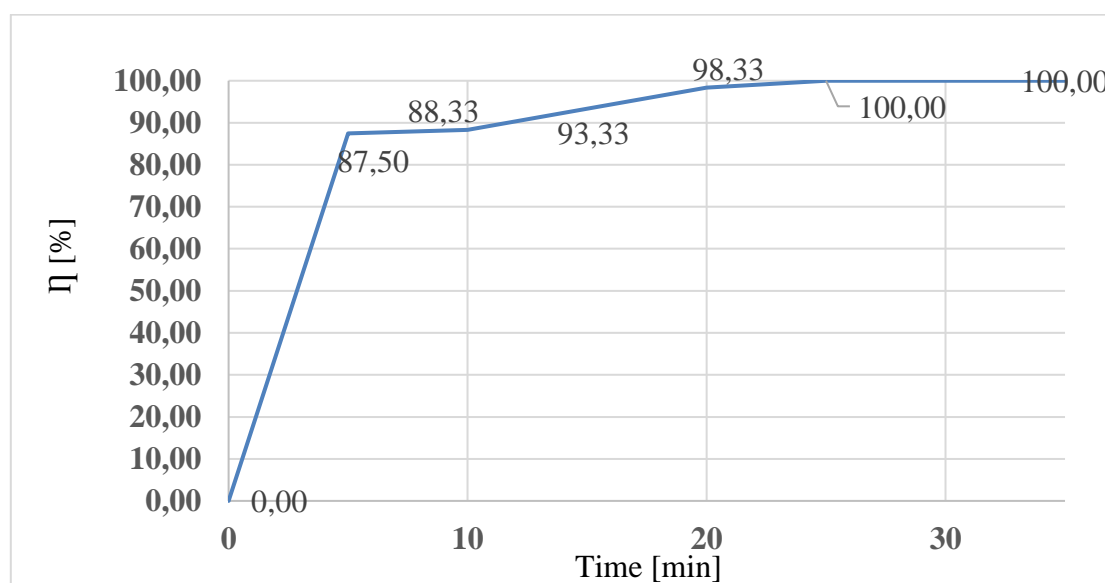

Figure 4.50. Variation of treatment efficiencies over time for the removal of 1.20 mg/L Cu^{2+} using 0.20 g Fe_3O_4, pH 11.5.

Figure 4.50. shows the rapid increase in wastewater treatment efficiencies and shows that the complete removal of copper ions was achieved in a time period of only 25 minutes, reaching a treatment efficiency of 100.00%.

In the following figures (Figures 4.51, 4.52 and 4.53) the time required for treatment for each experiment is plotted as a function of the concentration of copper ions in the wastewater and the quantities of magnetite used in the experimental investigations.

PhD student:
Oana Stoian (Păunescu)

Scientific coordinator:
Prof. habil. dr. ing. Cristina-Ileana Covaliu-Mierlă

Figure 4.51. Treatment time required for 0.70 mg/L Cu^{2+} concentration using 0.20; 0.02 and 0.01 g Fe_3O_4, pH 11.5.

Figure 4.51. shows that the time required to remove a copper ion concentration of 0.70 mg/L was a maximum of 20 minutes using 0.20 g of Fe_3O_4 oxide nanomaterial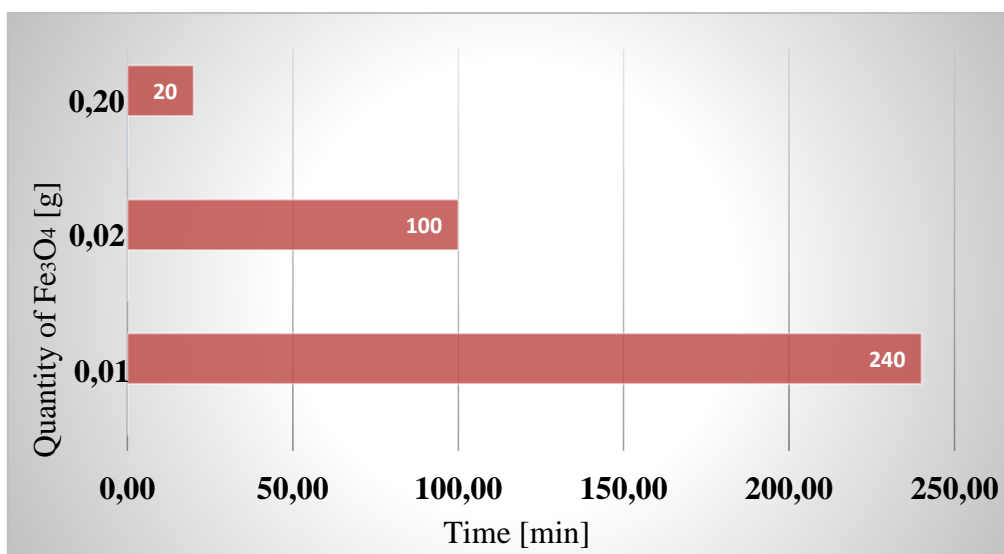, a maximum of 100 minutes using 0.02 g of Fe_3O_4 oxide nanomaterial and a maximum of 240 minutes using 0.01 g of Fe_3O_4 oxide nanomaterial.
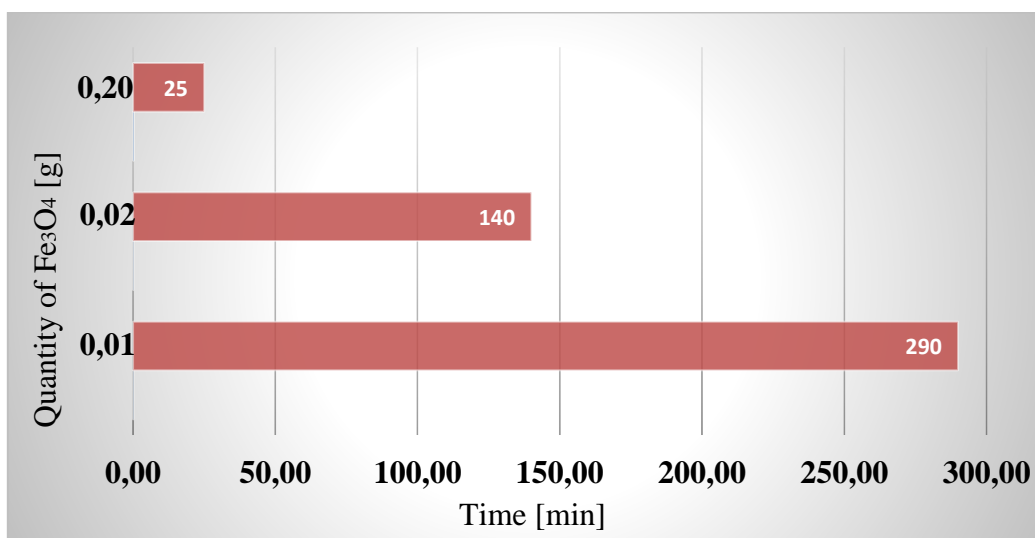
Figure 4.52. Treatment time required for 1.00 mg/L Cu^{2+} concentration using 0.20; 0.02 and 0.01 g Fe_3O_4, pH 11.5.

From Figure 4.52. it can be seen that the time required to remove a copper ion concentration of 1.00 mg/L was a maximum of 25 minutes using 0.20 g of Fe_3O_4 oxide nanomaterial, a maximum of 140 minutes using 0.02 g of Fe_3O_4 oxide nanomaterial and a maximum of 290 minutes using 0.01 g of Fe_3O_4 oxide nanomaterial. It can be seen that, compared to the results shown in Figure 4.51., the treatment time using an amount of 0.20 g of Fe_3O_4 oxide nanomaterial is close, while in the other two cases the required treatment time increased.

PhD student: *Scientific coordinator:*
Oana Stoian (Păunescu)   *Prof. habil. dr. ing. Cristina-Ileana Covaliu-Mierlă*

Figure 4.53. Treatment time required for 1.20 mg/L Cu^{2+} concentration using 0.20; 0.02 and 0.01 g Fe_3O_4, pH 11.5.

Figure 4.53. shows that the time required to remove a copper ion concentration of 1.20 mg/L was a maximum of 25 minutes using 0.20 g Fe_3O_4 oxide nanomaterial, a maximum of 160 minutes using 0.02 g Fe_3O_4 oxide nanomaterial and a maximum of 340 minutes using 0.01 g Fe_3O_4 oxide nanomaterial.
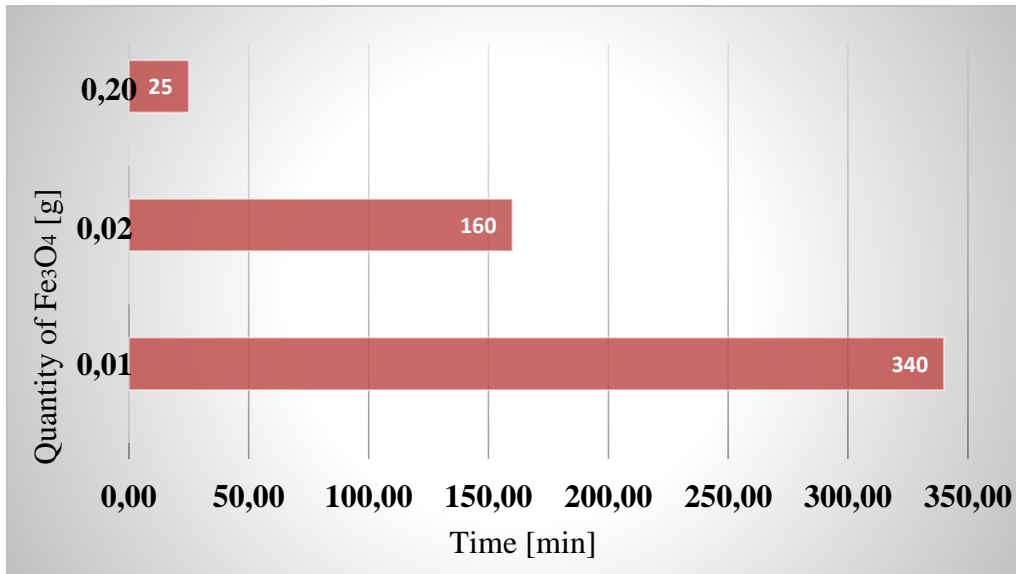
The removal efficiency of copper ions from wastewater was evaluated at two pH values, 8 and 11.5, in both cases reaching 100%, so the difference between them is the contact time. Figures 4.54. - 4.56. show the results for the three concentrations of copper ions (0.70, 1.00 and 1.20 mg/L respectively) as a function of wastewater pH and contact time required when using 0.10, 0.20 and 2.00 g/L magnetite (Fe_3O_4).

Figure 4.54. Influence of pH on removal of Cu^{2+} ions from wastewater for pollutant concentrations 0.70; 1.00; 1.20 mg/L when using 0.10 g/L Fe_3O_4.

PhD student: *Scientific coordinator:*
Oana Stoian (Păunescu)   *Prof. habil. dr. ing. Cristina-Ileana Covaliu-Mierlă*
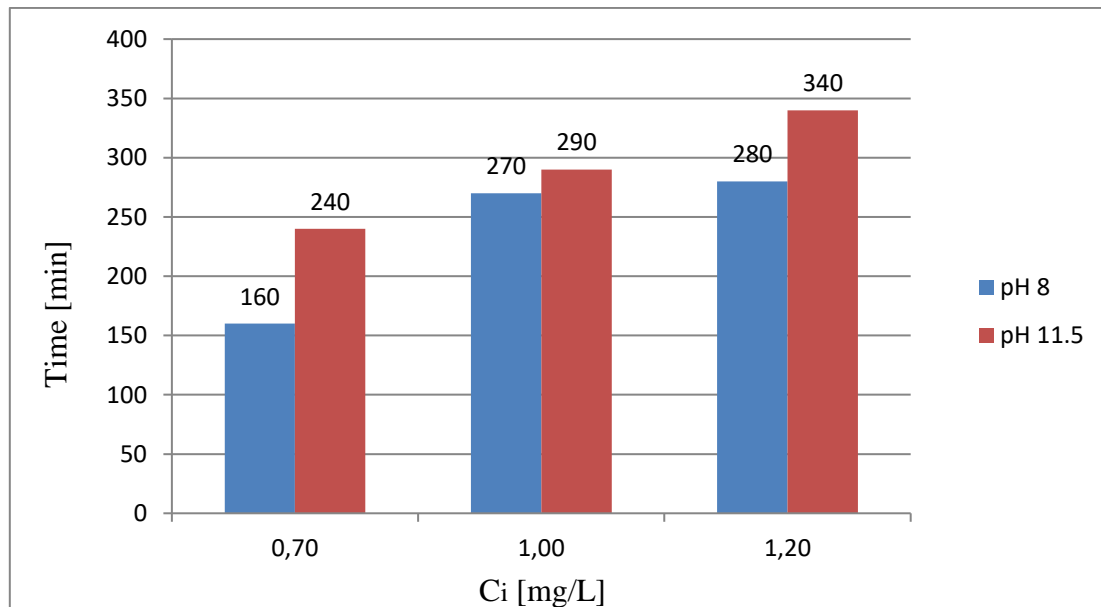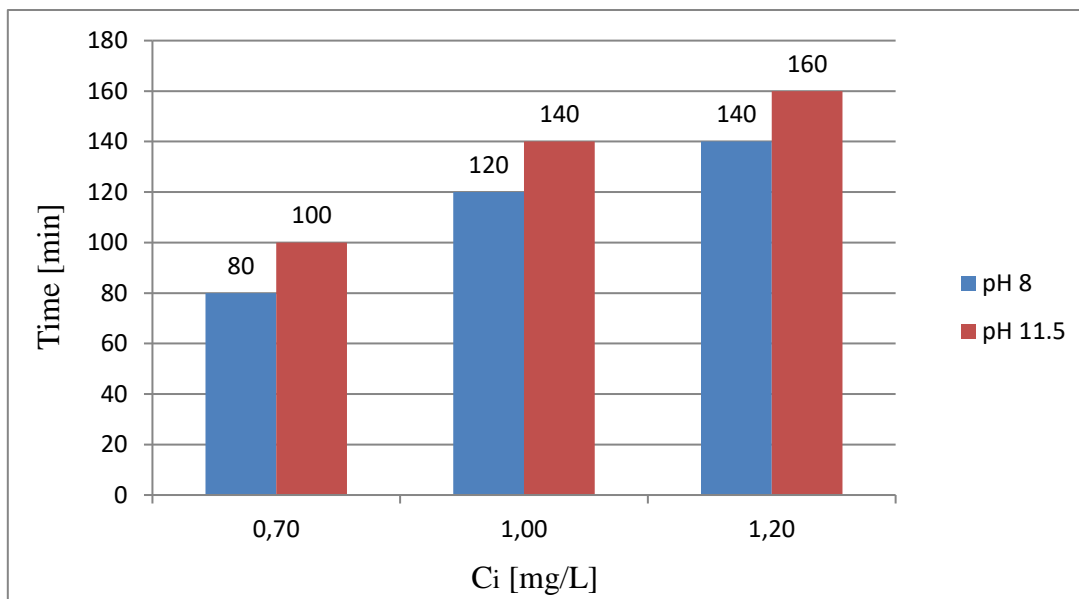
Figure 4.55. Influence of pH on removal of Cu^{2+} ions from wastewater for pollutant concentrations 0.70; 1.00; 1.20 mg/L when using 0.20 g/L Fe_3O_4.
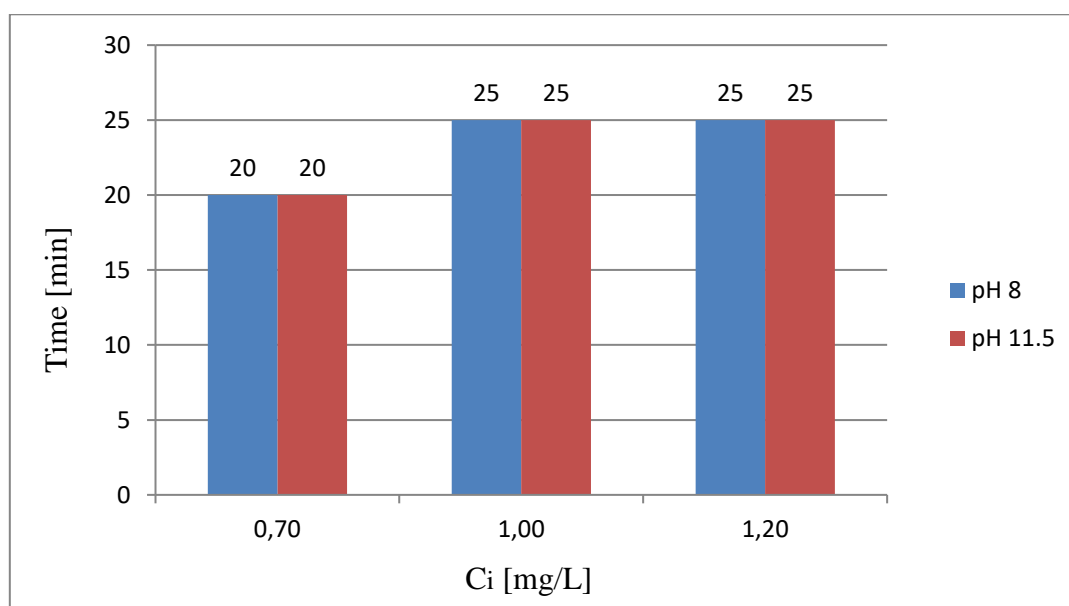
Figure 4.56. Influence of pH on the removal of Cu^{2+} ions from wastewater with pollutant concentrations of 0.70; 1.00; 1.20 mg/L when using 2.00 g/L Fe_3O_4.

From Figures 4.54. - 4.56. it can be seen that pH is an important parameter in this treatment process when the amount of magnetite used is lower because increasing the pH value to 11.5 leads to a higher treatment time, while keeping it at 8 leads to a lower treatment time. As the amount of magnetite used increases, the difference between the treatment time at the two pH values decreases until the required treatment time equalises (when using 2.00 g/L Fe_3O_4).

The influence of treatment time on wastewater at pH 8 and 11.5 has been studied and can be seen in Figures 4.57 - 4.59.

PhD student: *Scientific coordinator:*
Oana Stoian (Păunescu)   *Prof. habil. dr. ing. Cristina-Ileana Covaliu-Mierlă*

Figure 4.57. Influence of treatment time on removal of Cu^{2+} ions from wastewater for concentration 0.70 mg/L.

Figure 4.58. Influence of treatment time on removal of Cu^{2+} ions from wastewater for concentration 1.00 mg/L.

Figure 4.59. Influence of treatment time on removal of Cu^{2+} ions from wastewater for concentration 1.20 mg/L.
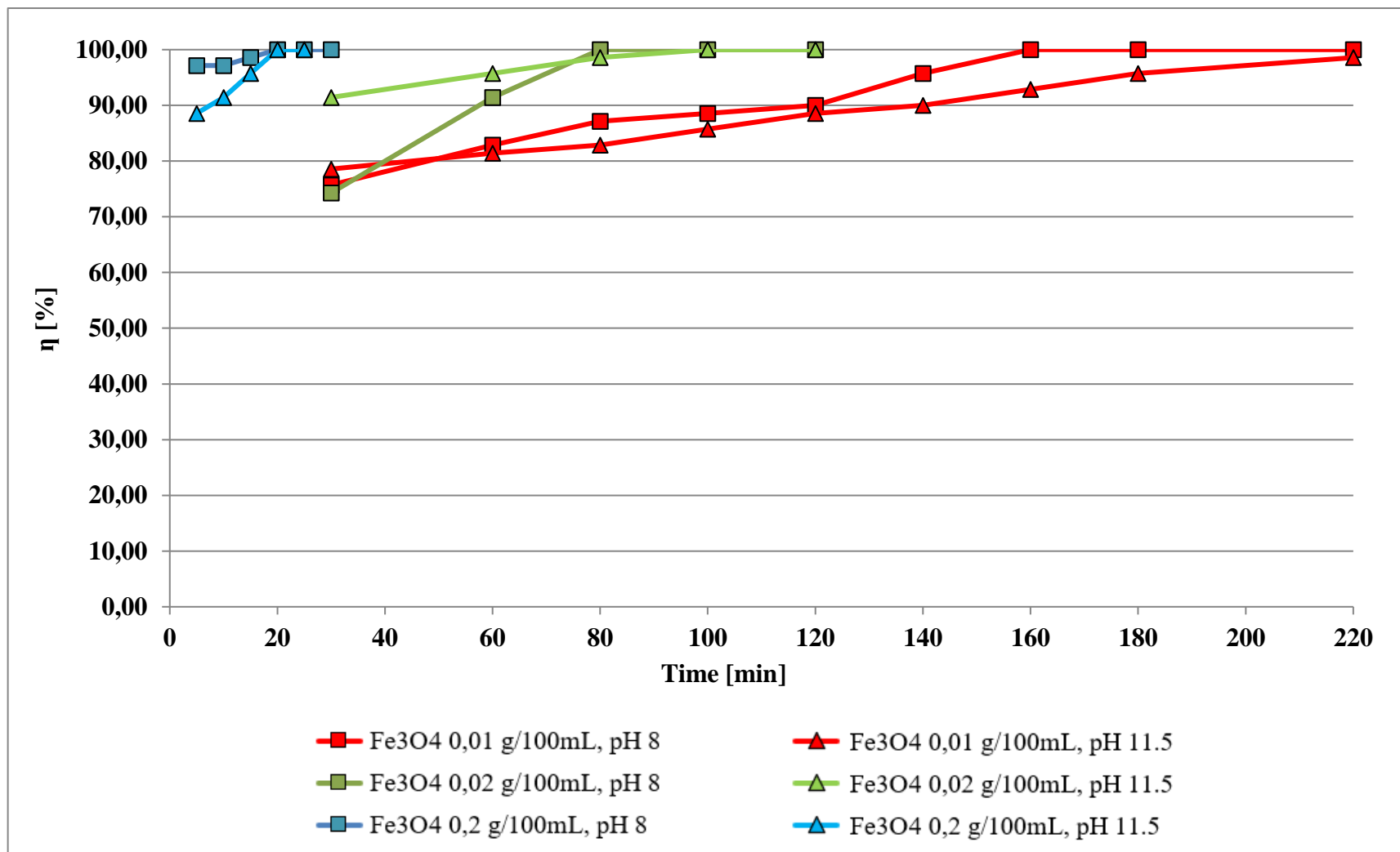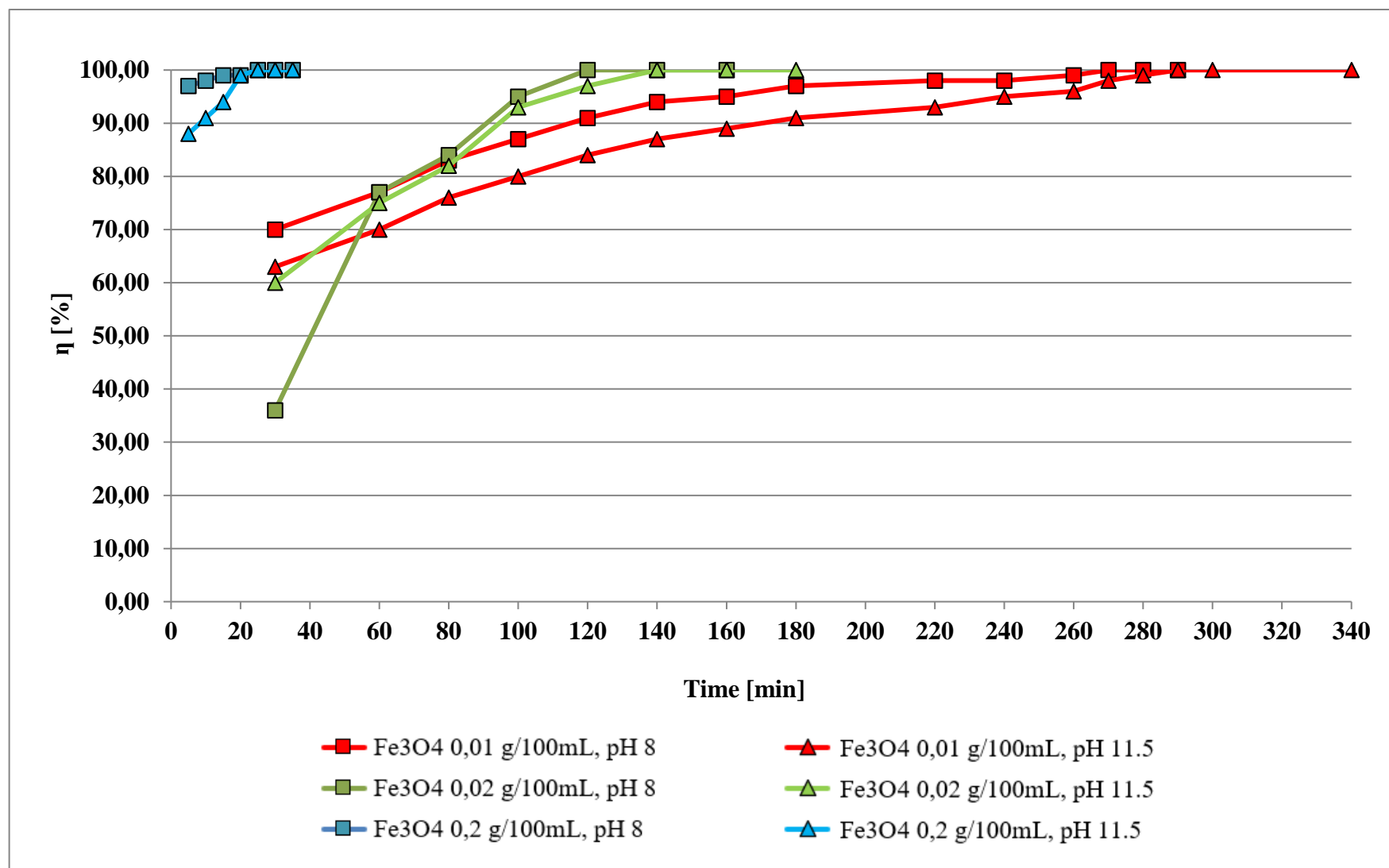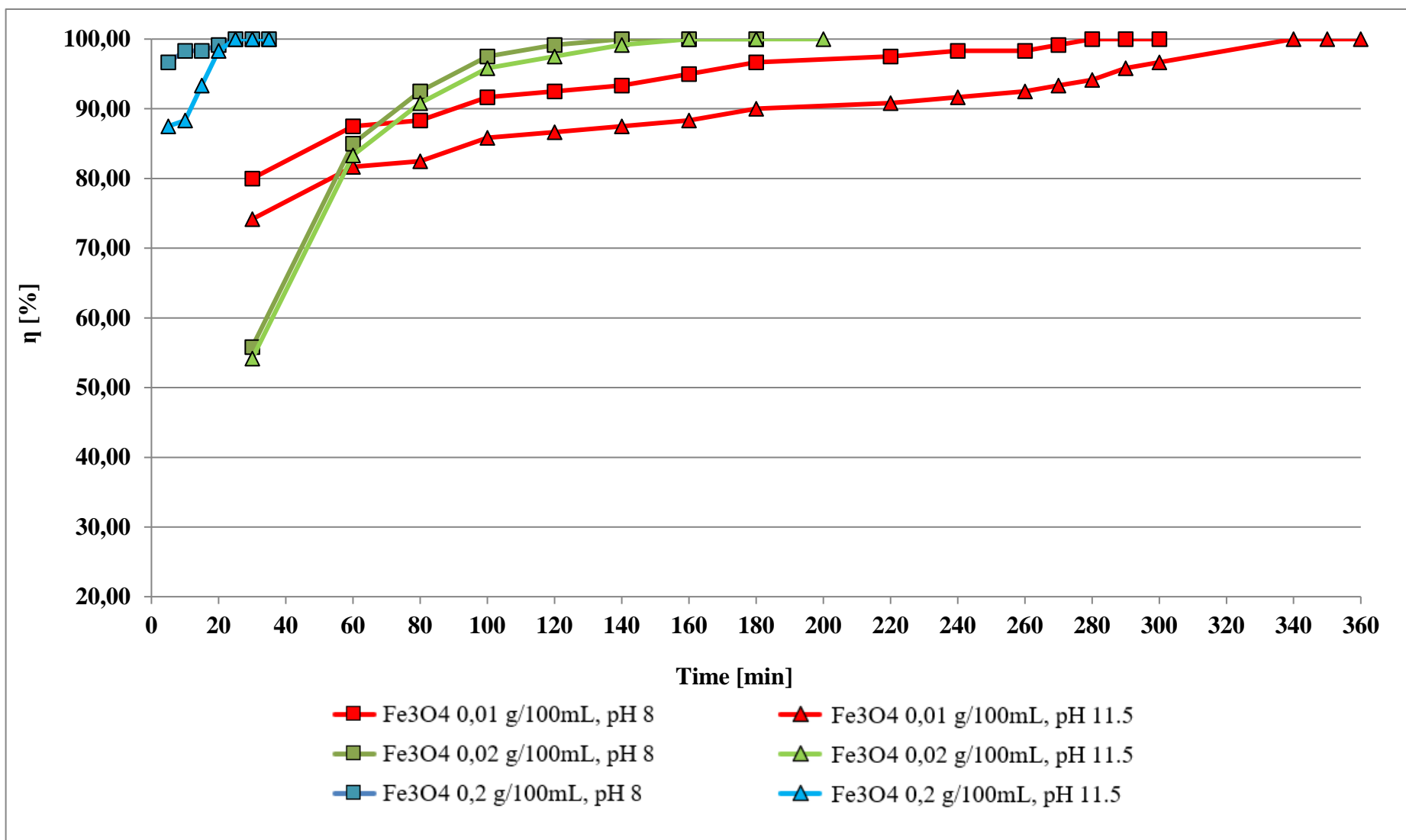
As can be seen in Figures 4.57. - 4.59., a magnetite quantity of 0.01g removes copper ions from wastewater in a longer period of time than a magnetite quantity of 0.20g which also leads to maximum treatment yields, but in a much shorter time. This is due to the fact that by using a larger amount of magnetite in this process, the existing adsorption centres on the surface of the magnetite nanoparticles are more numerous and thus the copper ions are adsorbed faster.

4.1.2.2. Lead (Pb^{2+}) ions adsorption experiments

Adsorption experiments to remove lead ions from wastewater were performed using magnetite (Fe_3O_4) as adsorbent nanomaterial. Wastewater was prepared from a 1000 mg/L lead standard solution at concentrations of 0.70; 1.00; 1.20; 1.45 and 1.64 mg/L Pb^{2+}. The amount of magnetite used for these experiments was 0.20 g. The pH was set at 4 and 6. The homogenization of the wastewater with the adsorbent nanomaterial was performed using an ultrasonic bath and a mechanical stirrer. The concentrations of lead ions in the samples (Figure 4.60.) were determined using the PhotoLab S12 photometer. The yields were calculated with the formula shown in equation (25).
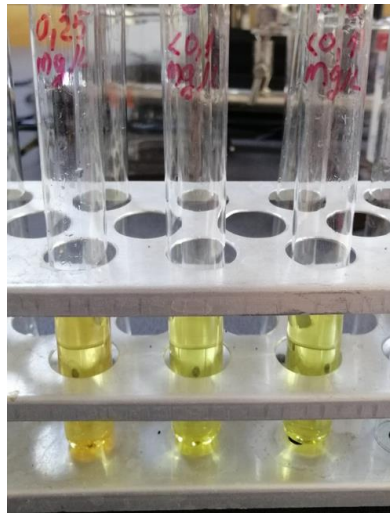
Figure 4.60. Preparation of solutions for the measurement of Pb^{2+} ions during treatment processes.

The equilibrium adsorption amount of Pb(II) ions was calculated using the following formula:

$$q_e = \frac{(C_i - C_e) * V}{W} \qquad (26)$$

where: q_e, the amount of adsorption at equilibrium [mg/g]; C_i, initial concentration of Pb(II) ions [mg/L]; C_e, equilibrium concentration of Pb(II) ions [mg/L]; V, volume of synthetic wastewater [L]; W, amount of magnetite [g].

The results obtained with the PhotoLab S12 photometer were determined according to ISO 8466-1 and DIN 38402 A51 (10 mm cell) with a measuring range of 0.1-5.0 mg/L Pb^{2+}.

The removal efficiency of lead ions from wastewater was evaluated at two pH values, 4 and 6. The results are shown in Figure 4.61.

a) Ci : 0,70 mg/L

b) Ci : 1,00 mg/L

c) Ci :1,20 mg/L

PhD student: *Scientific coordinator:*
Oana Stoian (Păunescu)   *Prof. habil. dr. ing. Cristina-Ileana Covaliu-Mierlă*
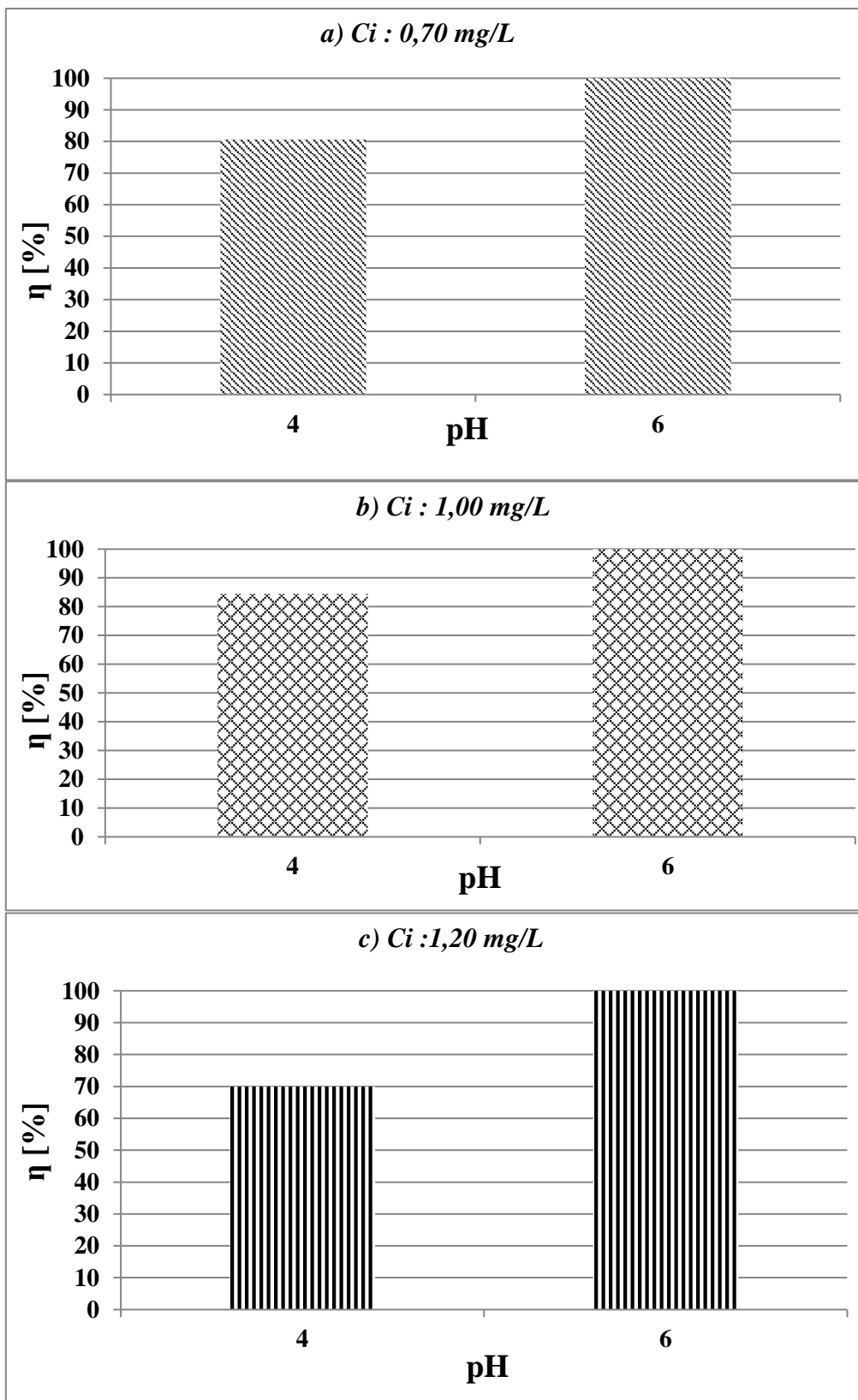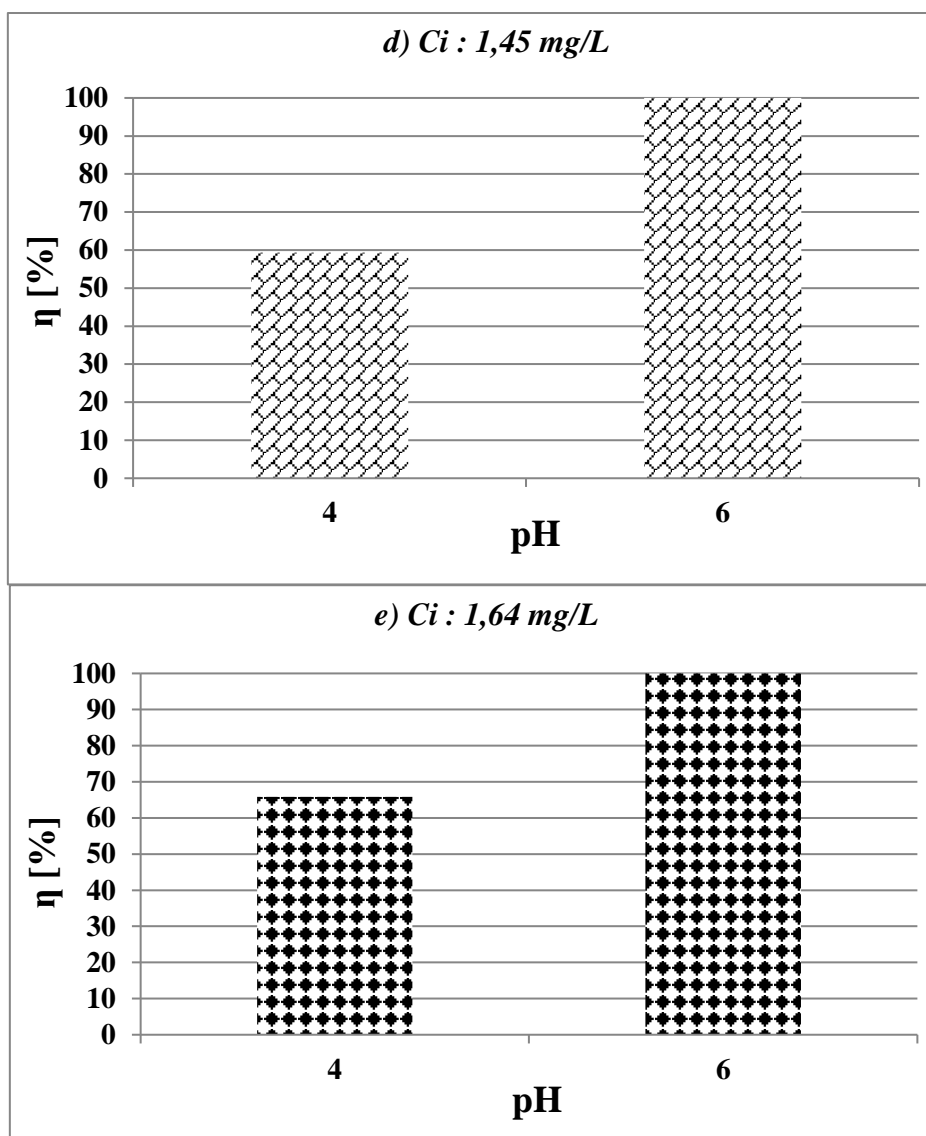
Figure 4.61. Effect of pH on the removal of Pb^{2+} ions from wastewater (Pb(II) ion concentrations: 0.70 (a); 1.00 (b); 1.20 (c); 1.45 (d); 1.64 (e) mg/L).

It can be seen that in the case of pH 4, the treatment efficiency reaches up to 84.40%, while at pH 6, yields of 100% were obtained. It is also observed that as the initial concentration of lead ions increases, the required contact time increases more in the case of pH 4 (from 180 to 420 minutes) than in the case of pH 6 (from 90 to 270 minutes). In the case of pH 6 the process is faster (up to 270 minutes) than in the case of pH 4 (up to 420 minutes). Experiments conducted at pH values higher than 6 do not show certainty that lead ions will be removed from wastewater by the adsorption process.

In the case of the interaction of lead ions with the nanomaterial magnetite, the literature shows that at pH greater than 6.5, Pb(OH)$_2$ is the dominant species, and at pH less than 6.5 we have Pb^{2+} and Pb(OH)$^+$ [319]. The reaction below demonstrates that the surface of the adsorbent nanomaterial can undergo protonation or deprotonation [320, 321]:

$$H_2O + M - O^- < \frac{H^+}{OH^-} > M - OH < \frac{H^+}{OH^-} > M - OH_2^+ \tag{27}$$

PhD student: *Scientific coordinator:*

Oana Stoian (Păunescu)   *Prof. habil. dr. ing. Cristina-Ileana Covaliu-Mierlă*
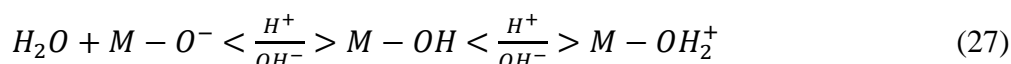
If the wastewater medium is basic, there will be a fairly strong electrostatic attraction between the surface of the negatively charged magnetite nanomaterial and the lead ions. When the pH of the wastewater decreases, the number of centres that are positively charged will increase and the number of centres that are negatively charged will decrease. Thus, the adsorption of lead ions is not favoured due to electrostatic repulsion. In an acidic environment, excess hydrogen ions present will compete with lead ions for adsorption centres and therefore the treatment efficiency is lower.

In water, magnetite nanoparticles show surface hydroxyl groups (Fe - OH). Depending on the pH of the wastewater, protonation or deprotonation of the hydroxyl groups is observed. At pH<pHpzc the nanoparticle surface is positively charged ($FeOH^{2+}$), and at pH>pHpzc the nanoparticle surface is negatively charged (FeO^-) [301]. As wastewater pH increases from 4.0 to 6.0, the adsorption of lead ions increases due to electrostatic attractions occurring between Fe^-O and Pb^{2+}. The low adsorption of lead ions at pH 4 is due to the competition for adsorption sites on the surface of magnetite nanoparticles available between H_3O^+ and Pb^{2+}.

The effect of contact time on wastewater at pH 4 and 6 has been studied and can be seen in Figures 4.62. and 4.63.
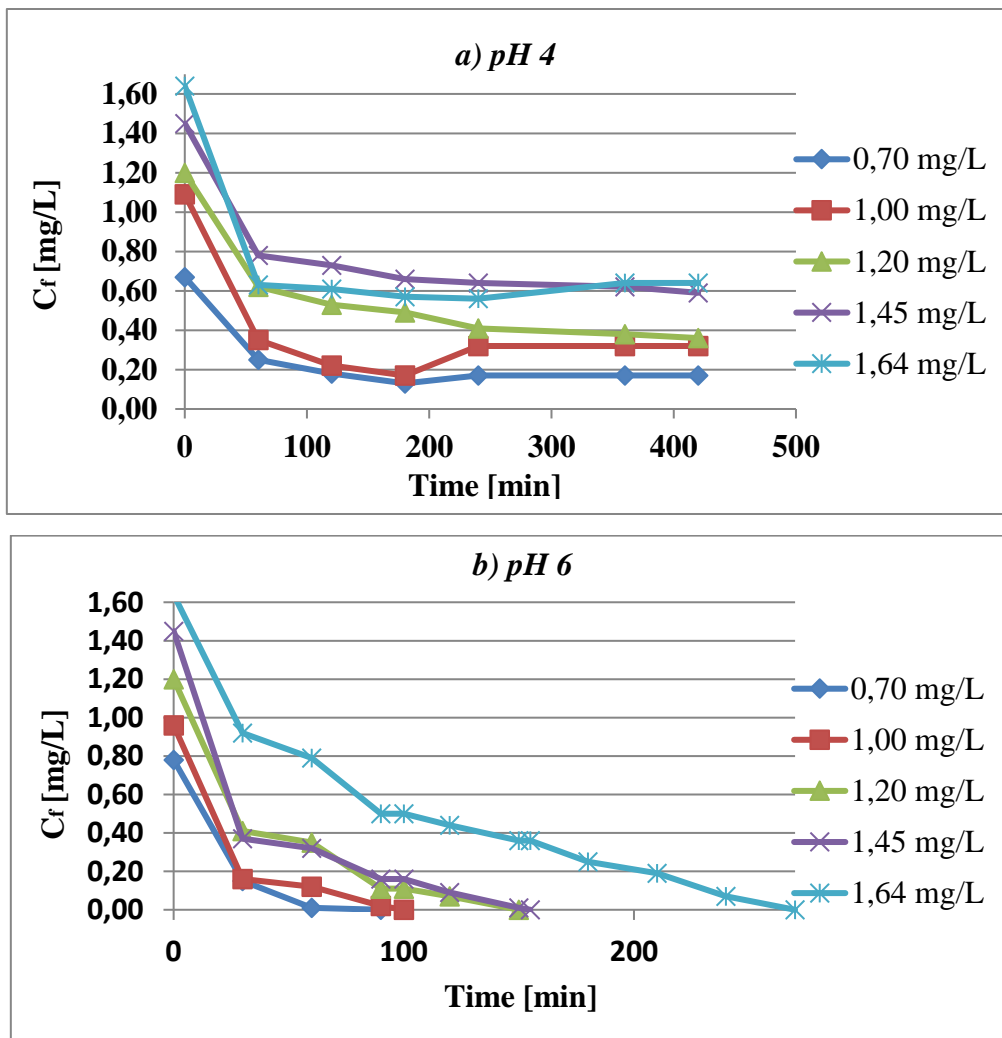

Figure 4.62. Final wastewater Pb^{2+} ion concentrations as a function of treatment time at pH 4 (a) and pH 6 (b).

PhD student:
Oana Stoian (Păunescu)

Scientific coordinator:
Prof. habil. dr. ing. Cristina-Ileana Covaliu-Mierlă
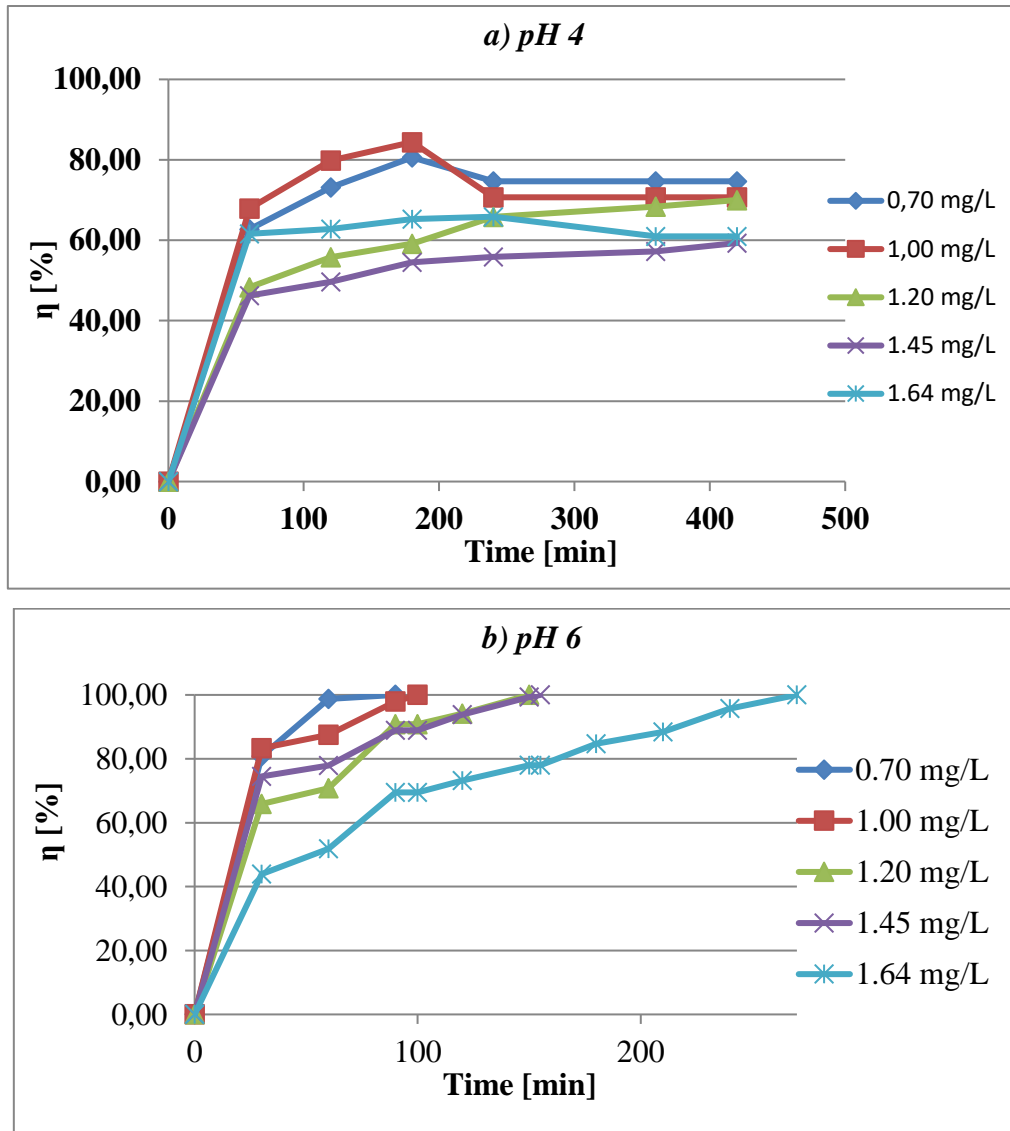
Figure 4.63. Treatment yields as a function of treatment time at pH 4 (a) and pH 6 (b).

From Figures 4.62. a) and b) it can be seen that in the case of pH 6 the equilibrium concentration is reached in a shorter treatment time (90 min for initial concentration 0.70 mg/L, 150 min for initial concentration 1.20 mg/L) than in the case of pH 4 (180 min for concentration 0.70 mg/L, 420 min for initial concentration 1.20 mg/L). Figures 4.63. a) and b) plot the treatment yields against the required contact time. The highest treatment efficiency for pH 4 was 84.40 %. For pH 6 of water it can be seen that the treatment efficiencies were maximum for all pollutant concentrations studied.

Adsorption isotherms

The experimental data were used for the Langmuir and Freundlich models (Figures 4.64., 4.65. and 4.66.). Adsorption isotherm modelling provides information about the adsorption process, surface properties of the adsorbent nanomaterial and its affinities.

Table 4.23. shows the Langmuir and Freundlich adsorption isotherm constants from the graphs in Figures 4.64. - 4.66.

PhD student: *Scientific coordinator:*
Oana Stoian (Păunescu)   *Prof. habil. dr. ing. Cristina-Ileana Covaliu-Mierlă*

Table 4.23. Adsorption isotherm constants

	Langmuir			Freundlich			
Adsorbent	K_L [L/mg]	R_L	R^2	1/n	n	K_F [mg/g]	R^2
Fe₃O₄	0.60	0.68	0.93	0.10	9.25	1.45	0.75

Due to the fact that the R_L value is between 0 and 1, we understand that the adsorption is favorable and that there is an effective interaction between the Fe_3O_4 adsorbent nanomaterial and lead ions according to the Langmuir model.

The Freundlich isotherm explains monolayer and multilayer adsorption. The values of K_F and n can be determined using a linear equation resulting from plotting the log q_e/log C_e curve (Figure 4.66.). Thus, the value of 1/n must be between 0 and 1 in order to apply the Freundlich model. In the present case, the value of 1/n is 0.10, which indicates that the adsorption process is favourable.
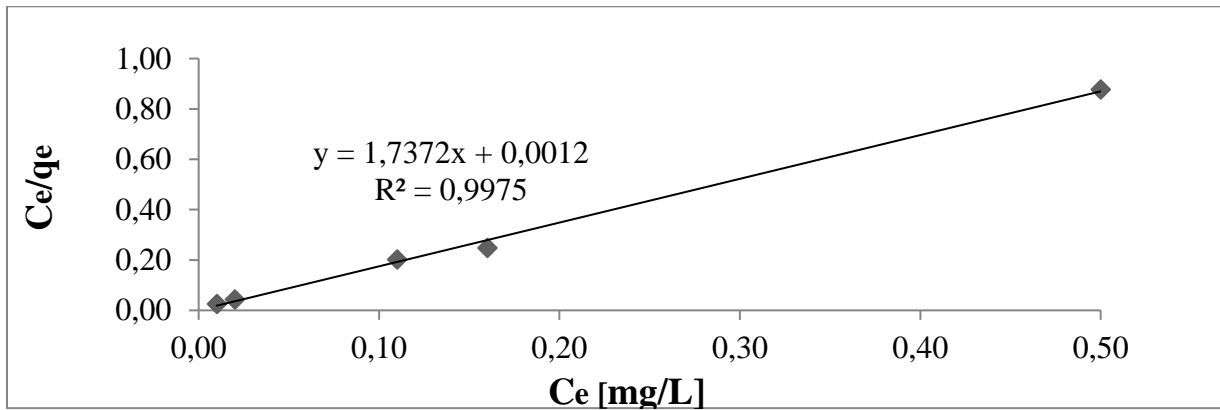

Figure 4.64. Adsorption isotherm for different Pb^{2+} ion concentrations (0.70; 1.00; 1.20; 1.45; 1.64 mg/L).
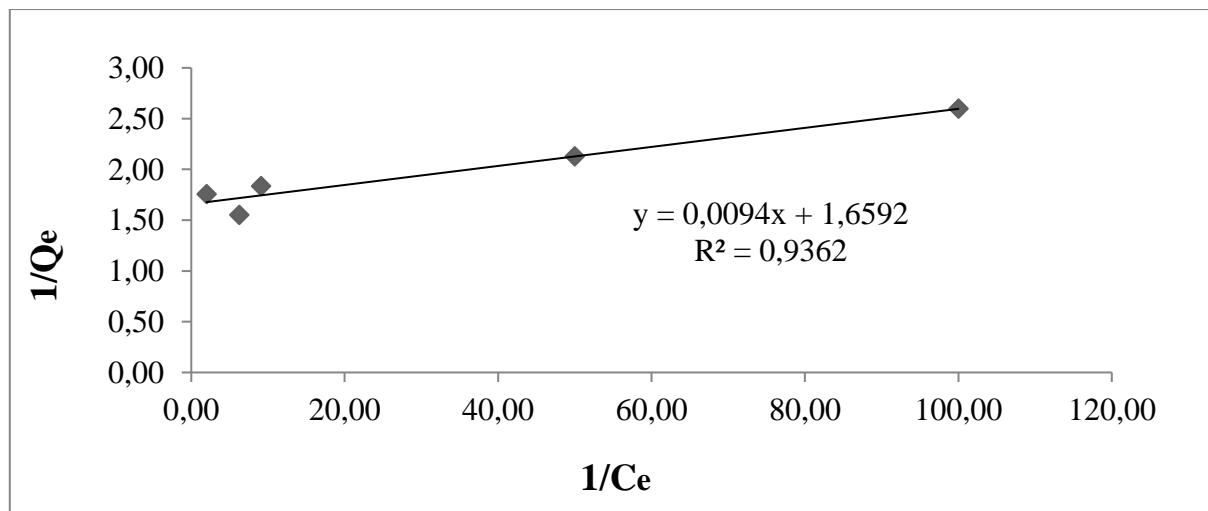
Figure 4.65. Langmuir model for the adsorption of Pb^{2+} ions in wastewater.

PhD student: *Scientific coordinator:*
Oana Stoian (Păunescu)   *Prof. habil. dr. ing. Cristina-Ileana Covaliu-Mierlă*
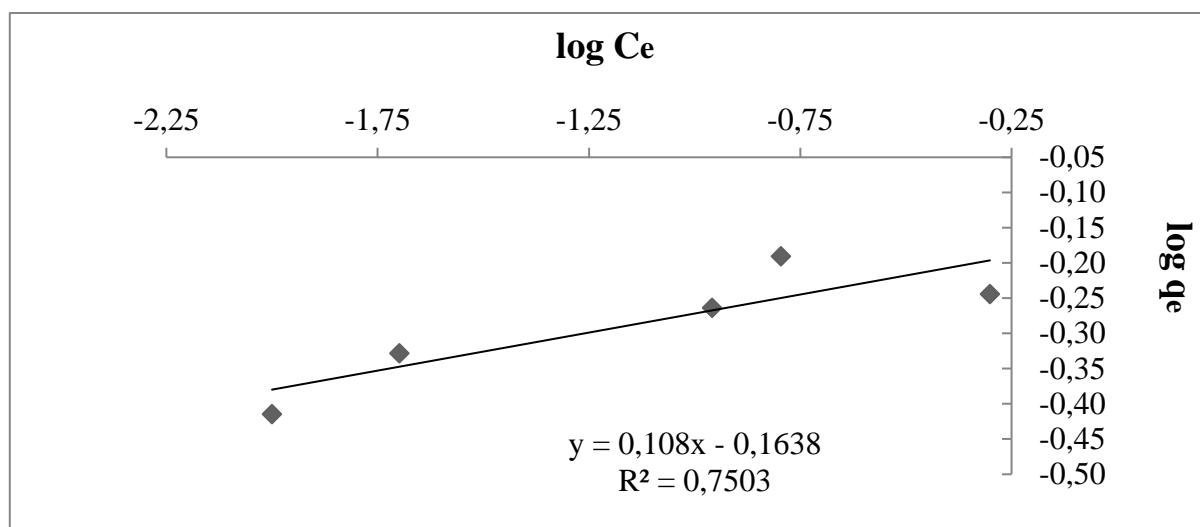
Figure 4.66. Freundlich model for the adsorption of Pb^{2+} ions in wastewater.

4.1.2.3.Manganese (Mn^{2+}) ions adsorption experiments

Adsorption experiments were performed as for copper and lead ions. The concentrations of pollutant prepared were 0.70, 1.00, 1.20, 1.40, 1.60, 1.80 and 2.00 at pH 8 and 0.70; 1.00 and 1.20 mg/L at pH 11.5 respectively. The amount of magnetite used was 0.20 g. Figure 4.67. shows the preparation of the samples taken for the determination of manganese concentrations in the wastewater.
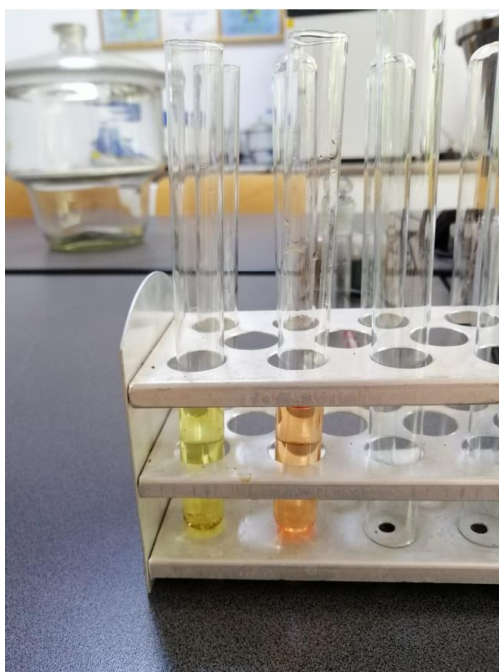
Figure 4.67. Preparation of solutions for the measurement of Mn^{2+} ions during treatment processes.

The results obtained with the PhotoLab S12 photometer were determined according to ISO 8466-1 and DIN 38402 A51 (10 mm cell) with a measuring range of 0.5 - 10.0 mg/L Mn^{2+}.

PhD student: *Scientific coordinator:*
Oana Stoian (Păunescu)   *Prof. habil. dr. ing. Cristina-Ileana Covaliu-Mierlă*

In Figures 4.68. and 4.69. are plotted the treatment yields at pH 8 and 11.5 respectively.
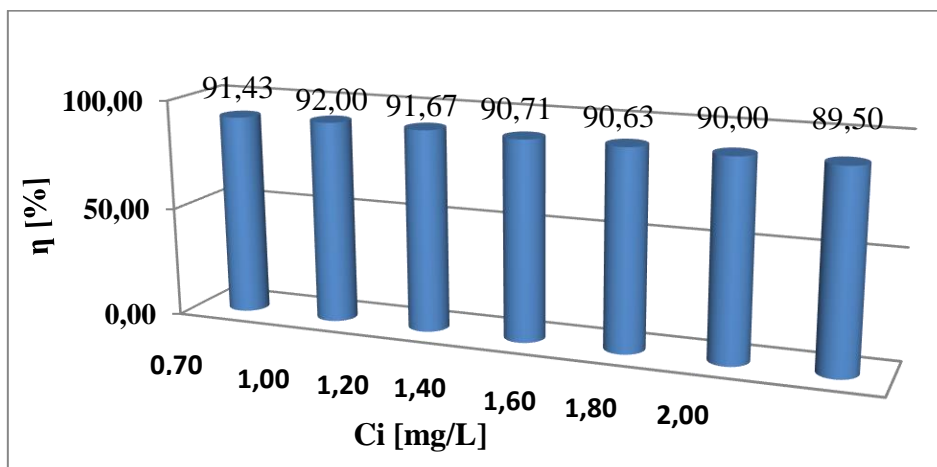
Figure 4.68. Treatment efficiency of water containing Mn^{2+} ions at pH 8.
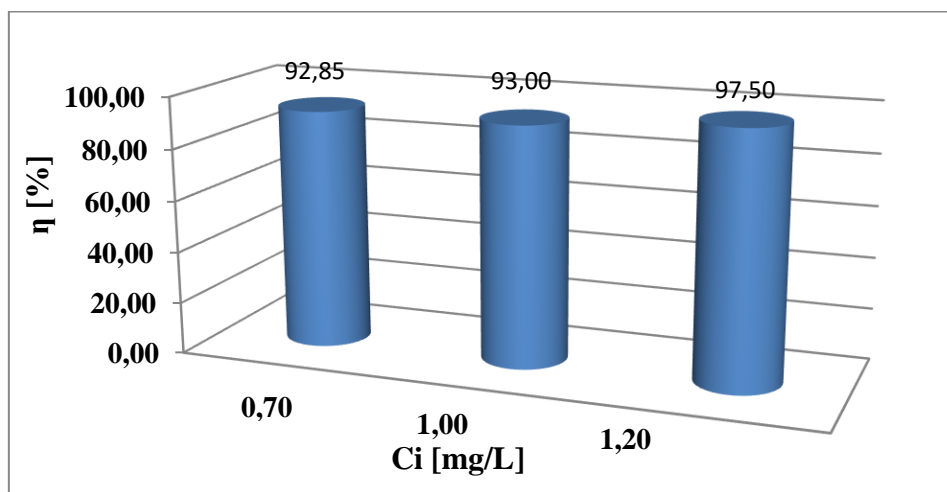
Figure 4.69. Treatment efficiency of water containing Mn^{2+} ions at pH 11.5.

The pH of the water is very important when talking about the pollutant-adsorbent system. Tests were carried out at different pH values (8 and 11.5) and different pollutant concentrations (0.70 - 2.00 mg/L). In the case of manganese ion removal at a concentration of 0.70 mg/L the treatment efficiency increases with increasing pH value from 91.4% to 92.8%, at a concentration of 1.00 mg/L the treatment efficiency increases with increasing pH value from 91.0% to 93.0% and at a concentration of 1.20 mg/L the treatment efficiency increases with increasing pH value from 90.0% to 97.5%. These observations lead to the conclusion that a basic medium is the most favourable for the removal of manganese ions from industrial wastewater.

Adsorption isotherms

Table 4.25. shows adsorption isotherm constants using magnetite (Fe_3O_4) as adsorbent nanomaterial for manganese ion removal. The constants are calculated using the graphs below (Figures 4.70., 4.71.).

PhD student: *Scientific coordinator:*
Oana Stoian (Păunescu)   *Prof. habil. dr. ing. Cristina-Ileana Covaliu-Mierlă*

Table 4.25. Langmuir and Freundlich adsorption isotherm constants

Adsorbent	Pollutant	LANGMUIR ISOTHERM			FREUNDLICH ISOTHERM			
		K_L [L/mg]	R_L	R^2	n	$1/n$	K_F [mg/g]	R^2
Fe_3O_4	**Manganese**	3,34	0,23	0,9818	1,27	0,78	3,15	0,9802
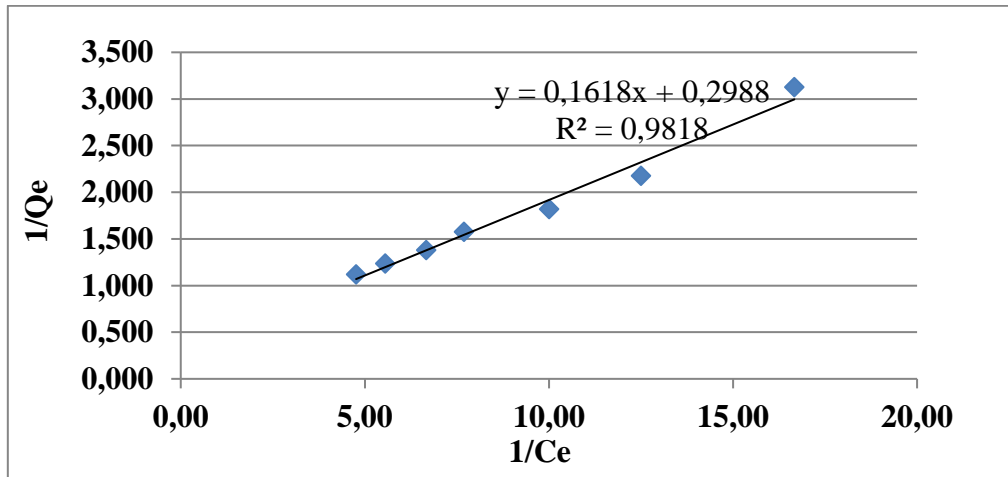
Figure 4.70. Graphical representation of the Langmuir model for Mn^{2+} ions in wastewater.
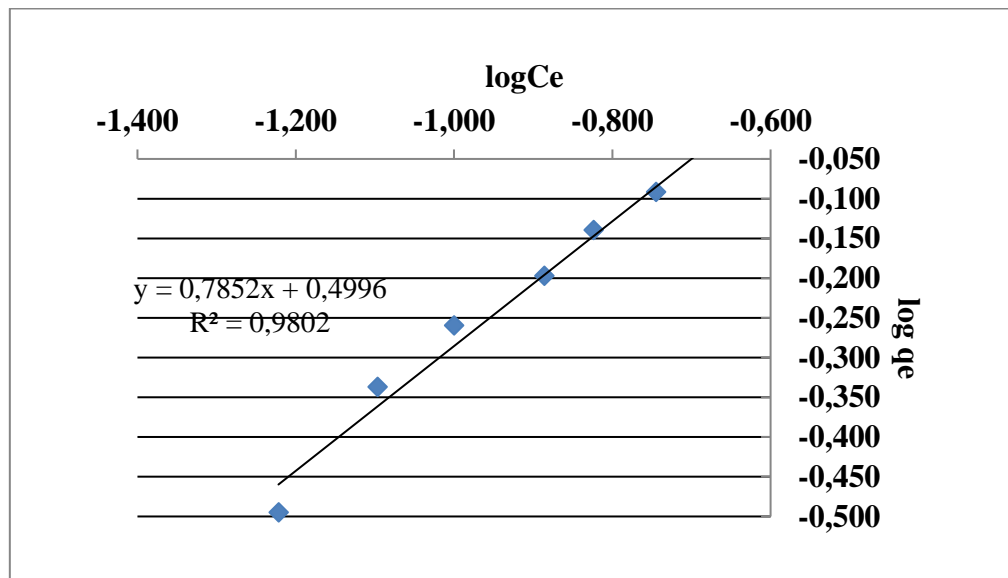
Figure 4.71. Graphical representation of the Freundlich model for Mn^{2+} ions in wastewater.

Langmuir and Freundlich models based on experimental data were plotted (Figure 4.70., 4.71.). The constants of both models are shown in Table 4.25. It can be seen that the experimental values fit well with the adsorption isotherms. In the case of the Langmuir model, its applicability indicates monolayer coverage of the magnetite surface by manganese ions. The Langmuir constant R_L is in the range 0-1, indicating that the Mn(II) ion retention process is favourable. The line graph between log (Ce) and log (Qe) confirms the applicability of the

49

Freundlich model. The value of 1/n is 0.78 (Table 4.25.) indicating that the adsorption process is favourable.

The results suggest that this type of magnetic nanomaterial could be successfully used to remove manganese ions from industrial wastewater. The possibility of rapid magnetic field separation of magnetite from wastewater at the end of treatment and the high removal efficiency recommend it as a useful nanoadsorbent.

4.1.3. Conclusions

In the case of pH 6 wastewater, the removal efficiency of lead ions from wastewater reached 100% at all concentrations studied at room temperature. The highest treatment efficiency for the removal of lead ions from pH 4 wastewater was 85.71% at the initial concentration of 0.70 mg/L at room temperature. The required contact time is longer at pH 4 than at pH 6. The minimum contact time at which maximum treatment efficiency was reached was 60 minutes and 150 minutes for pH 6 (100%) and pH 4 (85.71%) wastewater, respectively. There is also desorption (reversible adsorption).

As the pH of the wastewater increases (up to pH 6), adsorption of lead ions on the Fe_3O_4 surface is facilitated. On the other hand, if the pH rises above 6, the removal of lead ions can be achieved by the adsorption process, but precipitation can also occur due to metal hydrolysis of lead hydroxide.

Compared to the literature, the concentrations studied for lead ions were lower, but the importance of wastewater pH was observed and the treatment process was fast. The study of lower concentrations of lead ions under laboratory conditions demonstrates maximum treatment efficiency and the data can be reported on an industrial scale.

4.2. Adsorption of Cu^{2+} ions from wastewater using Fe_3O_4-PVP

4.2.1. General considerations

Although magnetite nanomaterials play an important role in many fields, uncoated nanoparticles may have some drawbacks, such as the fact that they easily form large aggregates or are not selective, so it is essential to coat them to overcome these limitations. Coating the surface of magnetic nanoparticles with various compounds can improve their chemical and mechanical properties, stabilise and determine their final shape, increase their dispersibility in various solvents and provide functional groups for the attachment of specific ligands or metals, so that coating can become a method of tailoring the properties of magnetic particles to subsequent applications [322].

Polyvinylpyrrolidone (PVP) is a commonly used water-soluble polymer that is readily soluble in ethanol and isopropanol and is widely used in foods, OTC drugs, wound dressings, cosmetics and other areas. It is also a polymer matrix commonly used in the preparation of nanofibers by electrospinning. Compared to conventional drug delivery systems, electrospun fibres have the characteristics of high specific surface area, high drug loading, low production costs and low residual organic solvents within the drug delivery field. Currently, PVP fibre membranes have been widely used. widely used for drug loading [323].

PhD student: *Scientific coordinator:*
Oana Stoian (Păunescu)   *Prof. habil. dr. ing. Cristina-Ileana Covaliu-Mierlă*

4.2.2. Experimental research

Adsorp̌ion experiments were carried out for the removal process of copper ions at different pHs and pollutant concentrations using Fe_3O_4-PVP (Figure 4.72.) as the adsorbent nanomaterial. Thus samples (100 mL each) were prepared from a 1000 mg/L copper standard solution with concentrations of 0.70, 1.00 and 1.20 mg/L. For these samples 0.017g nanomaterial composite was used (Figure 4.72.). PH was set at 8 and 11.5. Final concentrations were determined using the PhotoLab S12.
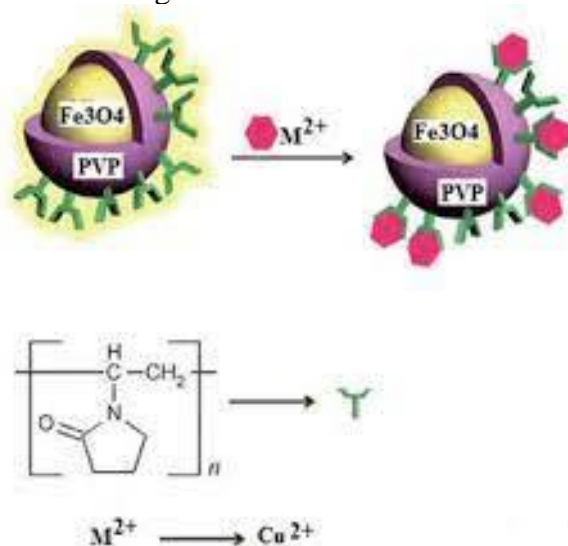
Figure 4.72. Composite nanomaterial used in the removal of Cu^{2+} ions from wastewater.

Figures 4.73., 4.74. show the variations of copper ion concentrations and treatment efficiencies over time using the Fe_3O_4-PVP composite nanomaterial for the removal of copper ions at a concentration of 0.65 mg/L from wastewater with pH 8.

Figure 4.73. Variation of Cu^{2+} ion concentrations in pH 8 wastewater using Fe_3O_4-PVP composite nanomaterial ($C_i = 0.65$ mg/L).

Figure 4.73. shows a decrease in the concentration of copper ions in the wastewater to 0.55 mg/L after 120 minutes, 0.49 mg/L after 1200 minutes and 0.28 mg/L after 2880 minutes of treatment time.

PhD student: *Scientific coordinator:*
Oana Stoian (Păunescu)   *Prof. habil. dr. ing. Cristina-Ileana Covaliu-Mierlă*

Figure 4.74. Variation of Cu^{2+} ion removal efficiencies from pH 8 wastewater using Fe_3O_4-PVP composite nanomaterial ($C_i = 0.65$ mg/L).

Figure 4.74. shows the variation of wastewater treatment efficiency over time, with efficiency reaching 15.38% after 120 minutes, 24.62% after 1200 minutes and 56.92% after 2880 minutes of treatment time.

Figures 4.75., 4.76. show the variations of copper ion concentrations and treatment efficiencies over time using the Fe_3O_4-PVP composite nanomaterial to remove copper ions at a concentration of 1.05 mg/L from wastewater at pH 8.
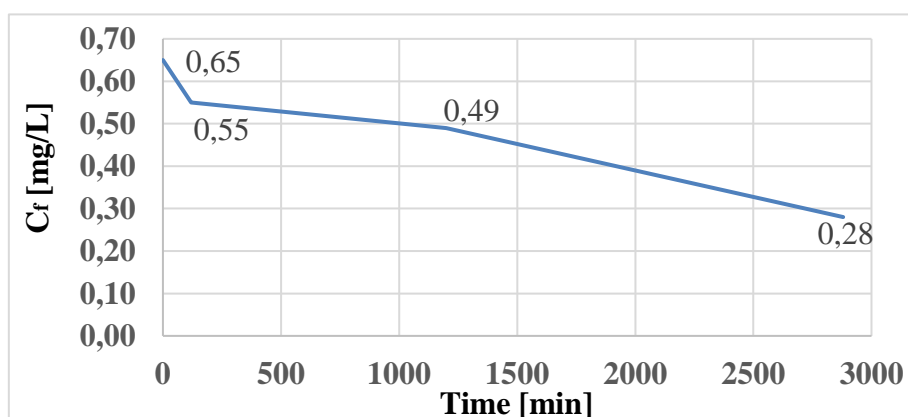

Figure 4.75. Variation of Cu^{2+} ion concentrations in pH 8 wastewater using Fe_3O_4-PVP composite nanomaterial ($C_i = 1.05$ mg/L).

It can be seen in Figure 4.75. that the final concentration of copper ions in the wastewater reached 0.83 mg/L from the initial concentration of 1.05 mg/L and after 48 hours it did not decrease further.

PhD student: *Scientific coordinator:*
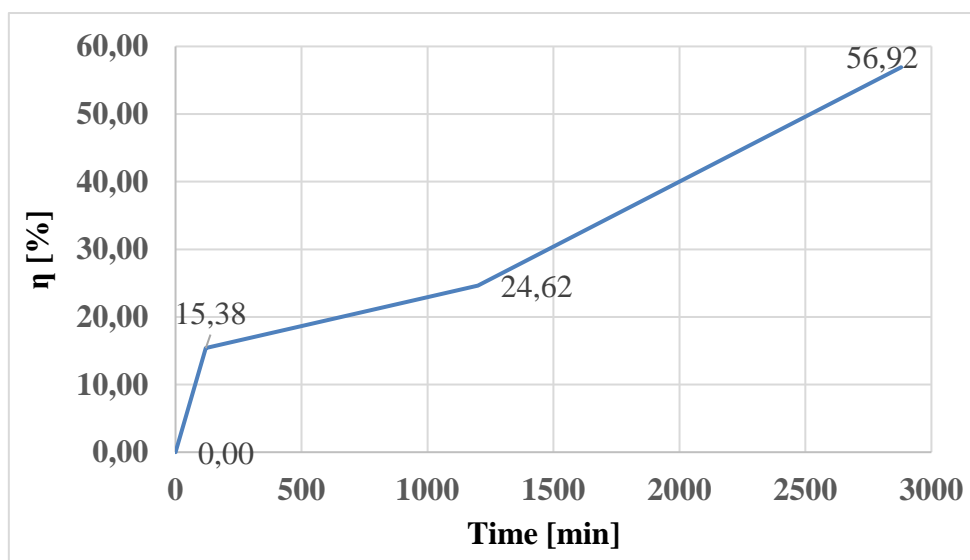*Oana Stoian (Păunescu)*   *Prof. habil. dr. ing. Cristina-Ileana Covaliu-Mierlă*

Figure 4.76. Variation of Cu^{2+} ion removal efficiencies from pH 8 wastewater using Fe_3O_4-PVP composite nanomaterial (C_i = 1.05 mg/L).

Figure 4.76. shows a treatment efficiency of 14.29% after 120 minutes, 19.05% after 1200 minutes and a treatment efficiency of only 20.95% after 2880 minutes of treatment time.

Figures 4.77., 4.78. show the variation of copper ion concentrations as well as the variation of treatment efficiencies over time using the Fe_3O_4-PVP composite nanomaterial to remove copper ions at a concentration of 1.20 mg/L from wastewater at pH 8.
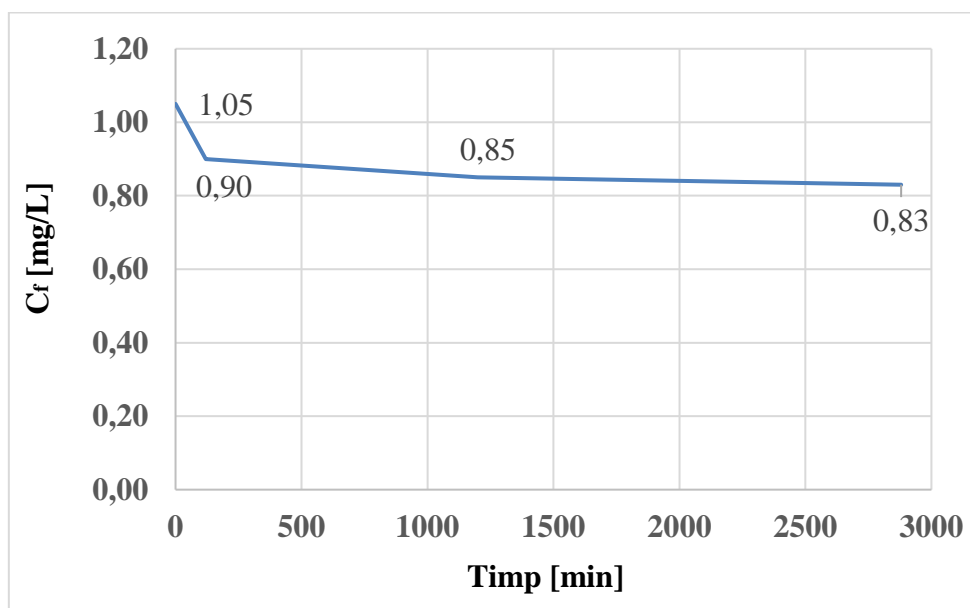

Figure 4.77. Variation of Cu^{2+} ion concentrations in pH 8 wastewater using Fe_3O_4-PVP composite nanomaterial (C_i = 1.20 mg/L).

Figure 4.77. shows the variation of copper ion concentrations and it can be seen that no concentration below 0.96 mg/L was reached after a treatment time of 2880 minutes.

PhD student: *Scientific coordinator:*
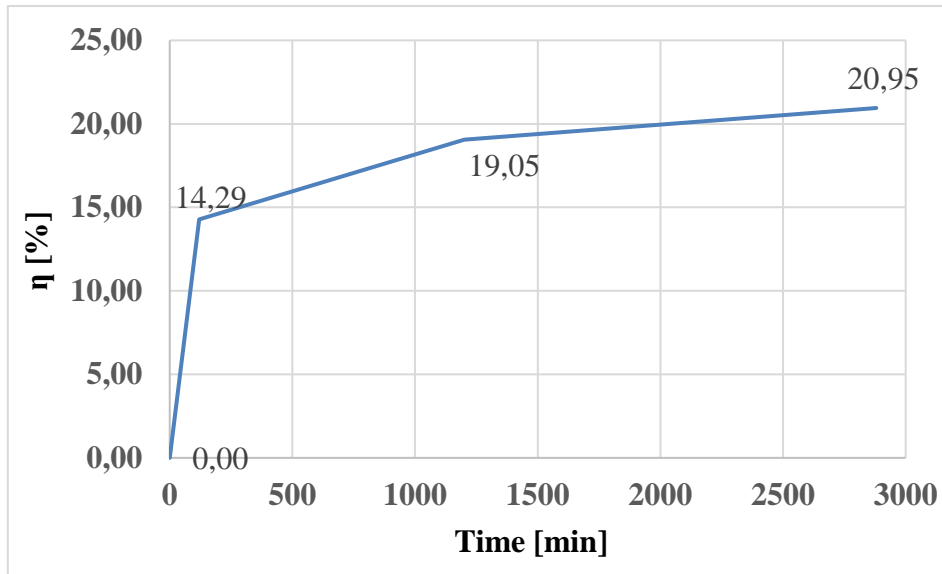*Oana Stoian (Păunescu)*   *Prof. habil. dr. ing. Cristina-Ileana Covaliu-Mierlă*

Figure 4.78. Variation of Cu^{2+} ion removal efficiencies from pH 8 wastewater using Fe_3O_4-PVP composite nanomaterial (C_i = 1.20 mg/L).

Figure 4.78. shows the variation of wastewater treatment efficiency over time, with efficiency reaching 10.83% after 120 minutes, 14.17% after 1200 minutes and 20.00% after a treatment time of 2880 minutes.

Figures 4.79., 4.80. show the variations of copper ion concentrations and the variations of treatment efficiencies over time using the Fe_3O_4-PVP composite nanomaterial for the removal of copper ions at a concentration of 0.70 mg/L from wastewater at pH 11.5.
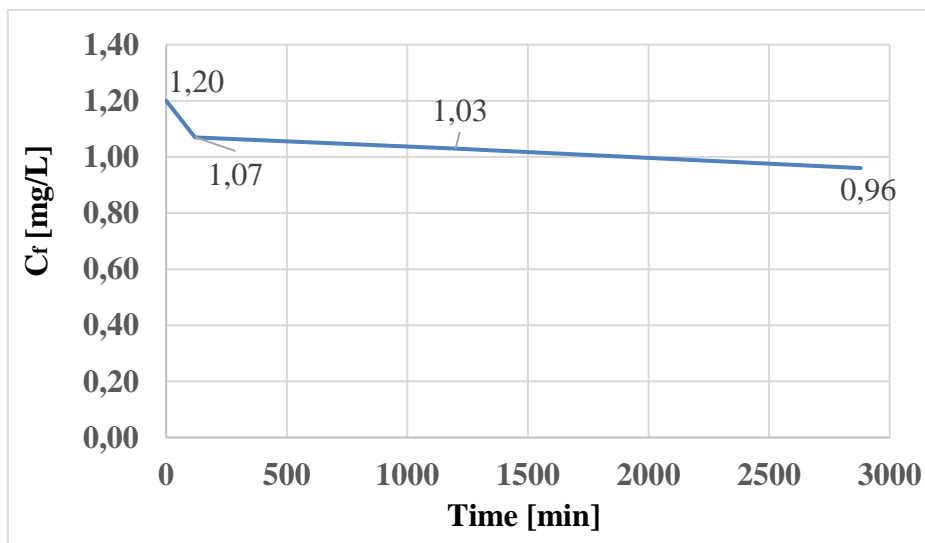

Figure 4.79. Variation of Cu^{2+} ion concentrations in wastewater at pH 11.5 using Fe_3O_4-PVP composite nanomaterial (C_i = 0.70 mg/L).

Figure 4.79. shows the variation of copper ion concentrations, reaching 0.48 mg/L after 120 minutes, 0.43 mg/L after 1200 minutes and 0.21 mg/L after a treatment time of 2880 minutes.

PhD student:
Oana Stoian (Păunescu)

Scientific coordinator:
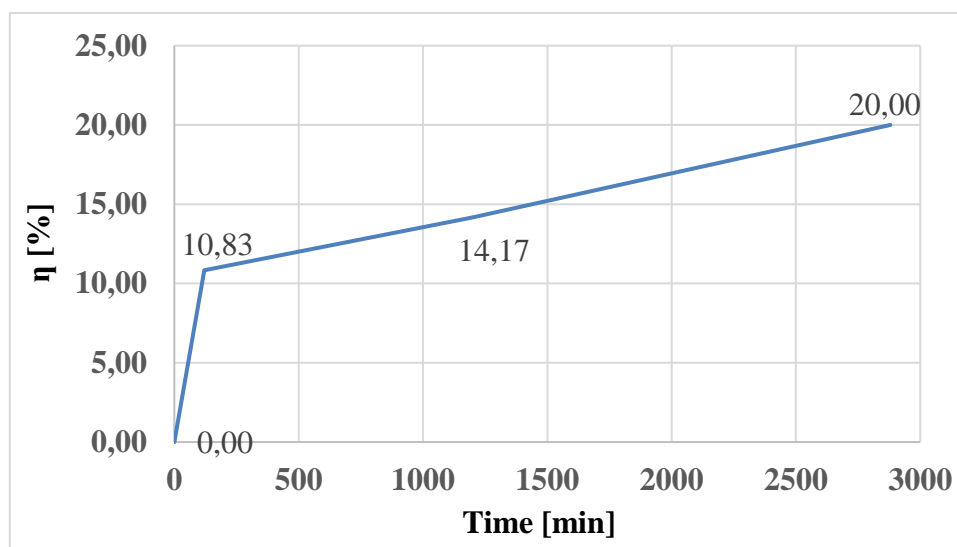*Prof. habil. dr. ing. Cristina-Ileana Covaliu-Mierlă*

Figure 4.80. Variation of Cu^{2+} ion removal efficiencies from wastewater at pH 11.5 using Fe_3O_4-PVP composite nanomaterial ($C_i = 0.70$ mg/L).

Figure 4.80. shows the variation of wastewater treatment efficiencies over time, with efficiency reaching 31.43% after 120 minutes, 38.57% after 1200 minutes and 70.00% after a treatment time of 2880 minutes.

The variation of copper ion concentrations is plotted in Figure 4.81 and the variation of treatment yields is plotted in Figure 4.82.
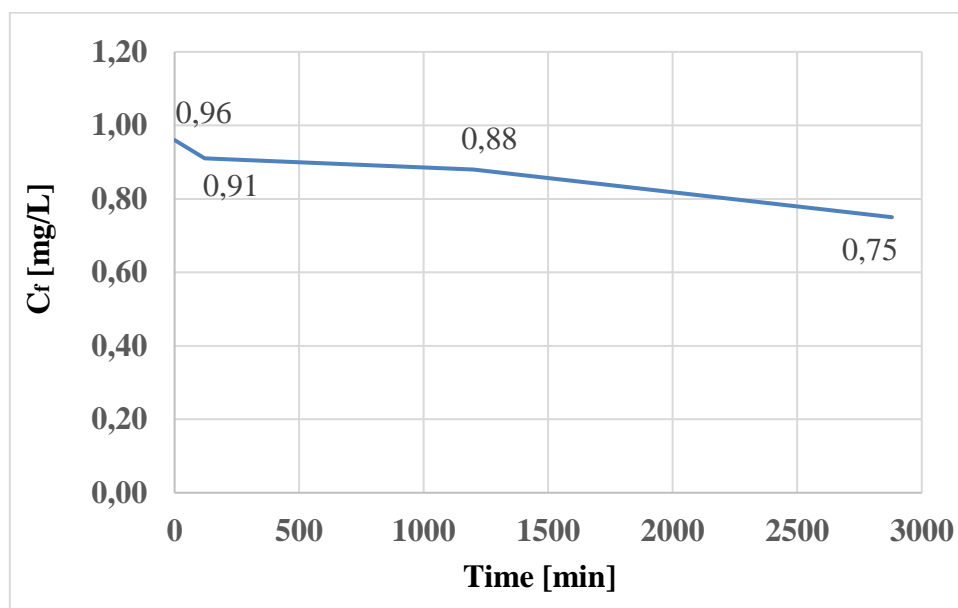
Figure 4.81. Variation of Cu^{2+} ion concentrations in wastewater at pH 11.5 using Fe_3O_4-PVP composite nanomaterial ($C_i = 0.96$ mg/L).

Figure 4.81. shows the variation of copper ion concentrations, starting from an initial concentration of 0.96 mg/L, reaching 0.91 mg/L after 120 minutes, 0.88 mg/L after 1200 minutes and 0.75 mg/L after a treatment time of 2880 minutes.

55
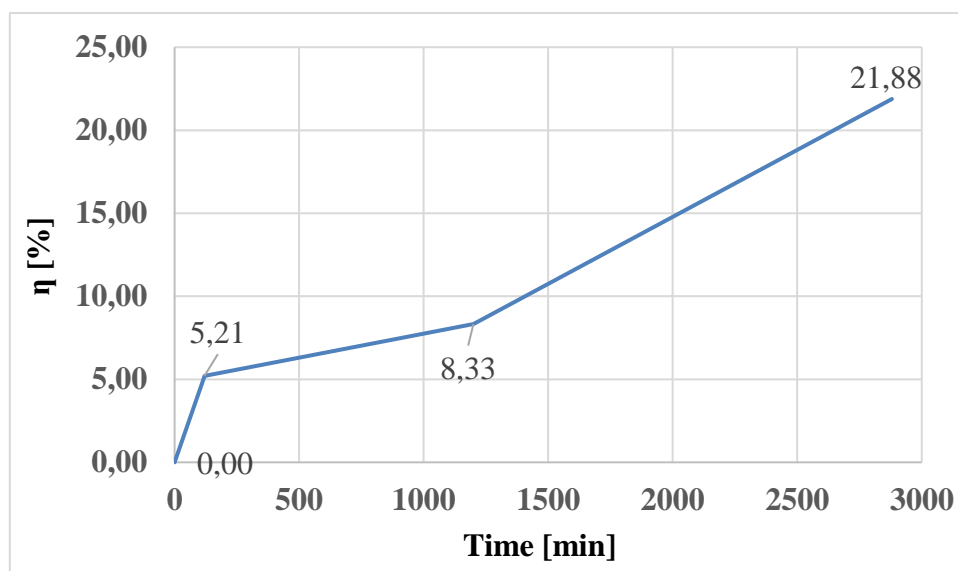
Figure 4.82. Variation of Cu^{2+} ion removal efficiencies from pH 11.5 wastewater using Fe_3O_4-PVP composite nanomaterial ($C_i = 0.96$ mg/L).

Figure 4.82. shows the variation of wastewater treatment efficiencies over time, with efficiency reaching 5.21% after 120 minutes, 8.33% after 1200 minutes and 21.88% after a treatment time of 2880 minutes.

Figures 4.83., 4.84. show the variation of copper ion concentrations as well as the variation of treatment efficiencies over time using the Fe_3O_4-PVP composite nanomaterial to remove copper ions at a concentration of 1.20 mg/L from wastewater at pH 11.5.
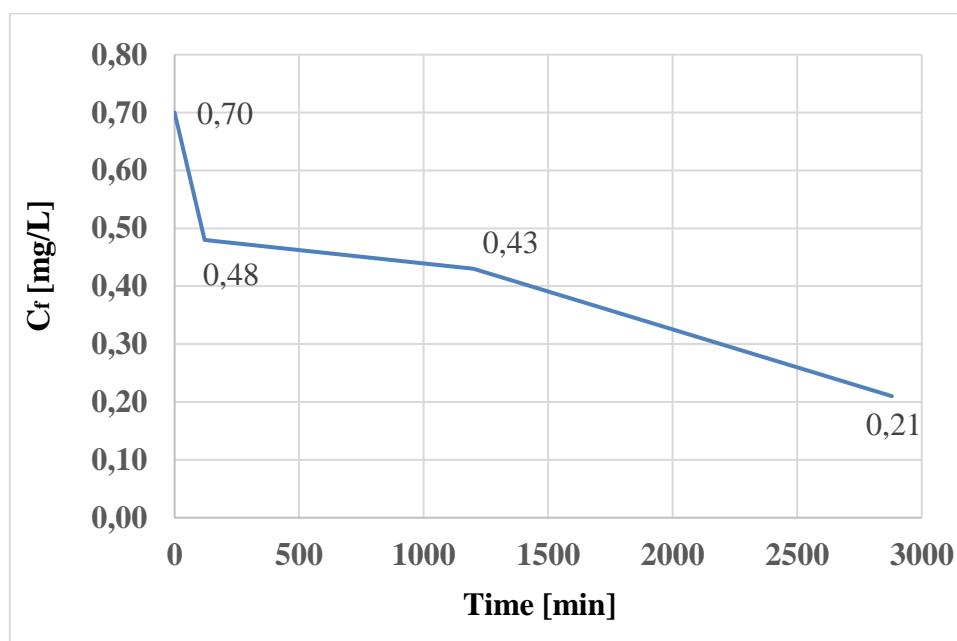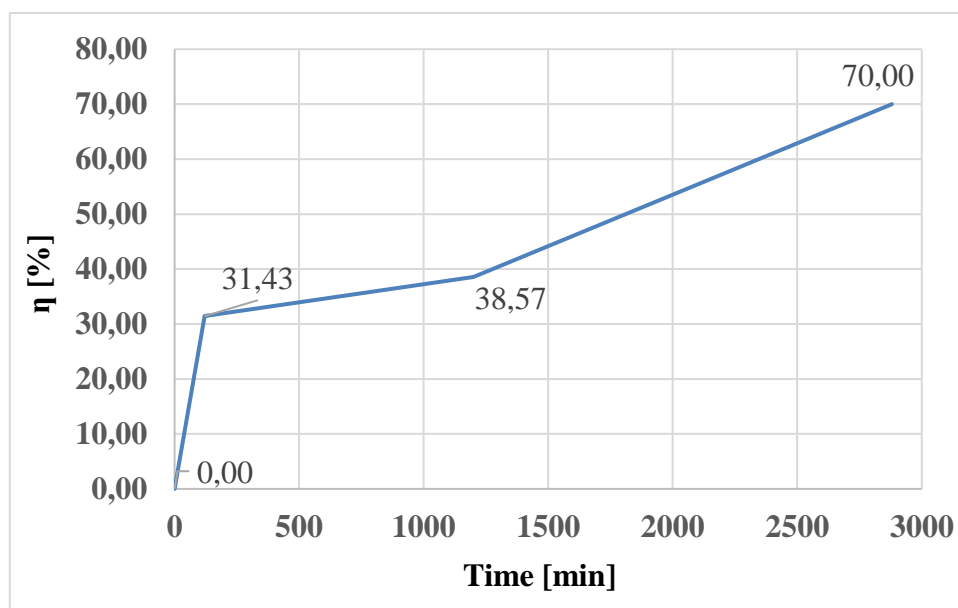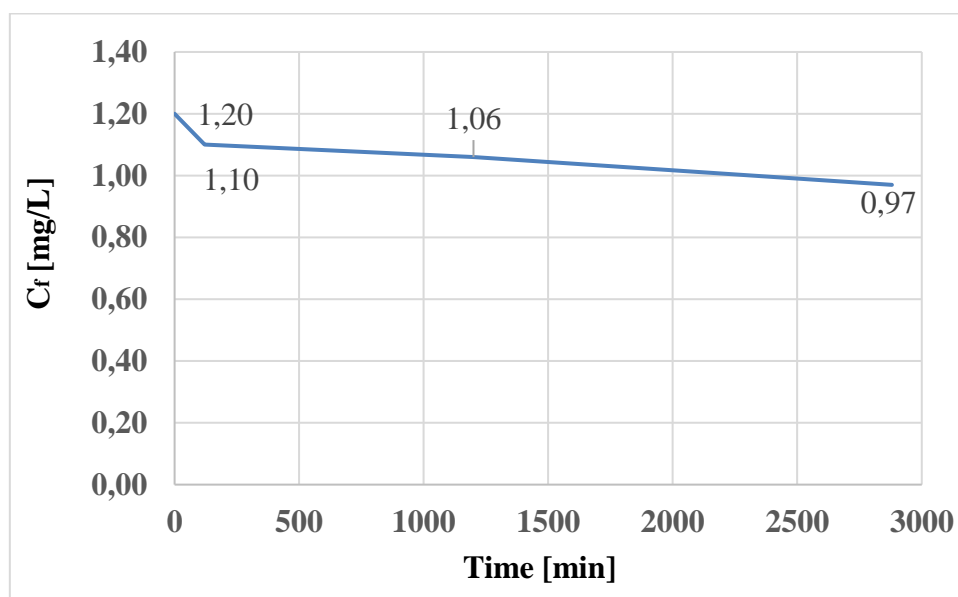

Figure 4.83. Variation of Cu^{2+} ion concentrations in wastewater at pH 11.5 using Fe_3O_4-PVP composite nanomaterial ($C_i = 1.20$ mg/L).

Figure 4.83. shows the variation of copper ion concentrations and it can be seen that no concentration lower than 0.97 mg/L was reached after 2880 minutes.

PhD student: *Scientific coordinator:*
Oana Stoian (Păunescu)   *Prof. habil. dr. ing. Cristina-Ileana Covaliu-Mierlă*
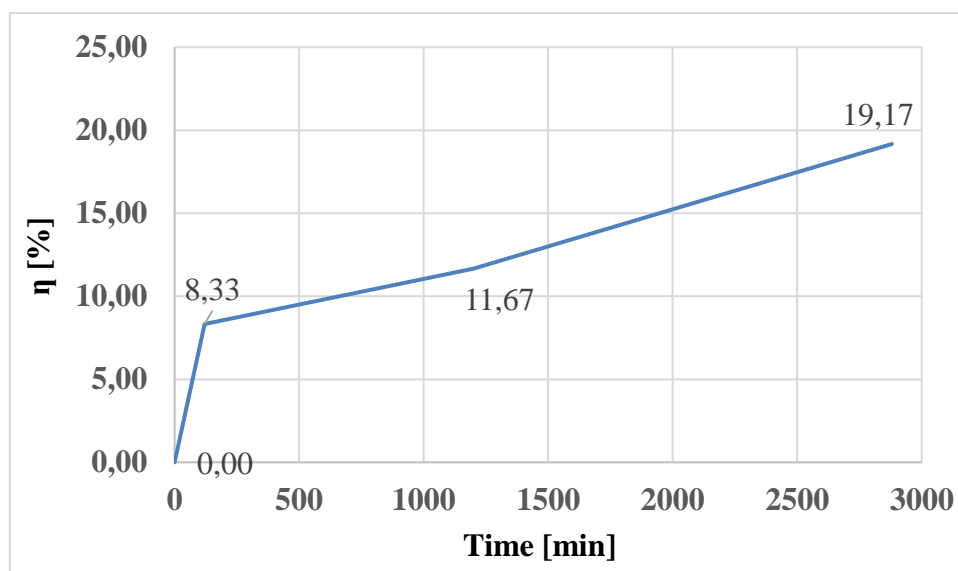
Figure 4.84. Variation of removal efficiencies of Cu^{2+} ions at a concentration of 1.20 mg/L from pH 11.5 wastewater using Fe_3O_4-PVP composite nanomaterial (C_i = 1.20 mg/L).

Figure 4.84. shows the variation of wastewater treatment efficiencies over time, with efficiency reaching 8.33% after 120 minutes, 11.67% after 1200 minutes and 19.17% after a treatment time of 2880 minutes.

PH plays an important role for the removal of copper ions from wastewater using Fe_3O_4-PVP composite nanomaterial. Acidic environment (pH 4) has a negative impact on the adsorption process. The resulting yield was only 1.45% after 1200 minutes. When the pH values were 8 and 11.5, changes in wastewater treatment yield were observed to 56.92% for pH 8 (Figure 4.85.) and 70.00% for pH 11.5 after 48 hours (Figure 4.86.).
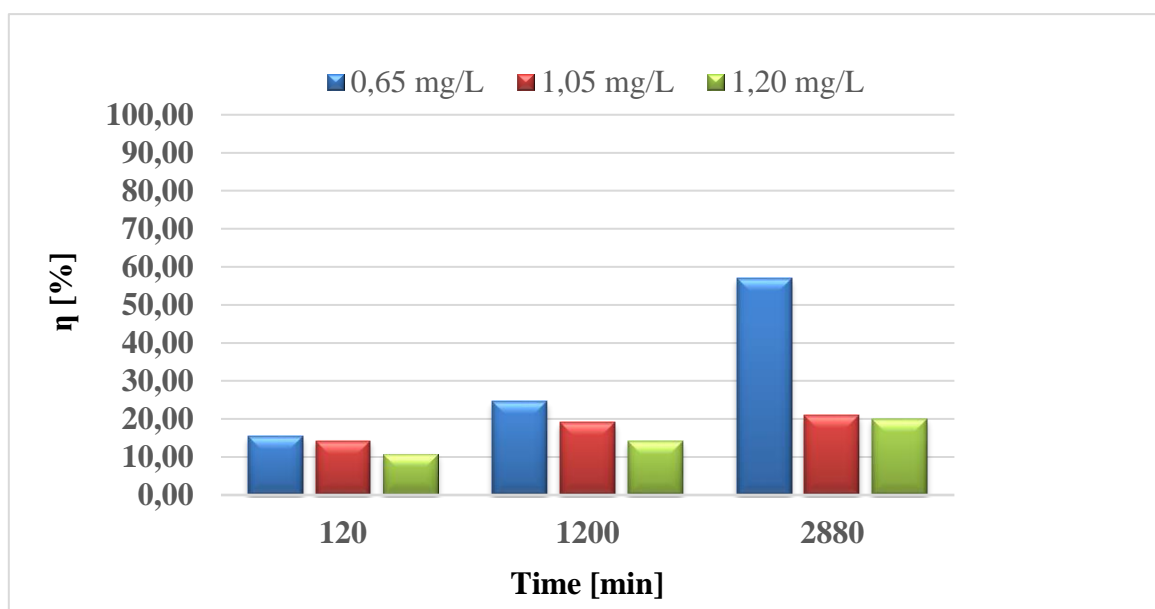
Figure 4.85. Removal of Cu^{2+} ions from wastewater at pH 8 using Fe_3O_4-PVP adsorbent composite nanomaterial.

PhD student:
Oana Stoian (Păunescu)

Scientific coordinator:
Prof. habil. dr. ing. Cristina-Ileana Covaliu-Mierlă

Figure 4.86. Removal of Cu^{2+} ions from wastewater at pH 11.5 using Fe_3O_4-PVP adsorbent composite nanomaterial.

4.2.3. Conclusions

In the case of adsorption of copper ions from wastewater using the Fe_3O_4 - PVP composite nanomaterial, the yield obtained in wastewater treatment was only 1.45% at pH 4, reaching values higher than 70% at pH 11.5.

The treatment process is dependent on the pH value of the wastewater, and it is observed that the acidic environment is not beneficial to the system with a treatment percentage of only 1.45% after a treatment time of 1200 minutes. Treatment efficiencies of 56.92% and 70.00% were observed at pH values of 8 and 11.5 respectively.

4.3. Adsorption of Cu^{2+} and Pb^{2+} ions from wastewater using halloysite nanotube composites
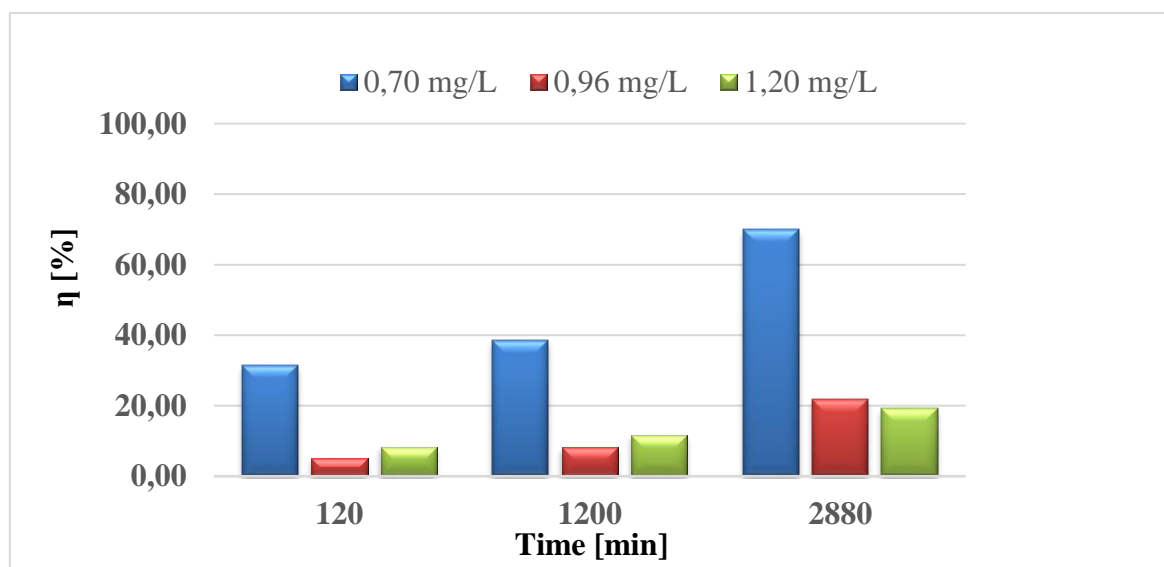
4.3.1. General considerations

Halloysite nanotubes (HNTs), a type of natural clay mineral with nanotubular structures, are increasingly the focus of research. As a type of well-crystallised kaolin, HNTs were first reported by Berthier in 1826 and are found widely deposited in soils around the world. Many countries such as China, France, Belgium and New Zealand have deposits of HNTs [324].

4.3.2. Experimental research

Adsorption experiments were performed for the removal process of copper and lead ions at pH 6 and pollutant concentration 1.00 mg/L using different composite nanomaterials (Figure 4.88.) based on halloysite nanotubes as adsorbent nanomaterials. The amount of nanomaterials used in the treatment processes was 0.20 g. After the wastewater was prepared, it was homogenized using a stirred screen (Figure 4.89.). Concentrations were determined at certain time intervals using the PhotoLab S12 photometer according to ISO 8466-1 and DIN 38402 A51 (10 mm cell) with a measuring range of 0.1-6.0 mg/L Cu^{2+} and 0.1-5.0 mg/L for wastewater polluted with lead ions. Yields were calculated with the formula shown in equation (25).

PhD student:
Oana Stoian (Păunescu)

Scientific coordinator:
Prof. habil. dr. ing. Cristina-Ileana Covaliu-Mierlă
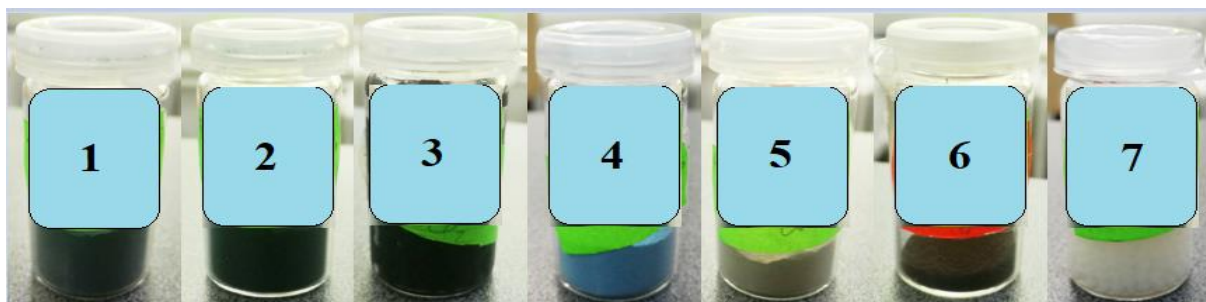
Figure 4.88. Composite nanomaterials. 1) HNTs:PANI (1:0.058), 2) HNTs-PANI (1:0.26), 3) PRGO HNT CoCl₂, 4) HNTs:Prussian Blue 5) HNTs:CoFe₂O₄ (1:0.058), 6) HNTs:CoFe₂O₄ (1:0.26), 7) HNTs:CaNaAlg.

Figure 4.89. Wastewater containing adsorbent composite nanomaterials.

The average size of halloysite-based composite nanoparticles corresponding to numbers 1, 2, 4, 5, 6 is 50 nm and the average size of halloysite-based composite nanoparticles corresponding to numbers 3 and 7 is 80 nm.

Figure 4.93. shows the treatment yields obtained for the removal of copper ions from wastewater after 900 minutes of contact.
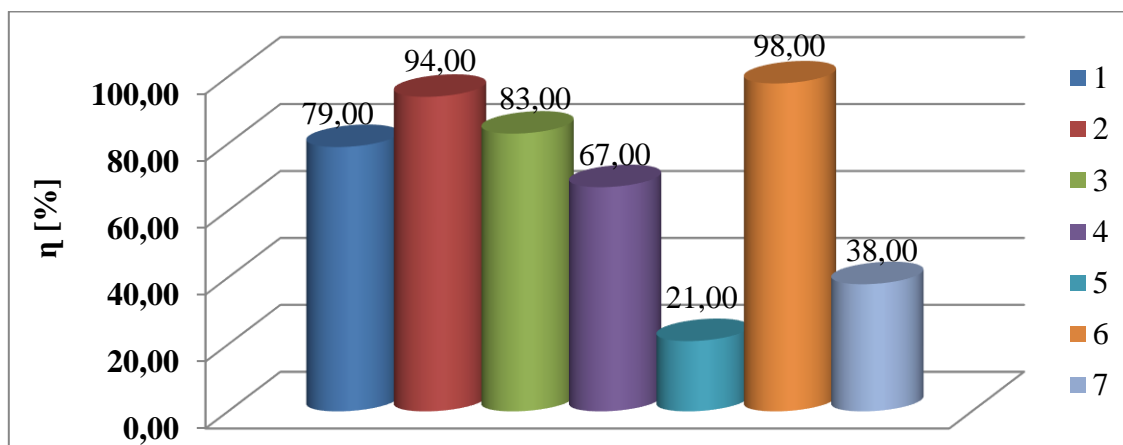
Figure 4.93. Treatment yields obtained after 900 minutes for the removal of Cu^{2+} ions from wastewater.

PhD student:
Oana Stoian (Păunescu)

Scientific coordinator:
Prof. habil. dr. ing. Cristina-Ileana Covaliu-Mierlă

Figure 4.94. shows the treatment yields obtained for the removal of lead ions from wastewater after 900 minutes of contact.
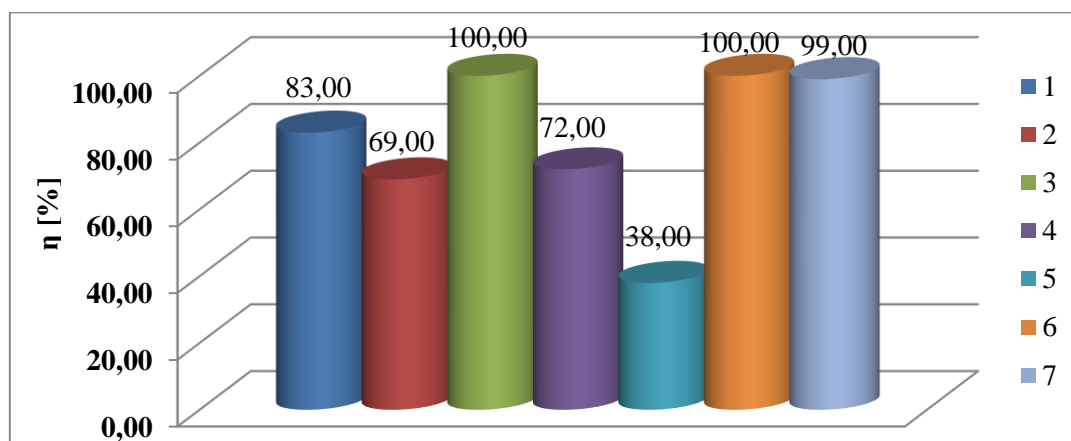
Figure 4.94. Treatment yields after 900 minutes for the removal of Pb^{2+} ions from wastewater.

4.3.3. Conclusions

It is observed that, in the case of composite nanomaterials consisting of halloysite nanotubes and polyaniline, increasing the amount of polyaniline influences the treatment efficiency positively in the case of removal of copper ions and negatively in the case of removal of lead ions from wastewater.

In the case of the composite nanomaterial containing partially reduced graphite oxide and cobalt chloride, maximum treatment efficiency was obtained for the removal of lead ions.

In the case of the composite nanomaterial containing Prussian Blue pigment, acceptable yields of up to 72% were obtained.

Synthesis of cobalt ferrite halloysite nanotubes influences the treatment yield for copper and lead ion removal depending on its concentration. When the concentration of cobalt ferrite is low, the treatment yield is negatively influenced, being no higher than 38%, and when the concentration of cobalt ferrite is higher, the treatment yield reaches 98% for copper ion removal and 100% for lead ion removal.

Halloysite nanotubes added to sodium alginate solution influence the removal process of copper ions in a negative way, and in the case of lead ions, the process is influenced in a positive way, the yield reaching 99%.

4.4. Removal of methylene blue from wastewater by photocatalysis using TiO_2-based composite materials

4.4.1. General considerations

The degradation of dyes in industrial wastewater has received increased attention and some remedial methods have been proposed. Traditional physical techniques (adsorption on activated carbon, ultrafiltration, reverse osmosis, coagulation with chemical agents, ion exchange on synthetic adsorbent resins, etc.) have been used to remove dye pollutants [338, 341]. These methods only succeed in transferring organic compounds from water to another phase, thus creating secondary pollution. This will require additional treatment of the solid waste and regeneration of the adsorbent, which will add additional costs to the process. Microbiological or enzymatic decomposition, biodegradation, ozonation and advanced oxidation processes such as Fenton and photo Fenton catalytic reactions, H_2O_2/UV processes have also been used for the removal of dyes from wastewater [337].

60

4.4.2. Experimental research

Methylene blue wastewater (50 mL) with a concentration of 0.01 mg/L was prepared from a 1% methylene blue solution. In the first system 0.80 g of TiO$_2$/AgPd Ca(Na)Alg gel beads were added and in the second a volume of 7 mL of TiO$_2$/AgPd Ca(Na)Alg microgel. The wastewater thus prepared (Figure 4.95.) was placed on the stirring plate at 120 rpm under the action of ultraviolet light.
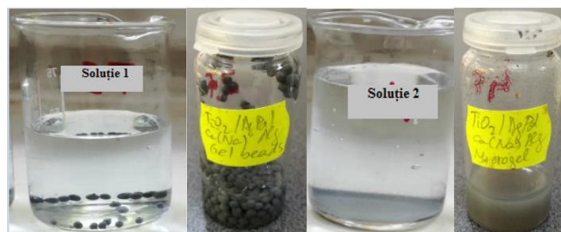
Figure 4.95. Removal of methylene blue from wastewater using TiO$_2$/AgPd Ca(Na)Alg.

The efficiency of the photocatalytic dye degradation reaction using the determined methylene blue concentrations is calculated with the relation (25).
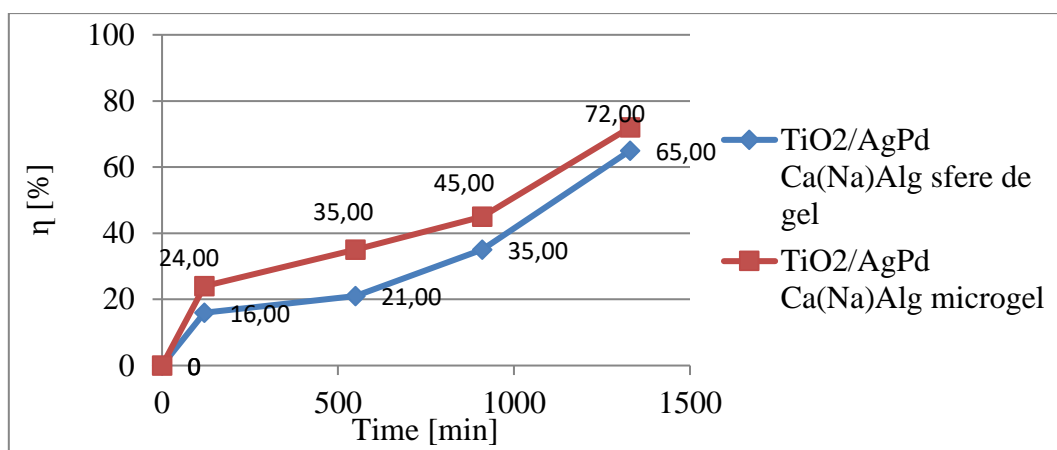
Figure 4.96. Treatment yields using the photocatalysis process.

A Philips UV lamp type HB 171/A 220-230V~50 Hz 75W UV Type 3 was used for these experiments and a SPECORD 200PLUS spectrophotometer was used to determine absorbance.

After 1330 minutes of contact the TiO$_2$ doped AgPd gel beads showed a yield of 65.00%, while the microgel showed a more efficient yield of 72.00%.

4.4.3. Conclusions

Different operational parameters influence the efficiency of TiO$_2$-based photocatalysts. Some dyes are degraded at a higher pH, while others at a lower pH; therefore, in the case of photocatalytic degradation of wastewater dyes, the reaction should take place at an appropriate pH. Oxidising agents, calcination temperature and catalyst loadings have been found to exert an individual influence on the photocatalytic degradation of any dye. It was also found that many methods are used in the preparation of TiO$_2$-based photocatalysts. However, the sol-gel method is widely used because the method facilitates the synthesis of crystalline TiO$_2$-based catalyst powder of nanometer size of high purity at relatively low temperature.

61

PhD student: *Scientific coordinator:*
Oana Stoian (Păunescu)   *Prof. habil. dr. ing. Cristina-Ileana Covaliu-Mierlă*

From our own experimental research using photocatalysis as a technique for photodegradation of wastewater pollutants using catalysts, a maximum degradation percentage of methylene blue of 72.00% is observed. TiO_2/AgPd Ca(Na)Alg in the form of gel beads and microgel was used and the steady degradation of methylene blue was observed over a time period of 1330 minutes. When using TiO_2/AgPd Ca(Na)Alg in the form of gel beads, a consistently higher efficiency was observed than when using TiO_2/AgPd Ca(Na)Alg in the form of microgel.

Composite nanomaterials (TiO_2/AgPd Ca(Na)Alg) in the form of gel spheres (average size 60 nm) and microgels were used to degrade methylene blue in wastewater and yields of 65.00% and 72.00% were obtained, respectively. Thus it was observed that the small size of the composite nanomaterials used positively influences the degradation efficiency of methylene blue due to the large specific surface area.

CHAPTER 5. ORIGINAL CONTRIBUTIONS. FINAL CONCLUSIONS. PERSPECTIVES

5.1. Original contributions

The original contributions, supported by the research activities carried out during the PhD internship, are as follows:

1) Extensive literature study on the application of conventional and non-conventional methods for wastewater treatment, application of nanotechnology in wastewater pollutant removal processes;

2) Testing of magnetite oxide nanomaterial for the removal of copper ions from wastewater using different concentrations of heavy metals than reported in the literature;

3) Performance evaluation of magnetite oxide nanomaterial for the removal of lead ions from wastewater using different concentrations of heavy metals than reported in the literature;

4) Testing of magnetite oxide nanomaterial for the removal of manganese ions from wastewater using different concentrations of heavy metals than reported in the literature;

5) Use of Fe_3O_4-PVP composite nanomaterial in experimental research for the removal of copper ions from wastewater;

6) Testing new composite nanomaterials based on halloysite nanotubes for the treatment of water containing copper ions;

7) Application of new composite adsorbent nanomaterials based on halloysite nanotubes for the removal of lead ions from wastewater;

8) Study of TiO_2-based composite nanomaterials in the form of gel spheres and myrogel for the removal of methylene blue from wastewater.

5.2. Final conclusions

The results suggest that the oxidative nanomaterial magnetite could be successfully used to remove copper, lead and manganese ions from industrial wastewater. The possibility of rapid magnetic field separation of magnetite from wastewater at the end of treatment and the high removal efficiency recommend it as a useful adsorbent nanomaterial. Regeneration studies will also be undertaken in the future to determine the lifetime of the magnetite adsorbent nanomaterial. There is a very high probability that the magnetite nanomaterial could be adapted to remove other types of heavy metals from wastewater.

Copper ions from wastewater were removed 100% by using the oxide nanomaterial magnetite when both pH 8 and pH 11.5 were used. pH 8 was found to be the optimal pH for these experiments to remove copper ions from wastewater because the treatment process was faster.

PhD student: *Scientific coordinator:*
Oana Stoian (Păunescu)   *Prof. habil. dr. ing. Cristina-Ileana Covaliu-Mierlă*

To remove a concentration of 0.70 mg/L Cu(II) the required treatment time was 20 minutes when 0.20 g magnetite was used. The longest treatment time recorded was 280 minutes and 340 minutes to remove a concentration of 1.20 mg/L copper ions using 0.01 g magnetite at pH 8 and 11.5 respectively.

Experiments were conducted for the removal of lead ions from wastewater at pH 4 and 6. We observed that the percentage of treatment in wastewater at pH 4 was maximum 84.40% and the time required was 180 minutes, while at pH 6 the treatment efficiency was maximum (100%) over a period of 90 minutes, the initial concentration of lead ions being 1.00 mg/L. It is found that with increasing pH value the adsorption of lead ions on the magnetite surface is facilitated. However, if the pH value increases above 6, precipitation may occur due to metal hydrolysis of lead hydroxide.

The removal process of Mn(II) ions from wastewater using the oxidic nanomaterial magnetite is strongly pH-dependent so that at pH 11.5 the removal efficiency was 97.50%, while at a lower pH of 8 the removal efficiency was 91.00%. The time required to remove manganese ions from wastewater was 500 minutes.

Using the Fe_3O_4 - PVP composite nanomaterial for the adsorption of copper ions from wastewater, it is observed that the acidic environment (pH 4) does not favour the treatment process, while increasing the pH to 11.5 is beneficial, the treatment efficiency reaching 70.00%.

Using composite nanomaterials containing halloysite nanotubes, the composite nanomaterial consisting of halloysite nanotubes and $CoFe_2O_4$ had the highest efficiency of 98% for the removal of copper ions from wastewater. Two composite nanomaterials, PRGO HNT $CoCl_2$ and $HNTs{:}CoFe_2O_4$, demonstrated maximum treatment efficiencies for the removal of lead ions from wastewater.

The use of photocatalysis to remove methylene blue from wastewater resulted in yields of 65.00% when using TiO_2-doped AgPd gel beads and 72.00% when using the microgel, respectively.

5.3. Perspectives

The work provides a solid basis for further research to develop the theory and refine wastewater treatment solutions through the application of nanotechnology.

Further experimental research can investigate the regeneration of nanomaterials and composites used to remove pollutants from wastewater. The number of cycles of operation of nanomaterials as well as the treatment efficiency after regeneration can be studied.

Nanomaterials and composite materials used in the studies presented in the PhD thesis can also be applied for the removal of other pollutants from industrial wastewater.

LIST OF PUBLICATIONS

Published articles related to the field of the PhD thesis

1. Cristina Ileana Covaliu, Gigel Paraschiv, Oana Stoian and Alexandru Vișan, Nanomaterials applied for heavy metals removal from wastewater, *IOP Conf. Series: Materials Science and Engineering* **572** (2019) 012074, 1-7;

2. Cristina Covaliu, Gigel Paraschiv, Oana Stoian, Bogdan Buzatu, Costin Mircea, Camelia Cristea, Halloysite nanotube applications for heavy metals removal from wastewater, *8th International Conference on Thermal Equipment, Renewable Energy and Rural Development (TE-RE-RD 2019),* **112**, (2019) 04010, 1-4;

PhD student: *Scientific coordinator:*
Oana Stoian (Păunescu)   *Prof. habil. dr. ing. Cristina-Ileana Covaliu-Mierlă*

3. Eugeniu Vasile, Cristina-Ileana Covaliu, Oana Stoian, Gigel Paraschiv, Ecaterina Matei, Gina-Alina Catrina (Traistaru), Alexandru Ciric, Manganese Ions Removal from Industrial Wastewater, *Revista de Chimie* **71 (7)**, (2020) 391-396;

4. Cristina Ileana Covaliu, Ecaterina Matei, Oana Stoian, Gigel Paraschiv, Magnetic Nanocomposite Material Containing Chitosan Polymer Used in Wastewater Depollution Processes, *Materiale Plastice* **57 (4)** (2020) 70-76, ***F.I. = 0,8***;

5. Cristina Ileana Covaliu, Oana Stoian, Ecaterina Matei, Gigel Paraschiv, Eugenia Tanasa, Gina Alina Catrina (Traistaru), Research on Copper Ions Removal from Wastewater Using Fe_3O_4 and Fe_3O_4- PVP Hybrid Nanomaterials, *Materiale Plastice* **58 (1)** (2021) 154-166, ***F.I. = 0,8***;

6. Oana Stoian, Cristina Ileana Covaliu, Gigel Paraschiv, Gina-Alina Catrina (Traistaru), Mihai Niță-Lazăr, Ecaterina Matei, Sorin Ștefan Biriș and Paula Tudor, Magnetite Oxide Nanomaterial Used for Lead Ions Removal from Industrial Wastewater, *Materials* **14** (2021) 2831, ***F.I. = 3,4***;

7. Oana Stoian, Cristina Ileana Covaliu, Gigel Paraschiv, Mihai Nita-Lazar, and Ioana-Corina Moga, Photodegradable organic pollutants from wastewater, *E3S Web of Conferences* **286** (2021) 03017, 1-8;

8. Oana Stoian, Cristina Ileana Covaliu, Gigel Paraschiv, Removal of copper ions from wastewater by adsorption using magnetite nanomaterial, *U.P.B. Sci. Bull.*, Series B, **83,** Iss. 3 (2021), 293-299, ***F.I. = 0,5***;

9. 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***;

10. 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* **4** (2022), 748-753;

11. Cristina Ileana Covaliu-Mierla, Oana Paunescu, Horia Iovu, Recent Advances in Membranes Used for Nanofiltration to Remove Heavy Metals fromWastewater: A Review, *Membranes* **13** (2023), 643, ***F.I. = 4,2***.

Other publications outside the field of the PhD thesis

1. Cristina Ileana Covaliu, Ancuta Nedelcu, Gyorgy Deak, Oana Stoian, Norazian Mohamed Noor, Biotechnology of Water Treatment Based on Algae Cultures, *IOP Conf. Series: Earth and Environmental Science* **616** (2020) 012081, 1-4;

2. Roxana Mitroi, Oana Stoian, Cristina Ileana Covaliu, and Dragoş Manea, Pollutants resulting from intensive poultry farming activities and their impact on the environment, *E3S Web of Conferences* **286** (2021) 03018, 1-6;

3. Paul-Octavian Stanescu, Ionut-Cristian Radu, Rebeca Leu Alexa, Ariana Hudita, Eugenia Tanasa, Jana Ghitman, Oana Stoian, Aristidis Tsatsakis, Octav Ginghina, Catalin Zaharia, Mikhail Shtilman, Yaroslav Mezhuev, Bianca Galateanu, Novel chitosan and bacterial cellulose biocomposites tailored with polymeric nanoparticles for modern wound dressing development, *Drug delivery*, **28,** 1 (2021) 1932-1950;

PhD student: Scientific coordinator:
Oana Stoian (Păunescu)   *Prof. habil. dr. ing. Cristina-Ileana Covaliu-Mierlă*

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.

REFERENCES

[1] Qu X., Alvarez P. J. J., Li Q., Applications of nanotechnology in water and wastewater treatment, *Water Research,* 2013, **47**, p. 3931-3946;

[2] Prachi, Gautam P., Madathil D., Nair A. N. B., Nanotechnology in Waste Water Treatment: A Review, *International Journal of ChemTech Research*, 2013, **5**, p. 2303-2308;

[3] Ravindra K. G., Sanjay K. S., Suresh M. and Mahesh C. C., CHAPTER 1: Contamination of Heavy Metals in Aquatic Media: Transport, Toxicity and Technologies for Remediation, in *Heavy Metals in Water: Presence, Removal and Safety,* 2014, p. 1-24;

[4] Roth, J.A., Homeostatic and toxic mechanisms regulating manganese uptake, retention, and elimination, *Biological Research*, 2006, **39**(1), p. 45–57;

[5] https://www.shutterstock.com/

[13] Cooper P., Color in dyehouse effluent, *Society of Dyers and Colourists*, 1995, p. 1-200;

[14] Forgacs E., Crestile T., Oros G., Removal of synthetic dyes from waste water. A review, *Environmental International*, 2004, **30**(7), pp. 953-971;

[15] Hao O.J., Kim O.J, Chiag P.C., Decolourisation of waste water critical review in environmental, *Science and Technology,* 2000, **30**, p. 449-505;

[19] https://www.carmenbusquets.com/journal/post/fashion-waste-water;

[20] Pyrzynska K., Removal of cadmium from wastewaters with low-cost adsorbents, *Journal of Environmental Chemical Engineering*, 2019, **7**, 102795;

[21] Khadr A.M., Copper concentrations and phases in polluted surface sediments of Lake Edku, Egypt., *The Egyptian Journal of Aquatic Research.,* 2005, **31**(2), p. 253–260;

[23] Fu F., Wang Q., Removal of heavy metal ions from wastewaters: A review, *Journal of Environmental Management*, 2011, **92**, p. 407-418;

[69] Kumar P. G. N. and Sumangala K. B., Fungal Degradation of Azo dye- Red 3BN and Optimization of Physico-Chemical Parameters, *International Journal of Environmental Sciences*, 2011, 1(6), p. 17-24;

[79] Alyüz B., Veli S., Kinetics and equilibrium studies for the removal of nickel and zinc from aqueous solutions by ion exchange resins, *Journal of Hazardous Materials,* 2009, **167**, p. 482-488;

[187] Nataraj S. K., Hosamani K. M., Aminabhavi T. M., Potential application of an electrodialysis pilot plant containing ion-exchange membranes in chromium removal, *Desalination*, 2007, **217**, p.181-190;

[195] Medina B. Y., Torem M. L., de Mesquita L. M. S., On the kinetics of precipitate flotation of Cr III using sodium dodecylsulfate and ethanol, *Minerals Engineering,* 2005, **18**, p. 225-231;

[271] Byrne C., Subramanian G., Pillai S. C., Recent advances in photocatalysis for environmental applications, *Journal of Environmental Chemical Engineering,* 2018, **6**, p. 3531–3555;

PhD student: *Scientific coordinator:*
Oana Stoian (Păunescu)   *Prof. habil. dr. ing. Cristina-Ileana Covaliu-Mierlă*

[277] Patil S. S., Shedbalkar U. U., Truskewycz A., Chopade B. A., Ball A. S., Nanoparticles for environmental clean-up: A review of potential risks and emerging solutions, *Environmental Technology & Innovation*, 2016, **5**, p. 10–21;

[278] Singh R., Bhateria R., Experimental and modeling process optimization of lead adsorption on magnetite nanoparticles via isothermal, kinetics, and thermodynamic studie, *ACS Omega,* 2020, **5**, p. 10826–10837;

[279] Bagbi Y., Sarswat A., Mohan D., Pandey A., Solanki P. R., Lead (Pb2+) adsorption by monodispersed magnetite nanoparticles: Surface analysis and effects of solution chemistry, *Journal of Environmental Chemical Engineering*, 2016, **4**, p. 4237–4247;

[280] Hong J., Xie J., Mirshahghassemi S., Lead J., Metal (Cd, Cr, Ni, Pb) removal from environmentally relevant waters using polyvinylpyrrolidone-coated magnetite nanoparticles, *RSC Advances*, 2020, **10**, p. 3266;

[301] Rajput S., Pittman C. U. Jr., Mohan D., Magnetic magnetite (Fe3O4) nanoparticle synthesis and applications for lead (Pb2+) and chromium (Cr6+) removal from water, *Journal of Colloid and Interface Science,* 2016, **468,** p. 334–346;

[319] Naiya T. K., Bhattacharya A. K., Das S. K., Adsorption of Pb (II) by sawdust and neem bark from aqueous solutions, *Environmental Progress,* 2008, **27**, p. 313–328;

[320] Roonasi P., Holmgren A., An ATR-FTIR study of sulphate sorption on magnetite; rate of adsorption, surface speciation, and effect of calcium ions, *Journal of Colloid and Interface Science,* 2009, **333**, p. 27–32;

[321] Johnson S. B., Franks G. V., Scales P. J., Boger D. V., Healy T. W., Surface chemistry–rheology relationships in concentrated mineral suspensions, International Journal of Mineral Processing, 2000, **58**, p. 267–304;

[322] Covaliu C. I., Matei E., Stoian O., Paraschiv G., Magnetic Nanocomposite Material Containing Chitosan Polymer Used in Wastewater Depollution Processes, *Materiale Plastice*, 2020, **57**(4), p. 70-76;

[323] Teng Y., Li Y., Li Y., Song Q., Preparation of Fe3O4/PVP magnetic nanofibers via in situ method with electrospinning, *Journal of Physics: Conference Series*, 2020, **1549**, 032087;

[324] Du M., Guob B., Jia D., Newly emerging applications of halloysite nanotubes: a review, *Polymer International,* 2010, **59,** p. 574–582;

[337] Akpan U. G., Hameed B. H., Parameters affecting the photocatalytic degradation of dyes
using TiO2-based photocatalysts: A review, *Journal of Hazardous Materials*, 2009, **170**, p. 520–529;

[338] Konstantinou I. K., Albanis T. A., TiO2-assisted photocatalytic degradation of azo dyes in aqueous solution: kinetic and mechanistic investigations—A review, *Applied Catalysis B: Environmental*, 2004, **49**, p. 1–14;

[341] Tang W. Z., An H., UV/TiO2 photocatalytic oxidation of commercial dyes in aqueous solutions, *Chemosphere*, 1995, **31**, p. 4158–4170.

PhD student: *Scientific coordinator:*
Oana Stoian (Păunescu)   *Prof. habil. dr. ing. Cristina-Ileana Covaliu-Mierlă*