VILNIUS GEDIMINAS TECHNICAL UNIVERSITY
FACULTY OF ENVIRONMENTAL ENGINEERING
DEPARTMENT OF ENVIRONMENTAL PROTECTION AND WATER ENGINEERING

Rima Dervinytė

APPLICATION OF EGG SHELLS TO THE REMOVAL OF LEAD FROM CONTAMINATED WATER

KIAUŠINIŲ LUKŠTŲ TAIKYMAS ŠVINUI IŠ UŽTERŠTO VANDENS ŠALINTI

Master's degree Thesis

Study programme of Environmental Protection Technology and Management,
state code 6211EX034
Study field of General Engineering

Vilnius, 2020

Vilnius Gediminas Technical University
Faculty of Environmental Engineering
Department of Environment Protection and Water Engineering

ISBN ISSN
Copies No. ....
Date ..........-.....-.....

Master Degree Studies **Environmental Protection Technology and Management** study programme Master Final Thesis

Title	**Application of Eggs Shells for the Removal of Lead from Contaminated Water**
Author	**Rima Dervinytė**
Academic supervisor	**Dainius Paliulis**

Thesis language: English

Annotation

In the Master thesis egg shell waste application opportunities were analyzed for lead ion adsorption from contaminated water. Aim of the thesis is to perform complex research and evaluation using organic waste (egg shells) as adsorbents to remove heavy metals from aqueous solutions. In the first chapter literature analysis for heavy metal sources, their effect to environment and possible methods for removing them from aqueous solutions is performed. In the second chapter multi–criteria decision analysis comparing methods like reverse osmosis, nanofiltration, adsorption, ion exchange and electrodyalisis is executed. In the third chapter preparation and methodology for adsorption parameter experiments is presented. In the fourth chapter the results for adsorption parameter experiments obtained are statistically processed and plotted graphically. At the end, the conclusions and recommendations as well as the author's publications are presented in the appendices. Thesis consists of 9 main parts: introduction, literature review, multi-criteria decision analysis part, methodological part, analysis of the results, conclusions, recommendations, references and appendices. Thesis volume: 72 pages without references and appendices, 34 figures, 21 tables, 78 references.

Keywords: Adsorption; adsorption isotherm; heavy metals; low cost adsorbent.

Vilniaus Gedimino technikos universitetas
Aplinkos inžinerijos fakultetas
Aplinkos apsaugos ir vandens inžinerijos katedra

ISBN ISSN
Egz. sk. ....
Data ..........-.....-.....

Antrosios pakopos studijų **Aplinkos apsaugos technologijų ir vadybos** programos magistro baigiamasis darbas

Pavadinimas	**Kiaušinių lukštų taikymas švinui iš užteršto vandens šalinti**
Autorius	**Rima Dervinytė**
Vadovas	**Dainius Paliulis**

Kalba: anglų

Anotacija

Magistro darbe išanalizuotos kiaušinių lukštų atliekų panaudojimo galimybės švino jonų adsorbcijai iš užteršto vandens. Darbo tikslas - atlikti tyrimus ir jų vertinimą naudojant organines atliekas (kiaušinių lukštus) kaip adsorbentus sunkiesiems metalams pašalinti iš vandeninių tirpalų. Pirmame skyriuje analizuojami sunkiųjų metalų šaltiniai, jų poveikis aplinkai ir galimi jų pašalinimo iš vandeninių tirpalų metodai. Antrame skyriuje atliekama daugiakriterinė sprendimų analizė, lyginant tokius metodus kaip atvirkštinė osmozė, nanofiltracija, adsorbcija, jonų mainai ir elektrodializė. Trečiajame skyriuje pateiktas adsorbcijos parametrų eksperimentų paruošimas ir metodika. Ketvirtame skyriuje gauti adsorbcijos parametrų eksperimentiniai rezultatai yra statistiškai apdoroti ir rezultatai pavaizduoti grafiškai. Pabaigoje pateikiamos išvados ir rekomendacijos, taip pat autoriaus publikacijos ir prezentacijos bei priedai. Darbą sudaro 9 pagrindinės dalys: įvadas, literatūros apžvalga, daugiakriterinė sprendimų analizės dalis, metodinė dalis, rezultatų analizė, išvados, rekomendacijos, literatūros sąrašas ir priedai. Darbo apimtis - 72 p. teksto be priedų, 34 paveikslai, 21 lentelė, 78 bibliografiniai šaltiniai.

Prasminiai žodžiai: Adsorbcija; adsorbcijos izotermos; sunkieji metalai; mažos kainos adsorbentas.

CONTENTS

LIST OF TABLES

LIST OF FIGURES

ABBREVIATIONS

AAS – Atomic Absorption Spectrometer;
AHP – Analytic Hierarchy Process;
ELECTRE – ELimination Et Choice Translating Reality;
ES – Egg Shells;
ESM – Egg Shell Membrane;
EU – European Union;
GFAAS – Graphite Furnace Atomic Absorption;
HM – Heavy Metals;
MCDA – Multicriteria Decision Analysis;
Me – Metals;
MPC – Maximum Permissible Concentration;
PROMETHEE – Preference Ranking Organization Method for Enrichment Evaluation;
PVC – Polyvinyl Chloride;
RO – Reverse Osmosis;
SCS – Sewage Collection System;
SEM – Scanning Electron Microscopy;
TOPSIS – Technique for Order Preferences by Similarity to an Ideal Solution;
US – United States;
US EPA – United States Environmental Protection Agency;
VIKOR – *VlseKriterijumska Optimizcija i Kaompromisno Resenje* in Serbian;
WHO – World Health Organization.

INTRODUCTION

Problem

Water is one of the most important components of the environment, which is of great importance to people's quality of life, health and development. Experience has shown that water has caused numerous illnesses and deaths. Pollutants are released into the atmosphere and eventually into precipitation, snow–melting, waste, industrial pollution, transport pollutants, farm fertilization materials, and so on. The major water–polluting contaminants are heavy metals, petroleum products, detergents, organic and natural compounds, acids and radioactive isotopes. Heavy metals are predominant among the contaminants listed.

Many anthropogenic variables, manufacturing, transport, agriculture, urbanization, have an effect on the biotic and abiotic environment. Technogenic pollution not only adversely affects the atmosphere, the hydrosphere, the soil, but also destabilizes the natural processes taking place there. Many of the harmful chemical compounds emitted into the environment from sources of contamination settle in the bottom sediments of the water body. Many of the biggest contaminants are heavy metals, which are a biggest anthropogenic concern today. The fastest metal migration in nature is ensured by the water medium, since most of these chemical compounds are soluble and have a high spread. The high level of interest in heavy metals is due to the fact that, in nature, metals have the capacity to accumulate by migrating from one natural system to another. These are the most harmful pollutants that join the metabolic cycle in a number of ways, depending on the rate and level of development in the biosphere, thus disrupting the physiological functions of organisms.

Actuality

Environmental contamination of toxic metals has been prevalent and widely includes significant volumes of wastewater. Due to the extent of the issue of heavy metal emissions, work into new and cheaper metal removal methods has recently increased. First of all, heavy metals have the potential to persevere in natural conditions for a longer period of time. In addition, they have the ability to occur at successive stages of the biological chain, contributing to acute and chronic diseases. It is established that chicken egg shells are convenient green and economic absorbents due to their simple availability and lack of toxic components. According to studies by the Lithuanian Department of Statistics, about 5895 tons of egg shell waste was generated in the country in 2018 and the quantity is increasing every year.

The method of activated carbon adsorption is appealing to many scientists, as heavy metal ions can be removed to scarcely detectable amounts. However, the procedure has not been used widely for its high costs. The use of low–cost materials as an adsorbent for metal removal from wastewater has therefore been emphasized. The amount of adsorption work as a method for eliminating heavy metals from contaminated water using low– cost adsorbents has increased exponentially in recent years, with scientists such as Ai Phing Lim and Ahmad Zaharin Aris in Malaysia and Tabatabaee Azam, Dastgoshadeh Fereshteh and Tabatabaee Akram in Iran making very useful contributions to research studies and experiments.

Heavy metal emissions and growing volumes of biological waste are major environmental problems in the world, so it is very important to develop the water treatment system for heavy metals by using waste products as low–cost, renewable and high–purity adsorbents.

Aim of the work

Perform complex research and evaluation using organic waste (egg shells) as adsorbents to remove heavy metals from aqueous solutions.

Objectives

- Complete literature analysis for heavy metal sources, their effect to environment, possible methods for removing HM;
- Determine the physical, chemical and adsorption properties of egg shell adsorbent used for selected lead ion removal;
- Perform multicriteria decision analysis on the methods for removing lead ions from contaminated water;
- Carry out experimental studies to evaluate the efficiency of egg shell adsorption by removing lead (Pb) ions from aqueous solutions;
- To evaluate the influence of adsorbent and HM contaminated solutions on adsorption properties by executing multicriteria analysis.

Novelty

The novelty of the study is complicated research involving experimental studies into the adsorbent effect of egg shells on relatively small amounts of lead. Multicirterial decision analysis on the methods of removal of lead from polluted water and analysis on adsorption parameters concerning adsorption is also carried out, depending on the results of the experimental evidence.

Practical value

The experimental studies conducted and the results obtained during these experiments would demonstrate whether natural egg shell waste can be successfully used to remove heavy metals from aqueous solutions. This work could be used to develop technologies for the removal of lead ions from wastewater (sewage, landfill filtrate, etc.) with an egg shell adsorbent load.

1. HEAVY METAL REMOVAL FROM WATER APPLYING EGG SHELL ADSORBENTS

1.1 Main sources of heavy metals release into environment

Heavy metals (HM) are generally described as natural elements of the environment with at least five times bigger density than water. The atomic weight of these elements is relatively high compared to other elements existing in nature. Due to the wide commercial, agricultural and technical usability of heavy metals, they have spread all over the world. However, the prevalence of heavy metals raises questions about their prospective adverse impacts on humans and the environment. The toxicity of the chemical compounds depends on several factors, including chemical dose, type of exposure, age, genetics and dietary patterns of the affected individuals. Due to its toxicity, arsenic, cadmium , chromium , lead and mercury are some of the most impactful heavy metals in human health (Tchounwou et al., 2012).

Heavy metal sources can be classified into two main parts – natural and anthropogenic. The main natural factors from which heavy metals enter the environment are shown in Fig. 1.1:

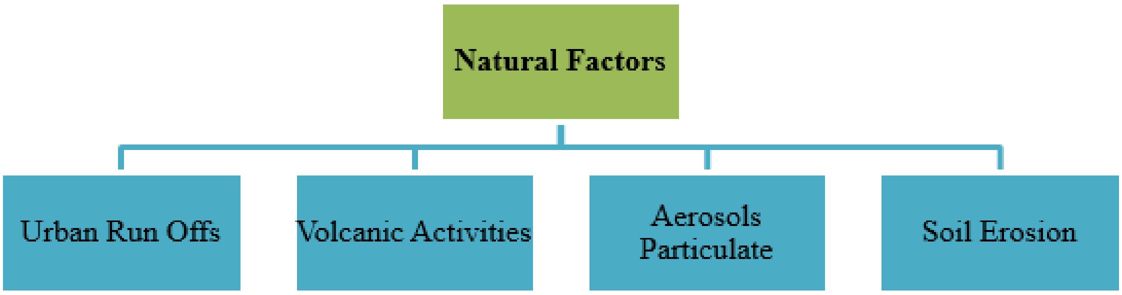

Fig. 1.1. The main natural factors

Volcanic eruptions have repeatedly been shown to have a catastrophic effect on the atmosphere, the climate, the environment in general and human health. Not only is the quality of the environment deteriorating due to the release of gases such as carbon dioxide, but also various organic compounds and heavy metals such as mercury, lead and gold, which contribute to environmental pollution. Mentioned heavy metals are known to greatly degrade water quality in water bodies (Akpor et al., 2014).

Some volcanic rocks are responsible for the accumulation of metals in soil and water. Due to the diffusion of acidic volcanic gases into permeable water rocks and the distribution of the hydrological amount in volcanic layers, heavy metals enter the environment. Volcanic activity is thought to lead to the spread of metals such as lead, magnesium, copper, arsenic, mercury, aluminum, zinc and many other HMs in the environment (Tabatabaee et al., 2014).

Dispersion of heavy metals is an important consequence of volcanic eruptions. Along with toxic SO_2 and H_2S gases, the elements of aluminum, zinc, manganese, lead, nickel, copper and mercury are also released during volcanic eruptions. These pollutants usually have a negative effect on the fauna and flora at the source of pollution, but are often distributed over longer distances (Akpor et al., 2014; Sauliutė, 2013).

Soil rock formation is also one of the natural sources of heavy metal dispersion. The soil layer is one of the most important natural sources of HM. Heavy metals are indeed natural elements that exist in nature, and their background concentrations vary in different parts of the world. The concentration of heavy metals depends on factors such as soil type and environmental factors that determine the severity of the erosion cycle. Scientific studies have found that volcanic rocks have higher concentrations of heavy metals than sedimentary rocks. Different forms of volcanic rocks contain different concentrations of heavy metals. For example, metal concentrations in serpentine rocks will be higher than in basalt or granite (Sauliutė, 2013).

The emissions of airborne pollutants (mercury or cadmium) from natural forests and steppe fires are another source of pollution. However, the amount of heavy metals entering the atmosphere from natural sources does not usually cause major harmful impacts on plants and other living organisms (Sauliutė, 2013).

Erosion of soil is also a cause of heavy metal contamination in water. Wind and water are two primary causes for soil erosion. Heavy metals accumulated in the sediment are released into the soil during precipitation. Heavy metals can be accumulated with runoff and spread to the atmosphere in the run–off due to erosion. During flooding, some HMs are wash away into faulty drainage structures. And then eventually pollutants are released into nearby rivers (Akpor et al., 2014).

HMs have the capability to remain in natural environments for a prolonged period of time. These can also cause various diseases due to the ability to accumulate at successive stages of the biological chain (Akpor and Muchie, 2010).

Some of the most polluting sources of anthropogenic heavy metals are electroplating, metalworking, clothing, and industrial operations. Therefore, anthropogenic influences include mainly those shown in Fig. 1.2. Electroplating and metal finishing include the deposition of thin protective layers on metal surfaces prepared using electrochemical processes. Toxic metals can be released into wastewater discharges during this process. This can be done either by rinsing the liquid or by spilling and dumping the process baths (Akpor et al., 2014).

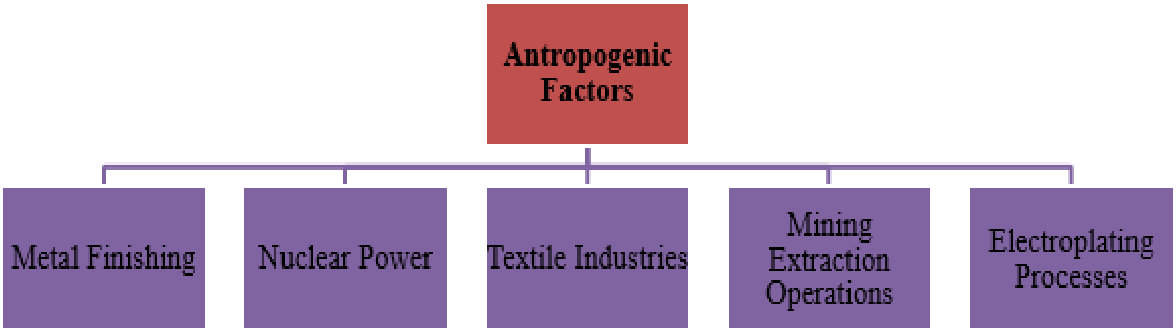

Fig. 1.2. The main anthropogenic factors

Wastewater from many factories and companies is responsible for the release of heavy metals into the natural environment. The removal of these metals is extremely important from both an environmental and an economic point of view. Wastewater generated by the activities of modern industries (refineries, non–ferrous metal plants, etc.) usually has a complex composition that includes metals, suspended solids, and other elements. Under ever–tightening environmental laws, these harmful by–products must be decontaminated because of their risk to humans, animals and plants (Martín et al., 2005).

Emission levels of heavy metals of anthropogenic origin from agriculture (fertilizers, pesticides), metalworking (metal mining and metal foundry), energy production and combustion, electronics manufacturing and waste disposal are growing (Wuana and Okieimen, 2011). Pollution sources of anthropogenic nature are shown in Fig. 1.3.

Heavy metal pollution in the world is recognized as an important environmental concern, which highlights the threat to life, health and genetics, holding one of the leading positions among other ecological concerns such as pesticides, acid rain, oil spills, chemical fertilizers, urban noise (Sauliutė, 2013).

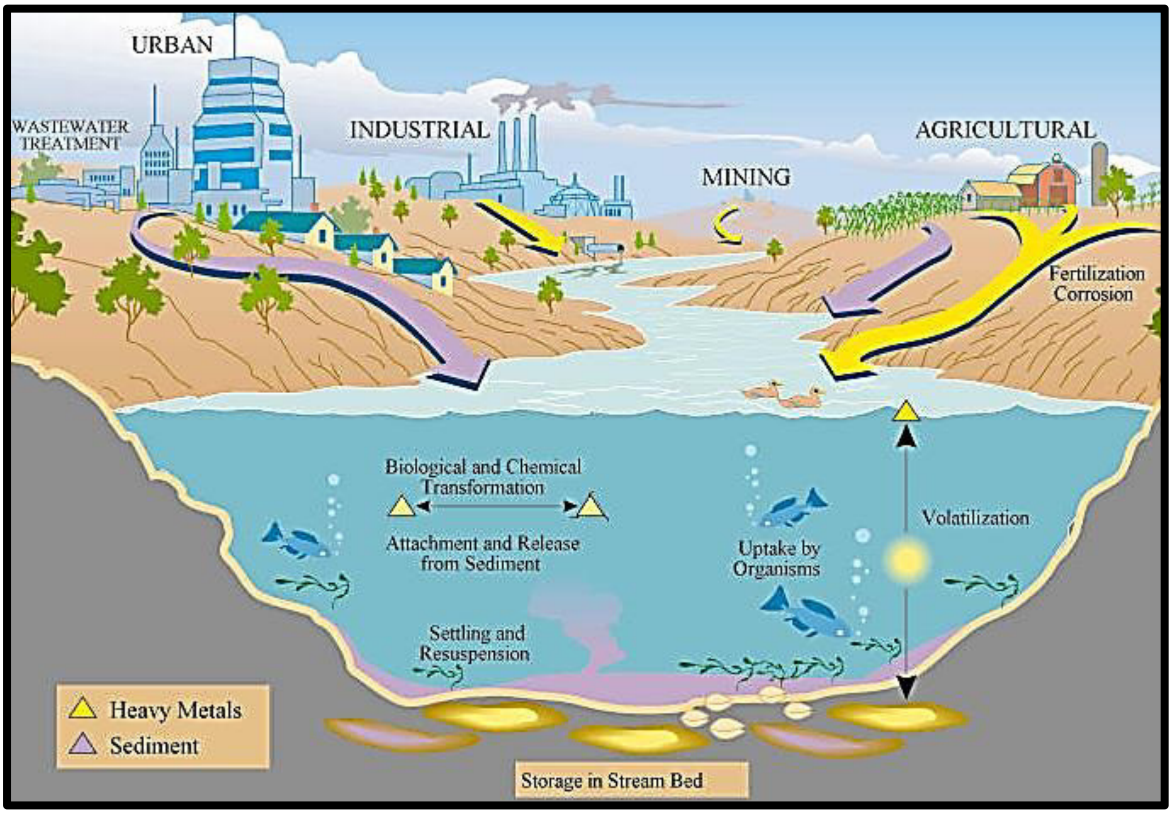

Fig. 1.3. Emissions of heavy metals of anthropogenic origin (Meade, 1995)

Anthropogenic emissions of heavy metals are often released into the environment in the form of gas. HM enters the environment in the form of waste during mining operations. The processing of steel, iron and sawn wood contributes to the formation of chromium. The combustion of fossil fuels (e.g. coal) and industrial waste, cement manufacturing and phosphate mining are another significant source of anthropogenic heavy metals in the atmosphere. The primary source of heavy metals in terrestrial and marine environments is sewage sludge, fertilizer used in agriculture, pesticides, animal waste and wastewater disposal (Sauliutė, 2013).

The concept of heavy metal applies to a cluster of components with an atomic weight of 63.5 to 200.6, such as lead, cadmium, chromium, nickel and copper. These metals are the most poisonous substances in freshwater systems, killing all water life and accumulating toxic substances for a long time. Most common HM manufacturing emissions are listed in Table 1.1. (Zhao *et al.*, 2016).

Cadmium enters the atmosphere mainly from radio, electrical engineering, metalworking, batteries, fertilizer production and several other companies. Cadmium and cadmium compounds are used in power plants, galvanized coatings, rubber, galvanic batteries, plastics and many other products. Cadmium, like silver, is used as one of the main indicators of environmental pollution (Vilniaus Aplinkos Informacinė… 2019).

Table 1.1. Various sources of HM pollution (Minister of Environment… 2006)

Branch of industry	Heavy metals
Pesticide factories	copper, common chromium, chromium (VI), zinc, arsenic;
Glass industry companies	lead, arsenic, antimony
Chemical industries	mercury, cadmium, copper, nickel, lead, common chromium, chromium (VI), zinc; tributyl tin
Surface metal coating (galvanic) companies	cadmium, mercury, common chromium, chromium (VI), zinc, tin, copper, lead, nickel, silver
Leather industry companies	common chrome
Textile industry companies	common chrome, chrome (VI), copper, zinc
Fertilizer industry factories	cadmium, mercury, zinc

Cadmium is one of the heavy metals that poses a significant risk to the environment and human health. It is usually found in the earth's crust at an average concentration of 0.1 mg/kg. The highest content of cadmium compounds in the environment is found in sedimentary rocks. Approximately 15 mg of cadmium/kg is found in marine phosphates (Tchounwou et al., 2012).

Although cadmium is known to be used in a variety of manufacturing applications, the most important uses of cadmium in industry are in the production of alloys, pigments and batteries. The use of cadmium in battery production has been growing significantly for a long time, but its industrial use in developing countries has declined in line with environmental requirements. The average US cadmium intake is about 0.4 μg/kg per day. This is half the value of the US Environmental Protection Agency (EPA) oral reference dose. Occurring decrease is due to the imposition of strict effluent volumes for coating works and the more recent general restriction on the use of cadmium in some countries (Tchounwou et al., 2012).

Lead is commonly used in cable printing, protective screens, pigment production, alloys, the glass industry, glazing, enamels, lubricants, plastics, insecticides, explosives, batteries, some paints, and finally, piezoelectrics (Vilniaus Aplinkos Informacinė… 2019).

Lead is generated in welding, roofing, leaded sewage and PVC pipes (as an impurity) and is also used as a fuel additive (although the production or use of such fuels is currently significantly reduced or banned in the EU), ammunition, chimney liners, some countries also use lead in fishing weights, yacht keel and other sources. Most of the lead is thought to enter the sewage from the lead sewer pipes (Patil and Puttaiah, 2013).

Chromium enters a variety of environmental media – air, water and soil from many natural and anthropogenic sources, but is mainly released from the manufacturing industry. The industries with the highest chromium emissions are metal processing, chromium product production, and pigment manufacture. Highest concentrations of chromium in the environment are related to the release of chromium from air and wastewater. This pollutant is mainly emitted from metallurgy, refractories and the chemical industry. Chromium exists mainly in the hexavalent form (Cr (VI)) due to anthropogenic activities. Hexavalent chromium is a hazardous industrial pollutant listed by various regulatory agencies as a human carcinogen. The health risk of chromium depends on its oxidation level. Chromium has a variety of forms of exposure, ranging from low metal toxicity to high hexavalent toxicity. All chromium–containing chemicals were previously considered man–made. In environment and biological materials, it was thought to exist only in the trivalent form of Cr (III). However, natural tetravalent chromium in soils and surface waters has recently been found to exceed the World Health Organization (WHO) water limit of 50 µg Hexavalent chromium per liter. It is extensively used in various manufacturing practices and is therefore considered a pollutant in most of the environmental structures. Chromium is often employed in chromium plating, dyeing and pigmentation, often used as an anti–corrosion cooking additive and compound for boiler protection (Tchounwou et al., 2012).

Nickel and its compounds are mainly used in the manufacture of stainless steel or nickel alloys under the influence of corrosion and high temperatures. Aforementioned alloys are widely applied in the metall, chemistry and food handling industries, especially in the production of catalysts and pigments. The most important nickel salts in production are:

- nickel chloride,
- sulfate, nitrate,
- carbonate, hydroxide,
- acetate,
- oxide (Žadeikytė, 2013).

Natural sources of nickel in the atmosphere are dust from decaying rocks and soil, volcanic emissions and forest fires. Nickel enters the ambient air through the combustion of coal, diesel, fuel oil, waste incineration and wastewater treatment (Žadeikytė, 2013).

Nickel is commonly used in the manufacture of alloys, catalysts, galvanic surfaces and Ni–Cd batteries. Nickel occurs in the environment mainly due to corrosion of laundry equipment, electroplating, jewelry, pigments and paints (Debabrata, 2013).

The last heavy metal analyzed is Copper, which is mainly released due to plumbing corrosion, copper chloride, pigments, wood preservatives, larvicides and paints. Copper is used in the electronics industry, in the coating industry, in the paper, textile, rubber, fungicide, printing, plastic, brass and other alloy industries. Copper can also be emitted into the environment from a variety of small commercial activities, as well as from heating systems in buildings (Patil and Puttaiah, 2013).

Table 1.2. Maximum permitted concentrations (MPC) of some priority hazardous and other controlled substances (Minister of Environment… 2006)

Heavy metal	MPC into the SCS	MPC into the natural environment	MPC into water body	Limit concentration in the SCS	Limit concentration into the natural environment
Cadmium	0.1	0.04	5	–	–
Lead	0,5	0,1	0,005	0,1	0,02
Cromium	2	0,5	0,01	0,4	0,1
Nickel	0,5	0,2	0,01	0,1	0,04
Copper	2	0,5	0,01	0,4	0,1

Note: All values are in mg/L;

Limit Concentration limit means the maximum calculated, measured or planned concentration limit of a substance below which it is not necessary to control that substance.

Maximum permitted concentrations of some heavy metals from Lithuanian Wastewater Management Regulation are provided in Table 1.2.

Sewage treatment regulations aim to reduce the exposure of humans and the environment to hazardous chemicals. This includes the types and concentrations of heavy metals that may be present in the effluent. However, it is very important to treat metal–contaminated wastewater before releasing it into the environment (Gunatilake, 2015).

1.2 Heavy metals effects on human health and environment

Various harmful organic and inorganic substances are constantly spreading in the air, water and soil, as technical human activities are constantly evolving and expanding. Various toxic substances enter the human body in various ways. Possible routes of poisoning – consumed with food, drinking water and even inhaled air. These organic and inorganic compounds are harmful to the human body and cause various chronic diseases and, in high doses, cause even life–threatening acute symptoms. Heavy metals are recognized as one of the most dangerous pollutants. Heavy metals are still considered to be one of the most persistent sources of water pollution. Unlike other contaminants, they are difficult to break down and can persist throughout the food chain and pose a potential risk to human health and the natural environment. At least 20 chemical elements in table metals are classified as toxic. Half of them are released into the environment in concentrations that pose a significant risk to human health (Foktas, 2014; Tabatabaee et al., 2014).

The more soluble HMs and their compounds are, the more toxic they are to the environment. When the body accumulates higher, in excess of physiological concentrations of heavy metals, toxicity occurs. Heavy metals can be classified as hazardous to most living organisms as follows: copper, mercury, arsenic, titanium, chromium, cadmium, zinc, manganese, iron, and lead. Heavy metals are characterized by mutagenic and carcinogenic effects, which are said to occur not immediately but over time and depend on the concentration of heavy metals in the body. Most HMs enter the body along with food. The excretion and accumulation of heavy metals and their compounds can be very different, for example, some are excreted through the digestive and urinary systems, others through sweat, others from the body, bones, skin, hair or internal organs (Foktas, 2014).

Toxic metals in vegetables and corn products have been reported to accumulate in the kidneys and cause dysfunction. Skeletal damage has been reported to be associated with heavy metals such as high levels of selenium (Akpor et al., 2014).

Although individual metals have been reported to have specific signs of toxicity, gastrointestinal disorders, diarrhea, tremors, and many other signs have been associated with signs of cadmium, lead, zinc, copper, and aluminum poisoning. Heavy metal poisoning is thought to cause depression and pneumonia upon inhalation of volatile vapors (Akpor et al., 2014).

Although heavy metals are natural components of the earth, they cannot be broken down, so they are toxic only if they are not metabolized in the body and are accumulated in the soft tissues of the body. Lead, for example, is seen as a major threat to children’s health, the effects of which can change their overall quality of life. Lead can affect a child's growth, nervous system damage and development, learning disabilities. It is now also linked to child crime and antisocial behavior (Akpor et al., 2014).

Lead has powerful neurotoxic, phytotoxic, bacterial, carcinogenic and mutagenic properties. Pb may cause blood, heart, blood vessels, gastrointestinal, nervous system, metabolic and endocrine disorders, many intoxications, including during pregnancy (Vilniaus Aplinkos Informacinė… 2019).

There is no agreement on the exact lethal single dose of Pb. Some literature suggests that it ranges from 155 mg/kg to 454 mg/kg body weight. Pb is a toxic metal used in many fields. Pb poisoning and mortality depend on many characteristics of the body: a certain dose of Pb can cause moderate poisoning in one person and can be fatal in another. Pb poses a serious threat to vital functions and normal development of the body. It is especially dangerous for children (Foktas, 2014).

Lead can enter the body by inhalation of its vapor, through the skin or simply by ingestion. The possible side effects of Pb entering the body depend on the characteristics of the person's diet and age. Therefore, although adults absorb an average of 10 to 15 % of the total intake, this amount can increase up to 50 % if Pb poisoning occurs in an infant, young child or pregnant woman. Intestinal absorption is further enhanced by low dietary intake of iron, calcium, phosphorus or zinc. Absorbed Pb is circulating to other tissues and is found mainly in soft tissues, blood, and bones. Approximately 99 % of Pb is found in erythrocytes in the blood and the remainder is distributed in plasma and blood serum. lead levels in plasma become higher than in blood when Pb is distributed to other organs such as brain, lungs, spleen, kidney cortex, teeth, bones. The uptake of Pb from the blood into soft tissues lasts about 4–6 weeks, with a half–life of about 35 days in the blood, about 40 days in the soft tissues, and 20 to 30 years in the bones. The half–life of Pb in various tissues and organs may depend on the age of the body: in children it is significantly longer (Foktas, 2014).

Lead–compound poisoning can cause severe pain and constipation. After poisoning, gastric lavage or, in some cases, activated charcoal may be prescribed. Heavy metal poisoning through the gastrointestinal tract is particularly dangerous. Heavy metal compounds are ionized in a variety of pH environments: both acidic, such as scandal, and alkaline, such as intestinal media. It is known that the most active heavy metal compounds are ionized in the duodenum and in the small intestine – in the jejunum. Heavy metals, complexed with plasma proteins, amino acids and fats, circulate throughout the human body (Foktas, 2014).

Heavy metals accumulate in all organs of the body. Most heavy metals have been found to accumulate in the kidneys and liver. This tendency to accumulate heavy metals is due to the fact that it is the liver and kidney that contain the most proteins with a large number of thiol groups, to which heavy metals bind particularly easily (Foktas, 2014).

Heavy metals and their compounds are excreted in a variety of ways and impair the functional function of a particular organ, such as the kidneys, skin, and intestines. Heavy metals enter cells and damage the envelopes of cellular structures and disrupt vital biochemical processes. It is known that fat–soluble heavy metal compounds enter the body much more easily through cell membranes. Other heavy metals enter by active transport, which requires energy or diffuse by passive transport, which does not require additional energy (Foktas, 2014).

Heavy metals also have irreversible effects on aquatic ecosystems. Several of them are associated with the death of aquatic species, algal blooms, habitat destruction due to the deposition of metals on the bottom of aquatic bodies, debris, increased water flow, and other short–term and long–term toxicity.

The high content of heavy metals in the soil degrades the quality and quantity of food, as it prevents plants from growing, absorbing nutrients, and interfering with physiological and metabolic functions. Adverse effects in animals have been associated with reduced development and growth, cancer, organ failure, nervous system damage and, in extreme cases, death (Akpor et al., 2014).

For example, lead in plants inhibits the activity of many enzymes, causing an imbalance of minerals (potassium, calcium, magnesium, iron, and other minerals). Lead also affects the structure and permeability of plant cell membranes, reducing the intensity of photosynthesis by disrupting the structure of chloroplasts and disrupting electron transport. With low concentrations of lead, plant cells can breathe, but as the concentration in plant cells increases, these processes proceed more slowly than normal. Visual changes in plants when exposed to lead occur through poor growth and a darkened root system (Foktas, 2014).

Improperly treated wastewater has various effects on the environment when it is discharged into the receiving environment. The number of living organisms in aquatic ecosystems is strongly affected by heavy metal pollution. Heavy metals not only have a serious negative impact on the development of aquatic organisms but can cause significant disruptions to biological wastewater treatment plants. High concentrations of heavy metals pose a significant threat to soil and plants, as animals and humans consume such plants due to their entry into the food chain through bioaccumulation, leading to significant adverse effects (Akpor et al., 2014).

1.3 Possible methods for removing heavy metals from contaminated water

Heavy metals are harmful to the environment and many different removal technologies are used to remove them. Fig. 1.4 presents the most well–known heavy metal removal technologies.

Numerous removal methods have been tested for the removal of lead ions from contaminated water, such as chemical precipitation, coagulation, complexation, application of activated carbon in the adsorption process, ion exchange, solvent extraction, foam flotation, electrodisposition, and membrane operations (Gunatilake, 2015; Tabatabaee et al., 2014).

Each technique has its advantages and disadvantages. Because of the need for efficient and cost–effective methods for removing heavy metals from aqueous solutions, there is still a search for a technology or method that can be useful in reducing the amount of heavy metals in the environment. Sewage treatment requires a focus on high throughput while keeping costs to a minimum (Gunatilake, 2015).

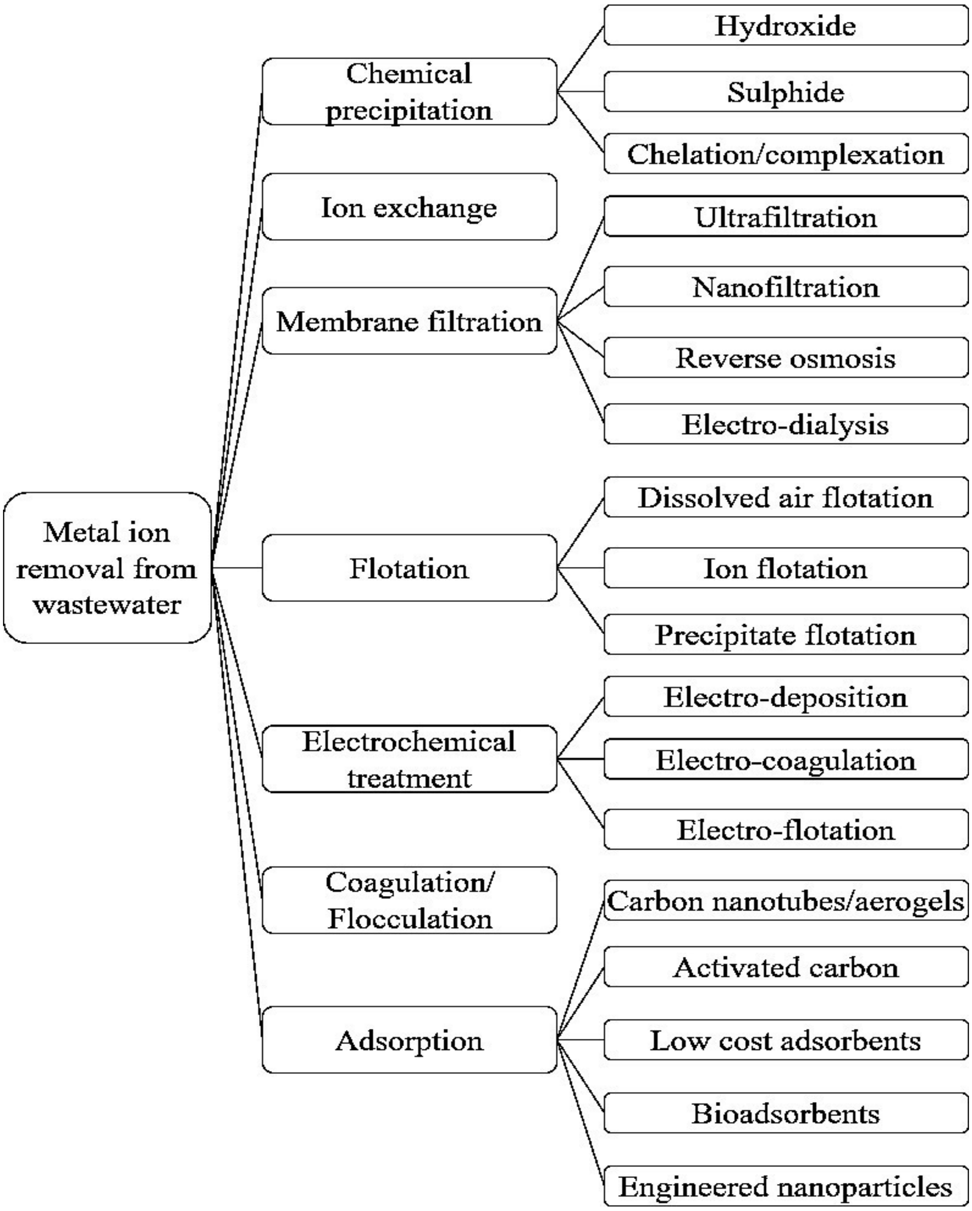

Fig. 1.4. Methods of removal of heavy metals from wastewater (Bilal et al., 2013)

Because most conventional methods are neither efficient nor cost–effective, especially when used to remove heavy metal ions to minimum concentrations, new separation methods are needed to reduce heavy metal concentrations to environmentally acceptable standards at an affordable price. Several new methods for developing cost–effective and efficient heavy metal adsorption methods have been investigated (Gunatilake, 2015).

1.3.1 Chemical Precipitation

One of the most commonly used methods in industry for the removal of heavy metals from inorganic wastewater is chemical precipitation. It is said to be the most common due to its extremely simple use. This chemical precipitation method typically combines insoluble heavy metals with compounds such as hydroxide, sulfide, carbonate, and phosphate into a precipitate. Therefore, the action of this process is based on the formation of insoluble metal deposits in solution or otherwise – the precipitation reaction of dissolved metals (Akpor and Muchie, 2010). Basic scheme of chemical precipitation is provided below in Fig 1.5.

During chemical precipitation, even very fine particles are precipitated. Chemical additives such as precipitants and coagulants are used to increase the particle size to make it easier to remove as sludge. A flocculation process can also be used to combine the particles into larger, more easily removed compounds. When contaminants such as metal ions settle to the bottom of the tank and form solid, tangible materials, they can be easily removed. In this way, contaminated water can be treated to a relatively low concentration of metals (Akpor and Muchie, 2010).

By changing parameters such as temperature, pH, initial concentration, or ion loading, the efficiency of metal ion removal in solution can be increased. In most cases, chemical precipitation in practice precipitates metals using hydroxides. This method is popular for its comparable simplicity and low sediment (lime) content, automatic pH control, cost and simplicity. From pH 8.0 to 11.0, the solubility of various metal hydroxides is reduced to a minimum (Gunatilake, 2015; Mashangwa, 2016).

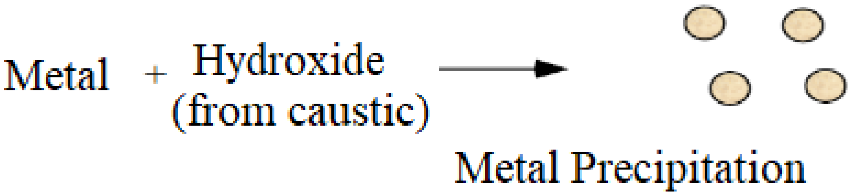

Fig. 1.5. Chemical metal precipitation (Gunatilake, 2015)

The efficiency of the method is determined by such factors as the minimum effort for hydrolysis of metal ions, the state of oxidation, pH, the presence or absence of complex ions, settling time, liquid mixing and other deposition and filtration properties. With the chemical deposition method, metal ions are slowly or poorly deposited, metal deposits accumulate and excess sludge (secondary pollution) is formed, which needs to be treated further (Mashangwa, 2016). Chemical deposition requires large amounts of chemicals to remove metals to the required standards. Some of the main disadvantages are high sludge formation, slow fall of metals, poor deposition, accumulation of metal deposits and long–term environmental impact of sludge removal. This turns the issue of water pollution into a matter of solid waste disposal, and metals are not recovered (Aziz et al., 2008; Gunatilake, 2015).

1.3.2 Ion Exchange

The ion exchange method is also considered to be one of the most widely used methods of removing heavy metals from wastewater. In a process based on this method, ions that are electrostatically linked to functional groups in one medium are replaced by other, mobile ions in solution (Mashangwa, 2016).

Ion exchange can draw soluble ions from liquid phase to solid one. Therefore it is widely used in the water treatment sector. The ion exchange process, as a cost–effective method, usually involves inexpensive materials and relatively easy maintenance. This method has been shown to be particularly effective in removing heavy metals from contaminated water. However, the best results are obtained by treating water with only low concentrations of heavy metals (Gunatilake, 2015).

The ion exchange method uses anions or cations to attract metal ions. Ion exchangers are used for easier removal of Me^{n+} from the contaminated solution. Synthetic resins usually applied as said ion exchanger. Unfortunately, ion exchange is most effective for small concentrations of metal ions and is very dependent on the pH of the solution (Hubicki and Koodynsk, 2012).

Ionic resins are usually water–impenetrable, solid elements that absorb positively or negatively charged ions from an electrolyte solution. Ionic resins release an equal amount of other ions of the same charge into the liquid. In solutions, ions such as H^+ and Na^+ are replaced by ions as nickel (Ni^{2+}), copper (Cu^{2+}), and zinc (Zn^{2+}). Similarly, negative ions, including OH^- and Cl^-, can be substituted by negative ions such as CrO^{2-}, SO_4^{2-}, or others (Gunatilake, 2015).

Frequently used ions are highly acidic (having a sulfonic acid group) or moderately acidic (having a carboxylic acid group). The following equations explain these reactions (Fu and Wang, 2011):

$$nR - SO_3H + Me^{n+} \rightarrow (R\text{-}SO_3^-)_n\, Me^{n+} + nH^+ \tag{1.1}$$

$$nR - COOH + Me^{n+} \rightarrow (R - COO^-)_n\, Me^{n+} + nH^+ \tag{1.2}$$

where

$nR–SO_3H$ and $nR–COOH$ – ion exchange resins;

Me^{n+} – metal ions in solution;

$(R–SO_3^-)_nMe^{n+}$ and $(R–COO^-)_n Me^{n+}$ – ionic and metal compound upon exchange reaction;

nH^+ – equivalent ions.

Minimal–cost natural zeolites are by far the most widely applied, but more recently, synthetic ions are more expensive but more effective for ion exchange reactions (Fu and Wang, 2011).

Nevertheless, the primary limiting factors of ion exchange application in practice for inorganic effluent treatment are high cost and the need for suitable pretreatment methods. The matrix gets quickly fouled in the wastewater by organics and other solids. This makes concentrated metal solution difficult to treat. In addition, the exchange of ions is nonsolic and extremely sensitive to the solution's pH. Ion exchange at high levels of competing Na and Ca ions is an almost completely inefficient method of water purification (Mashangwa, 2016).

This method has advantages such as high efficiency, selective removal, no generation of sludge, and disadvantages as – not broadly accepted, increased costs (Bolisetty et al., 2019).

1.3.3 Membrane Filtration

Membrane filtration has been recognized as one of the inorganic wastewater treatment methods. This method removes suspended solids, synthetic and inorganic pollutants (like heavy metals). Depending on the particle size of the contaminants that can be maintained, various forms of membrane filtration, such as ultrafiltration, nanofiltration, and reverse osmosis, can be used to remove inorganic elements from wastewater. (Gunatilake, 2015; Mashangwa, 2016). The principle of membrane filtration is shown in Fig. 1.6.

An impermeable membrane used to separate the solution from HM, macromolecules and suspended solids is used for ultrafiltration. Ultrafiltration reach more than 90 % removal efficiency, depending on membrane properties such as metal concentration (10 to 112 mg/L), pH (5 to 9.5) and pressure (2 to 5 bar). The advantages of ultrafiltration are low driving force and lower volume due to high packing density (Gunatilake, 2015; Roy, 2014).

Reverse osmosis is one way to separate contaminants from contaminated water. This process is based on pushing the solution through a membrane, which traps the solution on one side of the membrane and the contaminants on the other side (as shown in Fig. 1.7) (Gunatilake, 2015).

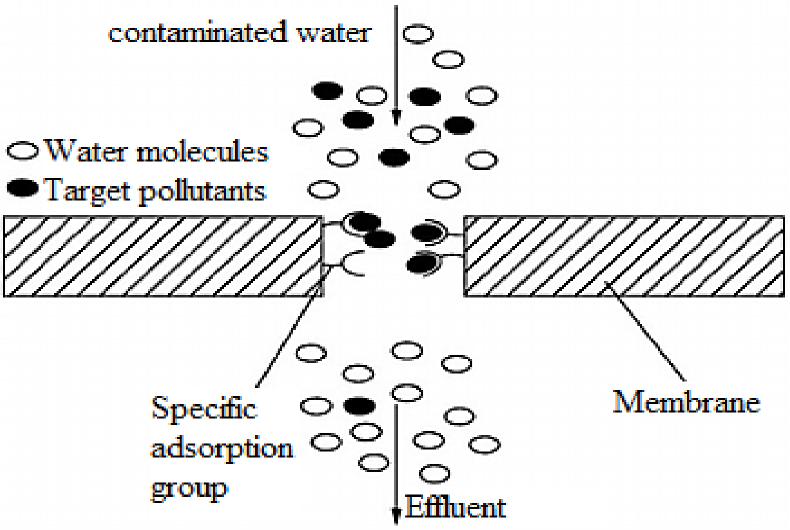

Fig. 1.6. The principle of membrane adsorbent (Khulbe and Matsuura, 2018)

The membrane is semi–permeable, which means that it allows solvent to pass through, while heavy metals do not. In their matrix, the membranes used during RO have a thick barrier layer in which most of the contaminant separation takes place. With the help of reverse osmosis, many types of molecules and ions, such as bacteria, can be extracted from solutions. Due to its advantages, this method can be used in industrial processes. Reverse osmosis requires a diffusion process, which means that the separation efficiency depends on the soluble substance concentration, pressure, and water flow rate (Gunatilake, 2015).

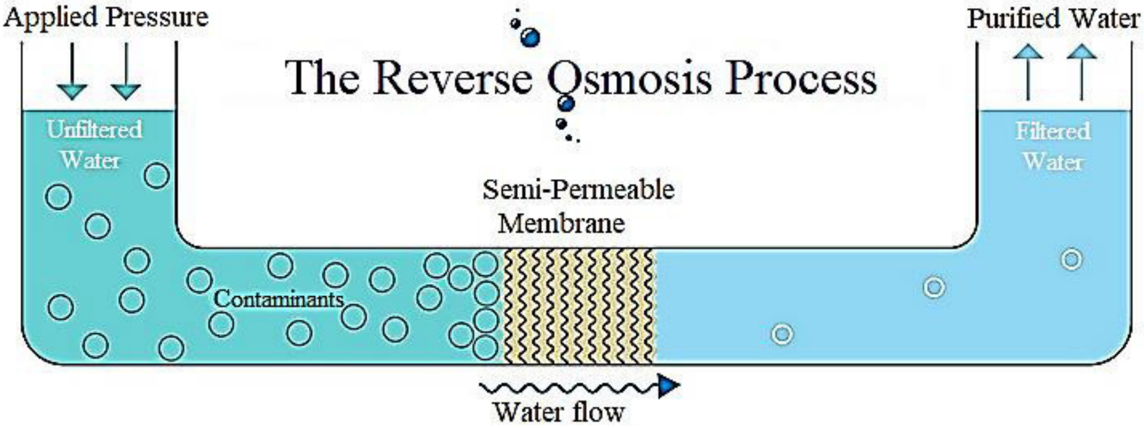

Fig. 1.7. The reverse osmosis process (Reliance Home Comfort, 2019)

Reverse osmosis is, in fact, one of the ways in which many dissolved organisms can be separated from water. This method represents more than 20 % of the planet’s desalination power. The research results revealed that the reverse osmosis cycle successfully separated copper and nickel ions from contaminated water, and the removal efficiency of the two ions was as high as 99.5 % (Roy, 2014).

The advantages of reverse osmosis include high removal efficiencies, no chemical or thermal additives, no phase change, no secondary emissions, ease of production and operation, and relatively little space required by the technology. Disadvantages of RO include – metal selectivity, permeability, high energy consumption due to the innate process caused by pressure (Bolisetty et al., 2019).

1.3.4 Flotation

Flotation is a method of removing heavy metals using bubbles formed in a liquid to separate heavy metals from water. The main flotation processes used in practice are dissolved air bubble flotation, ion compound flotation and sediment flotation. Air bubbles formed in water combine with suspended solids to form agglomerates with a relatively low density. For this reason, the formations rise to the surface of the solution and accrue as sludge. When pollutants are at the surface of solution. they can be easily extracted (Mashangwa, 2016; Roy, 2014).

The second way to extract HM ions from contaminated water is using flotation. This cycle involves the conversion of metal ions to hydrophobic compounds using surfactants in wastewater. After removing these compounds with the help of air bubbles (Mashangwa, 2016; Roy, 2014).

The researchers investigated the possibility of ion flotation to remove cadmium, lead and copper from an aqueous solution. Saponin, a plant–derived bioactive agent, was used for this study. The average removal efficiencies for cadmium (Cd), copper (Cu), and lead (Pb) were 71.17 %, 81.13 %, and 89.95 %, respectively (Yuan et al., 2008).

Sediment accumulation is alternative choice of flotation. This method is based on the development of sediments and later their removal by lifting the sediments with air bubbles. Sedimentation of contaminants depending on the concentration of the metal solution may occur upon release of the metal hydroxide or salts with a specific anion (Bilal et al., 2013; Mashangwa, 2016).

1.3.5 Electrochemical Treatments

A completely different technique applied to remove HM from contaminated water streams is electrolytic regeneration. Aforementioned method needs electricity power current that passes between a HM contaminated solution containing cathode and anode plates. When moving from anode to cathode, electrons generate electricity. The electrochemical treatment of heavy metal wastewater is the precipitation of HM in the form of hydroxides in a weakly acidic or neutralized catholyte (Gunatilake, 2015).

Electrolytic deposition, electrocoagulation, electric flotation and electro–oxidation are among the methods of electrochemical treatment for wastewater treatment. Application of electrolytic oxidation and destabilizing contaminants in the formation of coagulants is the formation of folks (Mollah *et al.*, 2001; Shim *et al.*, 2014). During this process, charged ionized metals that react with the anion are removed from the effluent. This process is beneficial due to the following properties: reduced sludge production, no use of chemicals and easy management (Aziz *et al.*, 2008; Gunatilake, 2015).

This method is most often applied to specifically eliminate HM ions from wastewater. Unfortunately, the use of this technology requires high investment and operating costs due to high electricity consumption, so this method is not widely used or recommended (Bilal et al., 2013).

Electrodialysis is a separation method which uses membrane. In electrodyalisis ionized metals migrate through an ion exchange membrane in solution to spread electrical potential. Membranes are made of thin layers of plastic. These layers have anionic or cationic properties accordingly. As the solution with ion elements moves between cell sections, anions move toward the anode and the cathodes to cathode, thus passing through the anionic and cationic exchange membranes. The most important negative features of this method are the removal of membranes as well as corrosion cycle (Bilal et al., 2013; Gunatilake, 2015).

The effects of different concentrations, flow rates, temperature, and voltage were investigated by lead removal. By applying two different commercial membranes and an electrodialysis cell. Experiments revealed that as the voltage and temperature was amplified, cell output efficiency improved and the removal decreased with increasing flow. This is very useful for cleaning very high concentrations of heavy metals (Gunatilake, 2015).

1.3.6 Coagulation and Flocculation

Coagulation can be also used to remove HM from wastewater. This method is based on destabilizing colloids by neutralizing bonds that hold them. Among the most used coagulants in traditional wastewater treatment systems are Al, $FeSO_4$ and FeCl (Mashangwa, 2016).

The coagulation–flocculation process is also used to remove metal ions. It is based on the zeta potential parameter as a criterion for determining the electrostatic relationship between contaminants and coagulants – flocculants. The coagulation process (shown in Fig. 1.8) reduces the surface load of colloidal elements to stabilize the electrostatic repulsion (Gunatilake, 2015).

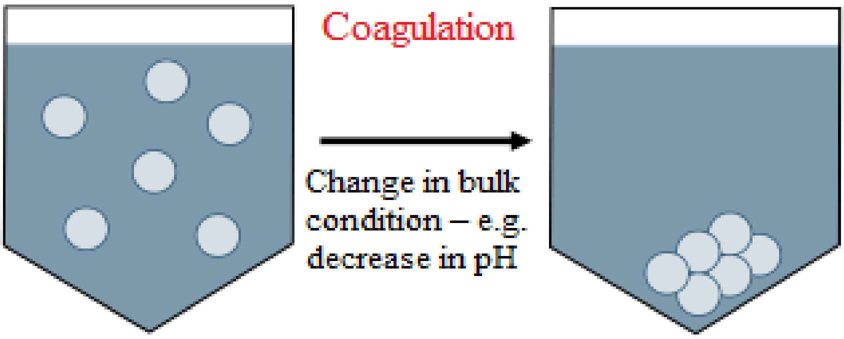

Fig. 1.8. Coagulation process (Aquarden Technologies, 2019)

During coagulation, chemicals are added to create positive charges that neutralize negative particle charges. The particles can then bond to form compounds that are easier to remove. The coagulation process also involves the addition of chemicals and mixing of the solution to dissolve the contaminant and distribute it evenly throughout the water (Gunatilake, 2015).

Research has identified several factors influencing the removal of HM by coagulation. These include the type of coagulant used, the pH, the dosage of the coagulant, and the concentration of metal ions. As a fairly common coagulant in the industry, aluminum sulfate, polyaluminum chloride, ferric chloride, or hydrated lime are often used to purify contaminated water. The presence of several different metal ions in the solution can affect the removal of certain metal ions and adversely affect the efficacy of metal ion removal in this process (Bolisetty et al., 2019).

Coagulation is amongst the most relevant methods of wastewater treatment. It destabilizes particles suspended in contaminated streams by adding coagulants or flocculants, causing the elements to settle. Both iron and aluminum salts are often used as coagulants or flocculants. Improved sludge deposition process and removal of biological contaminants are advantages of this technology, and their disadvantages are high costs of chemical consumption and sludge removal (Bolisetty et al., 2019).

However, the flocculation process (shown in Fig. 1.9) is based on the continuous incorporation of particles into larger derivatives, with the additional use of organic polymers to form inorganic polymers (Gunatilake, 2015).

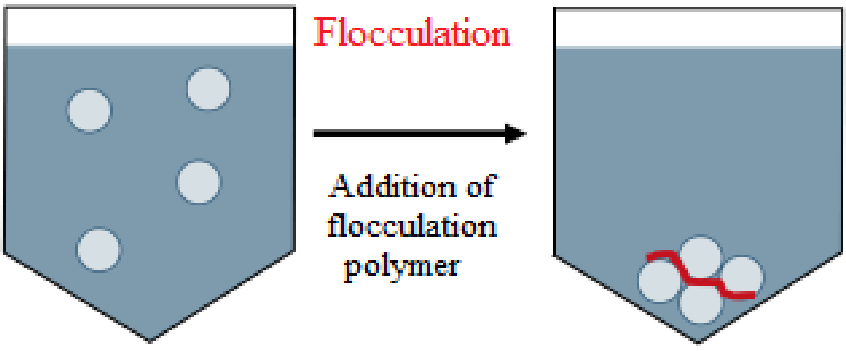

Fig. 1.9. Flocculation process (Aquarden Technologies, 2019)

When individual elements are flocculated into bigger compounds, they can be easily separated from solutions by ether filtration or flotation. Some of the main disadvantages of this process include formation of sludge, application of chemicals, the transfer of toxic compounds to the solid phase (Gunatilake, 2015).

Polyethylene sulfate and polyacrylamide are among the most widely applied flocculants used in sewage treatment. But macromolecular heavy metal flocculants should be used to remove heavy metals (Mashangwa, 2016).

1.3.7 Adsorption

One of the most efficient and high–potential methods for wastewater, groundwater and industrial wastewater treatment is known to be adsorption. This treatment method is one of the most economically attractive and aims at relatively high efficiency of contaminated water treatment. However, the engineering of the adsorption process involves many factors that need to be investigated and optimized in order to develop economically and technically sound wastewater treatment systems. The complex nature of multiphase systems in current life poses challenges in controlling water pollution through adsorption processes. Therefore, in order to control aquatic environment pollution which is initiated by anthropogenic and natural sources, it is essential to improve the adsorption (Bonilla-Petriciolet et al., 2017).

Adsorption has received much attention for its high efficiency, cost–effectiveness, adaptability, and ease of maintenance. Unlike some other contaminant removal methods, adsorption leaves no toxic by–products (Mittal et al., 2016).

As global environmental standards continue to tighten, technical adaptability and financial viability have become key factors in assessing the proper cleaning process. Traditional physical and chemical treatment methods can also involve relatively efficient decontamination, but also high energy requirements and expensive additives and reagents that increase treatment costs, reduce overall process efficiency, and generate other hazardous wastes. Therefore, adsorption has been adopted as the most appropriate technology–method, which is widely accepted by environmentalists around the world for elimination of toxic inorganic or organic pollutants in various wastewaters (Mittal et al., 2016).

The economic and technical plausibility of adsorption systems is based on various features such as the adsorbent form, solution properties and contaminant removal. As well as operational requirements, recovery and disposal of the waste. Both partial and continuous technologies may be used for sewage treatment. Both alternatives offer different adsorption skills and abilities. Partial adsorption reactors are useful when the adsorption rate, high adsorption capacity, and convenient detection of thermodynamic processes are important, including adsorbent–adsorbate interaction analysis. Meanwhile, adsorbent–loaded columns are suitable for large amounts of water when the process period is a relatively short time (Bonilla-Petriciolet et al., 2017).

Adsorption experiments in columns are considered necessary to calculate the breakthrough and saturation times, the adsorption potential of the charge and to establish the mass transfer criteria. This adaptation of the process also makes it possible to define the biggest efficiency of the method. Determining dynamic conditions is important because it indicates whether the adsorption residence time is less than the equilibrium time. It is also important that in this process, mass transfer resistance plays a key role in removing contaminants. Nevertheless, it is worth remembering that the efficiency of a continuous adsorption system is generally lower than that achieved with column systems (Bonilla-Petriciolet et al., 2017).

Activated carbon is the most commonly used for wastewater treatment. Nonetheless it is costly, so it is of great importance to find cheap alternatives to this material. The range of low – cost adsorbents already studied consists of clay, zeolites, silicon – based materials, coffee – based activated carbon, reduced coffee beans, seaweed, and other materials. These adsorbents are already considered to be commonly applied to remove toxic contaminants from wastewater (Borhade and Kale, 2017). Although adsorption is not a novel method in the water treatment industry, it is clear that there are still areas where the efficiency of this method could be improved. (Bonilla-Petriciolet et al., 2017).

Adsorption can be used for removing contaminants such as lead ions from wastewater. Adsorption by various constituents such as agricultural waste and minerals, among others, has been studied by removing Pb (II) ions. These studies have shown positive results in determining the choice of this process. When selecting an adsorbent material, it is desirable that it be general in nature, available in large quantities, economical and easily renewable in its source, and that it be capable of being used in multiple adsorption operations (Zhao et al., 2016).

Heavy metal adsorbents targeted at specific metal ions can also include agricultural by–products. In addition to traditional methods, adsorption using natural adsorbents is an inexpensive and reasonable way to remove HM. Advantages of adsorption – in addition to its low cost, it has a wide range of pH, great metal binding forces and simple operational conditions. However, the adsorption materials have the greatest influence on the adsorption efficiency (Babel and Kurniawan, 2003; Crini et al., 2018; Zhao et al., 2016).

The main advantages of adsorption:

- High heavy metal removal efficiency,
- Regeneration potential of the adsorbent,
- Versatility of technological design and actual application (Bolisetty et al., 2019).

The main disadvantages of the method:

- Disposal of used adsorbents,

- Wastewater generated during regeneration,
- Difficult cleaning the adsorption column,
- Adsorption quality decrease with each regeneration cycle (Bolisetty et al., 2019).

1.4 Adsorption Isotherm Modelling

The need to develop inexpensive adsorbents for industrial wastewater treatment has been an important goal for many environmental researchers. Therefore, modeling of adsorption processes is a very efficient and important way to predict the mechanisms of different adsorption systems (Ayawei et al., 2017).

The entry of contaminants into the aqueous medium and the development of containment measures have contributed to the use of adsorption instead of other methods. Adequate analysis of the adsorption process can be done using adsorption equilibrium data. Careful understanding and analysis of adsorption isotherms is essential for the overall development of adsorption process pathways and the successful design of an adsorption plant (Ayawei et al., 2017).

Linear regression analysis has long been one of the most commonly used methods for determining the most appropriate adsorption models because it quantifies the distribution of adsorbates, evaluates the adsorption mechanism, and verifies the correctness of the theoretical assumptions of the adsorption isothermal model. Due to the inherent discrepancy caused by linearization, several error functions were used to correct this shortcoming. At present, non–linear isothermal modeling, which solves linearization problems, has been widely used since the improvement of computer technology (Ayawei et al., 2017).

1.4.1 Equilibrium Modeling

The evaluation of the system's adsorption rate is a key factor in the development of the adsorption system. If the adsorbent and the contaminated water stream have been in contact for a sufficient period of time, a balance should be struck between the adsorbed contaminant and the amount remaining in the solution (Carvalho et al., 2011).

Adsorption equilibrium is usually described by isotherms, which are plotted as a diagram of the equilibrium absorption and the corresponding concentration of an aqueous solution at a given temperature (Volesky, 2003).

Isothermal adsorption models were used to evaluate the ability of the adsorbent to remove the contaminant up to a certain regulated value. Adsorption isotherms are the ratio of the weight of a solid adsorbent unit adsorbed to the volume adsorbed in the equilibrium solution (Carvalho et al., 2011).

Although a myriad of different isothermal models have been analyzed in the literature, the Langmuir and Freundlich models are most commonly used because of their simplicity (Maurya and Mittal, 2006). Both isothermal models have been shown to be valuable in explaining momentary single–component adsorption of toxic ions by specific adsorbents (Carvalho et al., 2011).

1.4.2 Langmuir Isotherm

Langmuir adsorption was originally designed to characterize adsorption between gas and solid phase. But now it is often used to measure and characterize the adsorption potential of a number of adsorbents. According to a literature review, the Langmuir isotherm reflects the surface coating, balancing the relative rates of adsorption and desorption. The adsorption is proportional to the surface area of the adsorbent and the desorption is proportional to the surface of the adsorbate–coated adsorbent (Ayawei et al., 2017).

The following equation will define the Langmuir Isotherm (Bonilla-Petriciolet et al., 2017):

$$q_{eq} = \frac{bX_m C_{eq}}{1+\mathrm{b}C_{eq}} \tag{1.3}$$

where
q_{eq} – accumulated metal content per gram on adsorbent material, mg/g;
b – Langmuir constant, L/mg;
C_{eq} – initial concentration of the pollutant in the solution, mg/L;
X_m – maximum specific absorption, mg/g.

Langmuir's theory is based on a single–molecular layer of adsorbed material, so it is best suited when the surface of the adsorbent is solid and smooth (Ayawei et al., 2017).

Graphically, Langmuir’s isothermal curve can be illustrated as follows (Fig. 1.10):

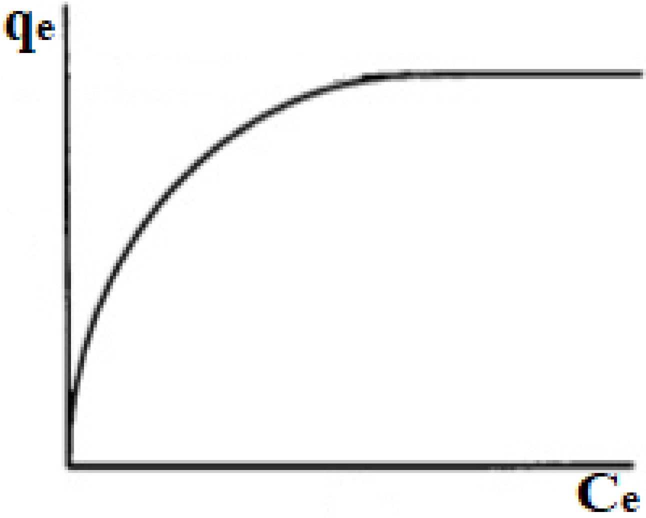

Fig. 1.10. Langmuir isotherm (Bonilla-Petriciolet et al., 2017)

Although the Langmuir isotherm model does not explain the mechanism of the adsorption process, it provides a rationale for some equilibrium adsorption behavior. Because this empirical model is simple and easy to apply, it is commonly used to explain how much adsorbent will be needed to remove a particular contaminant (Ladshaw et al., 2015).

Langmuir isotherms are usually applied in the soluble adsorption of contaminated water. Preliminary form of the equilibrium curve corresponds to the main assumption of this model – when the concentration of pollutant is high, adsorption capacity rises too. There is competition between soluble molecules for the adsorbent sites used (Bonilla-Petriciolet et al., 2017).

Research has shown that when adsorption occurs according to the Langmuir model, the molecules are adsorbed on a flat surface. Also in such a process, the molecules have a particularly strong intermolecular attraction. The Langmuir isotherm type indicates when adsorption occurs due to very weak forces (Bonilla-Petriciolet et al., 2017).

The simplicity of isotherm is based on the following 4 presumptions:

- Adsorption cannot take place outside the homogeneous layer;

- There may be only one molecule of adsorbate in each adsorbent pore (site);
- Adsorbent surface is homogeneous and adsorbent gaps (pores) are actively equivalent;
- The deposition of the adsorbed molecule at a particular site of the adsorbent is independent of the behavior of the other molecules (Bonilla-Petriciolet et al., 2017).

1.4.3 Freundlich isotherm

According to Freundlich's isothermal analysis, adsorption is assumed to occur on a heterogeneous surface. The increase in concentration significantly increases the amount of adsorption (Bonilla-Petriciolet et al., 2017). This isotherm explains the heterolyticity of the adsorption surface, which defines the accelerating distribution of active sites and their energy (Ayawei et al., 2015). The Freundlich isotherm is mathematically expressed as (Bonilla-Petriciolet et al., 2017):

$$q_{eq} = k \cdot C_{eq}^{1/n} \tag{1.4}$$

where

q_{eq} – the sorption uptake;

k and $1/n$ – Freundlich constants;

C_{eq} – the equilibrium concentration of sorbate remaining in the solution.

Graphically, Freundlich isothermal curve can be illustrated as follows in Fig. 1.11.

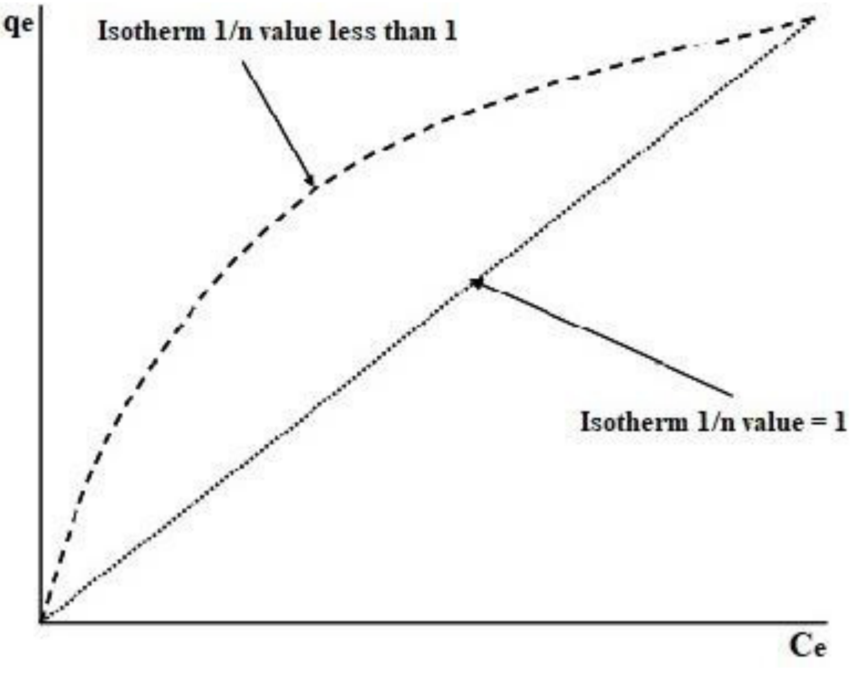

Fig. 1.11. Freundlich isotherm (Ecetoc, 2020)

The Freundlich isotherm is more valued as an empirical model. Freundlich isotherm is most commonly used to describe the equilibrium consumption of adsorption processes (Volesky, 2003). Langmuir's model is more theoretical, and Freundlich's isotherm is, as already mentioned, empirical. The main difference between these models is that Langmuir covers the surface so that only the surface of the material can be used for adsorption (Ayawei et al., 2017).

The Freundlich empirical model can be applied to multilayer adsorption by unequally distributing the heat and bonds of adsorption in a heterogeneous layer. This model has historically been developed for the adsorption of carbon dioxide of animal origin. Studies have shown that the weight ratio of adsorbate to adsorbent obtained in the soluble material was not constant at different solution concentrations. Therefore, the amount adsorbed is the total amount of adsorption at all sites (adsorbent pores). First, of course, stronger binding sites are occupied until, finally, the adsorption energy decreases exponentially with the implementation of the adsorption process (Foo and Hameed, 2010).

Nowadays, the Freundlich isotherm is often used in heterogeneous systems, especially in organic compounds or highly interacting organisms, on activated carbon and molecular sieves.

The slope of the isothermal curve from 0 to 1 is a rate of surface adsorption efficiency or heterogeneity. Surface becomes more heterogeneous when the value is close to zero. A value less than 1, meanwhile, indicates a chemosorption cycle, where 1 / n above one indicates addressing for cooperating adsorption (Foo and Hameed, 2010).

1.4.4 Henry’s Isotherm

This isotherma explains the suitability of adsorption at relatively low concentrations to separate all adsorbing molecules from the nearest neighbors (Ayawei et al., 2017).

When the correlation between the equilibrium concentration of the liquid phase and the adsorbed phase is linear, the proportionality constant is equivalent to the adsorption balance constant. This constant in literature is usually called Henrys’ constant (K_H). And linear correlation of the isotherm is simply called Henry's law. Henry constant (K_H) can be simply defined by the terms of concentration (Ayawei et al., 2017):

$$q_e = K_H C_e \tag{1.5}$$

where

q_e – amount of the adsorbate at equilibrium (mg/g),

K_{HE} – Henry’s adsorption constant,

C_e – equilibrium concentration of the adsorbate.

In the case of physical adsorption, the molecular status of adsorption does not change. In other words, during adsorption on a homogeneous surface and at relatively inferior concentrations, molecules are separated from the nearest neighboring molecules (Ayawei et al., 2017).

In this case bond between the concentration of the solute and the adsorbed phase should be linear. Therefore relationship with the surface concentration (n_s) can be described in Eq.1.6.

$$n_s = \frac{K_H}{a} C_e \tag{1.6}$$

where a is specific surface area per /volume of the pollutant (Bonilla-Petriciolet et al., 2017).

There are also many other adsorption models in the literature. Some of them are presented in Table 1.3.

Table 1.3. Adsorption isotherm models (Ayawei et al., 2017)

Isothermal model name	Model equation/ Linear expression of the model	Equation no.
Temkin Isotherm	$q_e=\frac{RT}{b}\ln K_T+\frac{RT}{b}\ln C_e$ or $q_e=B\ln K_T+B\ln C_e$ where $B=\frac{RT}{b}$	(1.7)
Redlich –Peterson Isotherm	$\ln\left(\frac{C_e}{q_e}\right)=\beta\ln C_e-\ln A$	(1.8)
Jossens Isotherm	$\ln\frac{C_e}{q_e}=-\ln H+Fq_e^p$	(1.9)
Elovich Isotherm	$\ln\frac{q_e}{C_e}=\ln K_e q_m-\frac{q_e}{q_m}$	(1.10)
Harkin–Jura Isotherm	$\frac{1}{q_e^2}=\frac{B}{A}-\frac{1}{A}\log C_e$	(1.11)

The presented adsorption isothermal models are classified into:

- One–Parameter Isotherm (Henry's Isotherms);
- Two–Parameter Isotherm (Langmuir Isotherm, Freundlich Isotherm, Temkin Isotherm, Harkin–Jura Isotherm, Elovich Isotherm);
- Three–Parameter Isotherms (Redlich–Peterson Isotherm, Langmuir–Freundlich Isotherm, Jossens Isotherm);

There are also models with more parameters, such as:

- Four–Parameter Isotherms (Fritz–Schlunder Isotherm, Baudu Isotherm, Weber–Van Vliet Isotherm, Marczewski–Jaroniec Isotherm);
- Five–Parameter Isotherms;
- Multilayer physical sorption isotherms (Brunauer–Emmett–Teller) (Ayawei et al., 2017).

1.5 Use of organic waste for adsorption

The use of organic waste for sorption of HM has been increasing rapidly recently. Consequently, many scientists used natural waste products to treat Pb (II) from aqueous solutions (M. Ahmad et al., 2012; Babel and Kurniawan, 2003; Park et al., 2007). The process may involve the use of organic fractions from agricultural, manufacturing and service companies in the region. Preparing adsorbents for metal removal does not require high costs, as waste is usually only washed and dried, but in some cases it is further crushed to the required particle size. Therefore, the most important advantage of these adsorbents is the low price.

But few considerations should be in mind when deciding on the adsorbent. First of all, due to unreadily available types of adsorbents, some pre–treatments are needed to improve adsorption capability. Second, the selectivity of such adsorbents continues to be studied and discussed. Eventually, the rejuvenation of adsorbents for future use should be taken into account (Zhao et al., 2016).

Table 1.4 shows the sorption capacity of sorbents of natural origin for the removal of Pb.

Table 1.4. Comparison of adsorbent capacities for Pb (II)

Adsorbent	Pb (II) adsorption capacities (mg/g)	References
Iron–ore sludge	1.31	(Nguyen et al., 2019)
Pistachio hull	142.00	(Hamidpour et al., 2018)
Banana peels	2.18	(Anwar et al., 2010)
Banana	20.90	(Mahmood-ul-Hassan et al., 2015)
Corn cob	29.17	
Sunflower	22.64	
Pine cone shell	25.40	(Martín-Lara et al., 2016)
Cork waste	13.57	(López-Mesas et al., 2011)

From the data in the table it can be determined that various organic waste can be used for the treatment of water from lead ions, and their adsorption capacity ranges from 1.31 to 142.00 mg/g.

Although organic waste used for HM removal has high cleaning efficiency, more and more research is done using chemically treated (modified) organic waste adsorbents. The adsorbents are treated with various acids, alkalis or salts to increase the adsorption capacity of the metals and thus extend the life of the adsorbent. Table 1.5 shows the adsorption capacity of modified organic waste for Pb removal.

Researchers Mahmood-ul-Hassan et al., (2015) conducted studies on the adsorption capacity of corn cobs. Respectively, in the first case, an untreated adsorbent was used, in the second case, corn cobs soaked in sodium hydroxide (NaOH), nitric acid (HNO_3) and sulfuric acid (H_2SO_4) were used. The Pb (II) adsorption capacity of untreated corn cobs was found to be 29.17 mg/g. After treatment of corn cobs, the adsorption capacity of NaOH increased 1.94 times (to 56.67 mg/g), HNO_3 – 1.77 times (to 51.75 mg/g), and H_2SO_4 – 1.14 times (only to 33.39 mg/g).

The data in the Tables 1.4 and 1.5 show that various solutions (Sodium hydroxide, sulfuric acid, nitric acid, etc.) are commonly used to treat adsorbents.

Lithuania also generates organic agricultural and industrial waste, such as husks of various grains (rye, wheat, buckwheat, etc.), rapeseed, sugar cane or apple pulp, etc., which can be used as adsorbents for the adsorption of HM. Chicken egg shells have been found to be beneficial ecological and economical absorbents due to their simple availability and lack of toxic elements (Ikram et al., 2016; Kalyani et al., 2010).

Table 1.5. The sorption capacity of modified organic waste used to remove Pb

Adsorbent	Material used for modification	Pb (II) adsorption capacities (mg/g)	References
Pineapple peel fibre	Succinic anhydride	70.29	(Hu et al., 2011)
Banana	NaOH	59.39	(Mahmood-ul-Hassan et al., 2015)
	HNO_3	39.91	
	H_2SO_4	36.45	
Corn cob	NaOH	56.67	
	HNO_3	51.75	
	H_2SO_4	33.39	
Sunflower	NaOH	39.23	
	HNO_3	27.87	
	H_2SO_4	23.60	
Orange peel	Grafted copolymerization	476.10	(Feng et al., 2011)

According to the research of the Lithuanian Statistics Department, in 2018, about 5,895 tons of eggshell waste was generated in Lithuania (OSP, 2020). Despite the advantages of modified agricultural and bio–waste as potential adsorbents, it also provides more opportunities for better waste management.

1.5.1 Description of egg shell adsorbent

Chicken eggs are widely consumed worldwide, resulting in large amounts of waste, mainly eggshells and shell membrane waste. Removal of eggshells remains one of the most important problems for food, bakeries and poultry businesses. Attempts have been made in recent years to use eggshells in the manufacture of biodiesel and collagen, but the outcome have shown that this use of shell waste is not financially viable (Mittal et al., 2016).

Eggshells can be adapted to the adsorption process as a non–toxic, durable and effective adsorbent for the removal of hazardous chemicals. Over the last 10 years, there has been an increase in research into eggshells as an adsorbent for the removal of a number of organic and inorganic hazardous chemicals, especially wastewater. A review of the literature shows that both natural and chemically or physically modified eggshells have given excellent results for the removal of various types of dyes, pharmaceuticals, surfactants, heavy or precious metals (Mittal et al., 2016).

Physically, the eggshell looks like crystalline calcium carbonate, which is partly derived from chicken bones. Consumption of eggs is essential for humans and the food industry as one of the most abundant sources of protein in life. However, this is precisely why a large amount of eggshells are generated on a daily basis as waste and these amounts are unlikely to decrease. This is why eggshell is one of the most relevant useful adsorbents for removing heavy metals from aqueous solution for wastewater treatment (Badrealam et al., 2018).

Research has shown that there are between 7,000 and 17,000 pairs in each egg shell. On average, a chicken egg shell weighs 5 to 6 g. The structure of the egg shell is a very important indicator in controlling the water and gas exchange in the egg (Carvalho et al., 2011).

Typically, a chicken eggshell contains about 6 grams of minerals. The mineralized shell consists of 96 % calcium carbonate. The remaining components consist of an organic matrix (2 %) as well as traces of magnesium, phosphorus and various other trace elements (Hincke et al., 2012). Full chemical composition of hen egg shell is provided in Table 1.6.

Table 1.6. Chemical composition of egg shell (Arunlertaree et al., 2007)

Element	Weight %
	Natural hen egg shell
$CaCO_3$	96.48
S	2.31
Mg	0.40
P	0.50
Sr	0.07

The thickness of the shell is a major factor contributing to the mechanical properties of the egg shell. Although the structural basis of the egg shell has the greatest influence on its mechanical properties (Hincke et al., 2012).

Egg shells are rich in calcium carbonate, therefore recycling of them can decrease environmental pollution as well as acting as a low cost adsorbent to decontaminate toxic substances (Bhaumik et al., 2012). Both the ultra–structural view and chemical structure of egg shell is shown in Fig. 1.12.

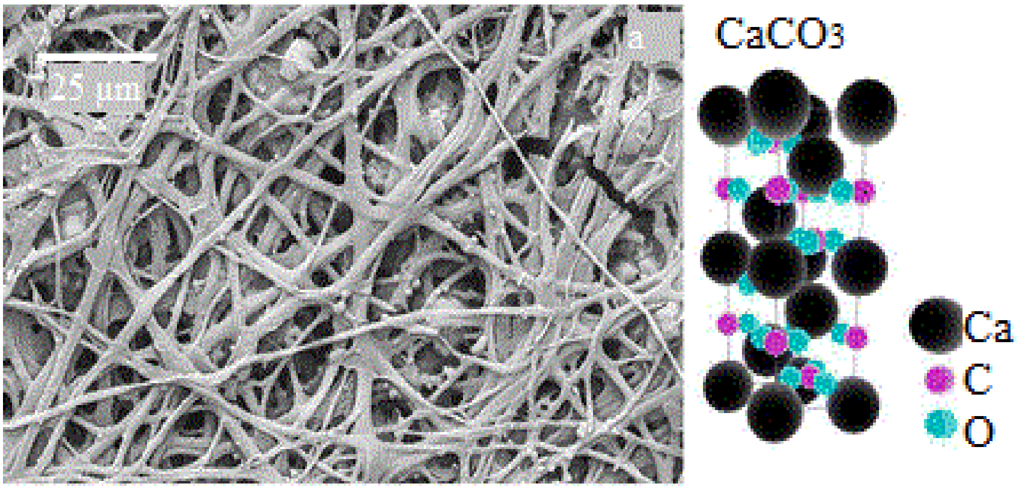

Fig. 1.12. Chemical egg shell structure (Carvalho et al., 2011)

One of the methods used to clean contaminated water from contaminants like heavy metals is adsorption. Metal removal has already been studied by foreign scientists by adsorbing various materials. Activated carbon, agricultural waste, moss peat, minerals are some of the many potential adsorbents already investigated. It is very important that the adsorbent is available in large quantities, easily recovered and cost–effective. Therefore, the application of eggshell to adsorption seems to be a very promising way to obtain a cheap material for the adsorption process but also to manage the amount of food waste. The adsorption of eggshells is mainly due to the exchange reaction and it should be possible to use it as a new biological metal ion adsorbent (Tabatabaee et al., 2014).

The by–product of the ES consists of $CaCO_3$ and the membrane of the eggshell. Egg has two membranes around it: thick external membrane, and thin inside membrane, as shown in Fig. 1.13. These egg shell layers are made of protein fibers. Bonded in this way membranes form a partially permeable layer. This property is the reason why the shell and the membrane have many applications, such as adsorption and support medium for immobilization of enzymes (Carvalho et al., 2011).

Studies show that the natural egg shell has some capacity to remove heavy metals from polluted water:

- 42 % removal for iron (Fe) ions,
- 37 % removal for copper (Cu) ions,
- 48 % for lead (Pb) ions,
- 24 % for cadmium (Cd) ions,
- and 30 % for chromium (Cr) ions (Choi and Lee, 2015).

Nevertheless, it is believed that a calcined egg is better adsorbent because it is a good medium that not only raises the pH of acidic effluents but also at the same time absorbs toxic heavy metal ions well (Choi and Lee, 2015).

Calcined (heat–treated above 100 °C) eggshell is a non–toxic, non–corrosive and safe material. Therefore, heat–treated eggshell can be widely used in contaminated water treatment technologies. This material is biocompatible and has favorable adsorption and polyelectrolytic properties. Also, calcined shell can be regenerated for many cleaning processes. The high cationic load density of eggshells allows strong adsorption of negative areas by other particles (Choi and Lee, 2015).

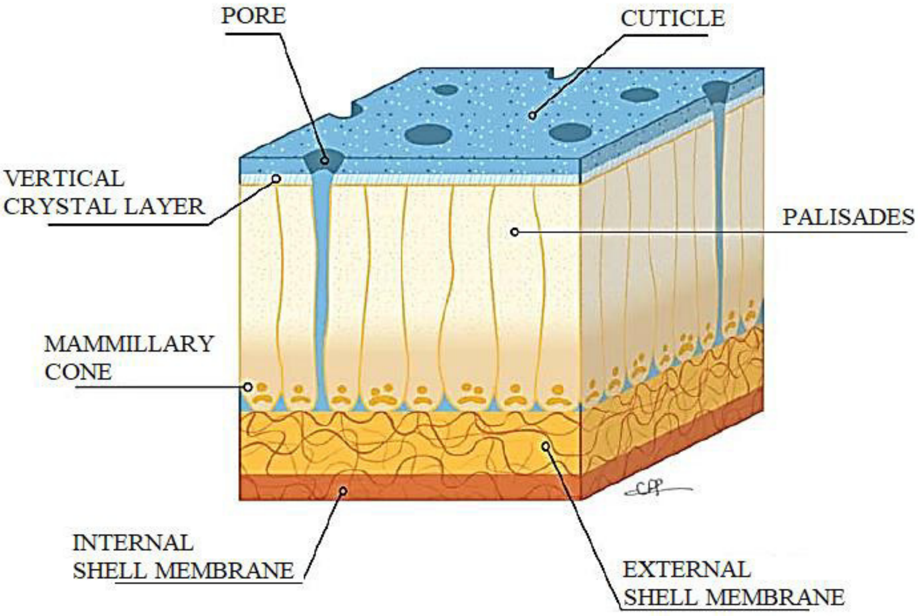

Fig. 1.13. Schematic view of the egg shell (Hincke et al., 2012)

According to M. Ahmad et al., (2012) the study of egg shell adsorption data was fitted to the linear shape of the Langmuir equation and was plotted in Fig. 1.14. These results showed that the formation of metal ions on the homogeneous surface of the adsorbents explains the adsorption of metal ions. The highest adsorption gained from the Langmuir equation may be useful in estimating the potential absorption capacity of the adsorbing eggshell for heavy metals (M. Ahmad et al., 2012).

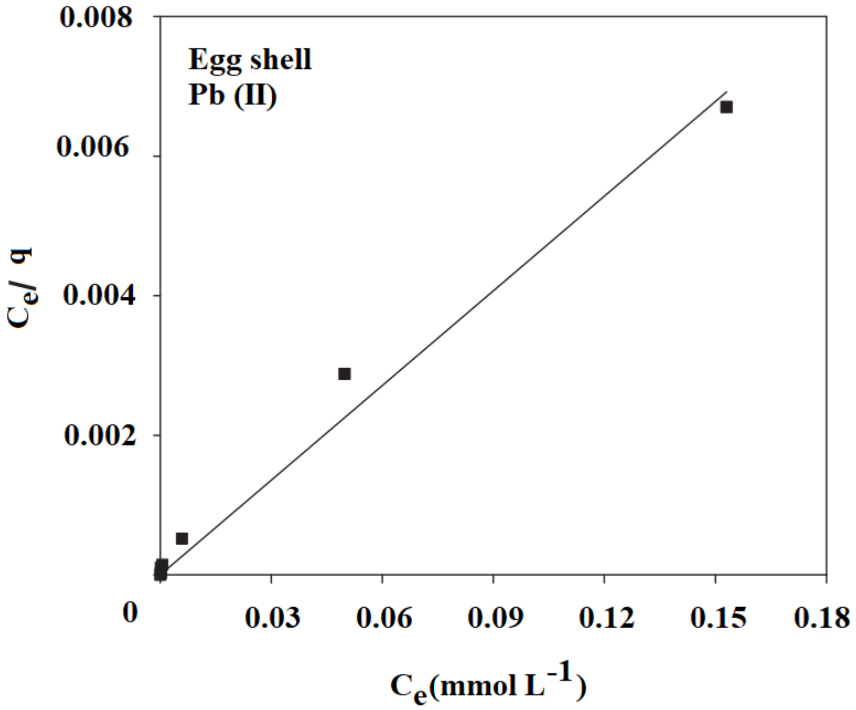

Fig. 1.14. Langmuir sorption isotherm of Pb (II) onto egg shell (M. Ahmad et al., 2012)

Given the graphically represented isothermal form of the adsorption process, the eggshell has a relatively high adsorption capacity (M. Ahmad et al., 2012). After these adsorption experiments, a clear change in surface structure was observed in the eggshells (Fig. 1.15).

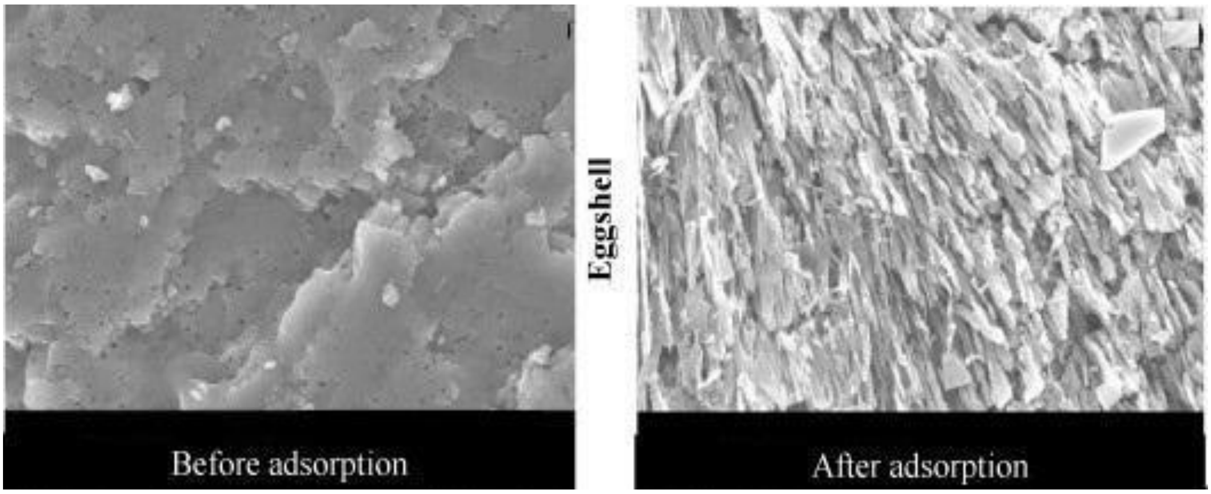

Fig. 1.15. Scanning electron microscopy of egg shells before and after Pb (II) ion adsorption (M. Ahmad et al., 2012)

Research has shown that metal ions adsorb on the surface of the eggshell, most likely due to the ion exchange reaction (M. Ahmad et al., 2012).

The absorption of metal ions in ES powder depends heavily on both the number of free pores and the amount of adsorbent functional groups. Poor adsorption of some metals may be directly related to the saturation of the adsorbent junctions or related to different types of metals, some have a stronger attraction to the eggshell adsorbent and others a lower one (Mashangwa et al., 2017).

The selectivity of the eggshell for different metal cations is related to the ability of the metals to form strong complexes between themselves and the eggshell. During the adsorption process, some metals displace other metals that have already been bound to the surface of the eggshell through ion exchange reactions or other interactions. Studies of the ion exchange mechanism have shown this dependence (Mashangwa et al., 2017):

$$\mathrm{Ca(surface)} + \mathrm{Me^{n+}(aq)} = \mathrm{Me(surface)} + \mathrm{Ca^{n+}(aq)} \tag{1.12}$$

The results obtained by the researchers showed that when the eggshell was combined with an contaminated solution, calcite began to dissolve in the eggshell, which also increased the alkalinity of the solution, as shown in the equations below (Mashangwa et al., 2017):

$$\mathrm{CaCO_3\,(S)} + \mathrm{H_2O} \rightarrow \mathrm{Ca^{2+}} + \mathrm{CO_3^{2-}} \tag{1.13}$$

$$\mathrm{CO_3^{2-}} + \mathrm{H_2O} \rightarrow \mathrm{HCO_3^{-}} + \mathrm{OH^{-}} \tag{1.14}$$

As already analyzed above, metal uptake is relatively reliant on the pH. Therefore, tendency of the eggshell to alkalinity of the solution may have resulted in a decreased percentage of adsorption efficiency for some metals. Due to the said dissolution of calcite according to Eq. (1.13) and the increased pH of the experimental solution, some metals are likely to be removed from the aqueous solution in the state of precipitated hydroxides, carbonates, heterogeneous or homogeneous metal compounds. (Mashangwa et al., 2017).

It is essential that the mechanisms of removal of separate metals may differ and may result from a complex combination of mechanisms, which may include precipitation, adsorption, sediment, or solid solution diffusion. The removal of metals could also be stopped by the fact that the effluent almost never contains only heavy metals, there are always organic and other inorganic substances (Mashangwa et al., 2017).

1.6 Regeneration of adsorbent material

No matter how advanced the adsorption process is, it can also waste resources and cause secondary pollution of heavy metals. Therefore, when adsorbing heavy metals from contaminated water, it is necessary to find cheap (or free) and effective adsorbents. It is also very important to investigate the methods of HM desorption and adsorbent recovery. Due to the small initial costs, high efficiency and biodegradability of adsorbents, adsorption has recently received a lot of attention in the removal of HM. Finally, it would still be useful to check whether the eggshell adsorbent can be regenerated. (Wang and Chen, 2009).

Most adsorbents can be reused several times after their regeneration. When regenerating the adsorbent, the absorbed materials must first be desorbed. Based on the experience of other scientists (Banerjee et al., 2010), acetic acid can be used in experimental studies on the regeneration of eggshell adsorbents. In the said regeneration study, the adsorbent was applied to the column and packed with a solution of acetic acid (very low concentration to prevent dissolution of the coating). The adsorbent was then immersed in 9.7 M acetic acid. After 24 hours, acetic acid was discharged through a valve at the bottom of the column. The second stage of regeneration was solvent desorption. The adsorbent was washed with a mixture of ethanol and deionized water to clean any residual matter. Then rinsed adsorbent was dried to constant weight. Adsorption capacity of the heavy metal was then determined and compared with the adsorption of the new adsorbent previously determined (Banerjee et al., 2010).

The recycling of spent adsorbents is an important step in assessing the economic viability of adsorption as a form of water treatment. Efficiency of the adsorbent gradually decreases due to the gradual accumulation of adsorbates on the surface of the adsorbent, which ultimately depletes it. The strength of the contact between the adsorbent and the purified pollutant is of great importance in the adsorbent renewal procedure. To remove adsorbates collected on the surface of adsorbent the adsorbent regeneration is used. It is important that the capacity of adsorbents decreases with each revival rotation. Recovery methods can be categorized into chemical, thermal, vacuum, and microbiological recovery (Bonilla-Petriciolet et al., 2017).

The mechanisms for the regeneration of adsorbents include heating, pH change, change of adsorbent medium, chemical reactions, and decomposition of contaminants. Many different reagents can be used in these recovery methods. Some of them include organic and inorganic chemicals, methods based on electricity power, physical processing, and microorganisms (Bonilla-Petriciolet et al., 2017).

The conditions of regeneration should be developed to increase the service life of the adsorbent. As well as to give priority to its use in multiple process cycles and to decrease the vulnerability of the adsorbent construction while evading substantial losses of mass and dynamic sites. New methods of adsorbent recycling have recently been suggested. Biggest potential is expected from the use of microwave or ultrasound. Electromagnetic and mechanical waves are used in aforementioned processes. Though application of these technologies in practice obliges additional research to evaluate their shortcomings (Bonilla-Petriciolet et al., 2017).

To sum up, cheap and not harmful for environment adsorbent regeneration methods are needed to improve the cost-effectiveness of water treatment adsorption developments. Lastly, renewal of adsorbents at the end of their service life is also a key aspect of reducing the environmental impact of solid waste generation (Bonilla-Petriciolet et al., 2017).

Conclusions of the first chapter

1. Pollution of the environment with heavy metals has a negative impact on human and animal and plant organisms, which manifests itself in oncological diseases, developmental disorders of biological organisms, impaired immune system and other severe effects. The main anthropogenic sources of heavy metals in the aquatic environment are factory effluents, industrial and domestic waste and transport.
2. The amount and variety of heavy metals in industrial wastewater depends on the company's production. Lead is mainly used in the manufacture of cables, pigments, the glass industry, explosives, batteries, some paints and the manufacture of PVC pipes (as an impurity). Lead has also long been used as a fuel additive in the ammunition industry, with some countries also using lead in fishing weights and other sources. It is estimated that most of the lead enters wastewater from lead sewer pipes.
3. Heavy metals are hazardous to the environment, so many different methods of removal from aqueous solutions are used (chemical precipitation, membrane filtration, sorption, and many other methods). The use of natural food waste for the adsorption of heavy metals is rapidly gaining popularity. Organic waste from agricultural, manufacturing and service plants, such as cereal waste, rapeseed, sugar beet pulp, etc., can be used for the adsorption process.
4. Eggshells collected from households, bakeries and other food establishments could also be used as adsorbents. According to the Lithuanian Department of Statistics, the amount of this waste is growing rapidly every year and in 2018 reached almost 6,000 tons.
5. Many different models have been developed to model adsorption processes, but it is very important to pay attention to the amount of parameters. One of the most important requirements is that the model must well reflect the process of metal adsorption from the solution. Langmuir and Freundlich isotherm models are most commonly used in practice to achieve this goal.

2. MULTIPLE–CRITERIA DECISION ANALYSIS FOR LEAD ION REMOVAL METHOD

Hwang and Yoon (1981) were first to propose method of The Technique for Order Preferences by Similarity to an Ideal Solution (TOPSIS) as an alternative for multi–criteria analysis. This method came from the idea of choosing the best alternative closest to the positive ideal solution and the alternative furthest from the negative ideal solution. Then choose the best arranging method, which will be the best choice (Tzeng and Huang, 2011).

MCDA approaches are designed to improve the quality of solutions by including a number of criteria to make choices clearer, more streamlined, and more effective. The goal of this approach is to create a structured process for setting goals, developing alternatives, and comparing them to different perspectives. MCDA processes are diverse and can therefore cover a large part of environmental processes: environmental planning, fisheries management, water management, forestry, nuclear accident management, climate policy, life cycle analysis, and more (Tzeng and Huang, 2011).

Numerous features of possible results are often considered in terms of possible profits. In order to substantiate the choices of certain decision makers, multiple criteria decision analysis (MCDA) is used to select the best solution taking into account several aspects. There are many multi–criteria solution analysis methods such as ELECTRE, AHP, VIKOR, PROMETHEE or TOPSIS (in order of preference for similarity to the ideal solution). However, the TOPSIS method was chosen in this thesis (Łatuszyńska, 2014).

Proper design of a set of criteria is the first and one of the most difficult parts of designing decision models. This part of the multi-criteria decision has a significant impact on the choice made. The literature provides the two most desirable features of such criteria:

- First, the analysis needs as few variables as possible to make the decision-making process as easy and short as possible and for the decision-maker to understand the impact of all the criteria on the decision;
- Secondly, there should still be sufficient criteria to provide all the relevant information that fully describes the problem raised (Łatuszyńska, 2014).

Multicriteria analysis is performed according to the following steps:

1) Establish system evaluation criteria related to system capabilities;
2) Generating alternatives using mathematical or physical models or performing experiments;
3) Evaluation of alternatives according to criteria (determination of the values of alternative criteria);
4) Determination of criteria weights;
5) Adoption of one "optimal" (preferred) alternative;
6) If the resulting analysis decision is not satisfactory to the decision maker, additional information describing the supplementary criteria is collected or other multi-criteria optimization is repeated (Łatuszyńska, 2014).

The alternative chosen in the TOPSIS method should be the smallest geometric distance from the positive decision and the furthest from the undesired–worst decision. The ideal solution consists of all the best criteria values. Accordingly, the worst case solutions are the values of all the worst case criteria. The main advantage of this method over other methods of multicriteria analysis is that it limits the subjectivity of decisions. Additional advantages of the TOPSIS analysis consist of:

- Coherent reason of decision maker selection of alternative,
- Calculation procedure is simple to transfer to computer systems,
- the results obtained can be quite easily visualized in various forms, such as using graphs (Łatuszyńska, 2014).

The pros listed above are the main reason why TOPSIS is one of the most favorable multi–criteria solution analysis methods. Nevertheless, this process also have some drawbacks. The main disadvantage of TOPSIS is the weighting of criteria and the need to check the reliability of decision–makers (Łatuszyńska, 2014).

2.1.1 Normalization

It is not necessary to always normalize the attribute values, but some methods, such as maximization, simple weighting of additives, ELECTRE, and others, may need to alleviate computational problems because of the occurrence of different units in the decision matrix. The goal of normalization is to obtain comparable rating scales. There are many different ways to normalize the values of attributes (Hwang and Yoon, 1981).

Vector Normalization: This procedure works by dividing each vector of the solution matrix row by its norm. Each normalized value r_{ij} of the normalized decision matrix could be determined as follows:

$$r_{ij} = \frac{x_{ij}}{\sqrt{\sum x_{ij}^2}} \tag{2.1}$$

where xij – is value of specific criteria.

The advantage of this method of standardization is that all criteria are measured in dimensionless units, thus facilitating comparisons between them. However, the disadvantage of this method is that this standardization procedure does not produce measurement scales of the same length. The minimum and maximum scale values are not equal for each criterion, so it is still difficult to compare them (due to the nonlinear scale transformation). This procedure is usually used using the TOPSIS method (Hwang and Yoon, 1981).

2.1.2 Determination of criteria importance

Based on the MADM problem solving, an analytical hierarchy process (AHP) was proposed to estimate relative weights according to the appropriate hierarchical system. The AHP approach has been proposed for modeling subjective decision–making processes using a large number of attributes in a hierarchical system (Balioti et al., 2018).

Table 2.1. Ratio scale in the AHP (Balioti et al., 2018)

Intensity	Description	Explanation
1	Equal	Equal importance
3	Moderate	Moderate importance
5	Strong	Strong importance
7	Demonstrated	Very strong importance
9	Extreme	Extreme importance
2, 4, 6, 8	Intermediate values	–

AHP is often used to compare the relative weight between the attributes of solution elements and to form a return matrix. In this way, individual subjective expert judgment is summarized and relative weight is estimated. To determine the best alternatives, the relative weights of the elements are combined (Tzeng and Huang, 2011).

Table 2.1. represents the ratio scale that is employed to compare the importance weight between criteria according to the linguistic meaning from 1 to 9 to denote equal

importance to extreme importance. Then matrix of elements is constructed (as shown in Eq. (2.2)).

$$\begin{bmatrix} c_{11} & c_{12} & c_{13} \\ c_{21} & c_{22} & c_{23} \\ c_{31} & c_{32} & c_{33} \end{bmatrix} \tag{2.2}$$

Then total amount of the values in each column of the matrix should be calculated according Eq. (2.3):

$$C_{ij} = \sum_{i=1}^{n} c_{ij} \tag{2.3}$$

Then each element in the AHP matrix is divided by its column total to generate a normalized matrix Eq. (2.4):

$$X_{ij} = \frac{C_{ij}}{\sum_{i=1}^{n} c_{ij}} \tag{2.4}$$

Finally, priority vector is calculated. The total of the normalized column of matrix is divided by the number of criteria used (n) to generate priority vector (criteria weight):

$$W_{ij} = \frac{\sum_{j=1}^{n} X_{ij}}{n} \tag{2.5}$$

After this, weighted normalized decision matrix is constructed by multiplying the normalized scores r_{ia} by their corresponding weights w_i :

$$v_{ai} = w_i \cdot r_{ai} \tag{2.6}$$

where

v_{ai} – weighted value;

w_i – criteria weight;

r_{ai} – normalized criteria value.

2.1.3 Determination of beast and worst criteria distances

Finally, the weighting results obtained are used to compare the ideal and anti–ideal solution. Each indicator is compared with the maximum and minimum values that meet the relevant criterion. To determine the total distance of the alternative to the ideal solution, the sum of the squares of the difference of the criteria of each alternative from the maximum value is used.

$$d_a^{+} = \sqrt{\sum_{j=1}^{n} (v_i^{+} - v_{ai})^2} \tag{2.7}$$

$$d_a^{-} = \sqrt{\sum_{j=1}^{n} (v_i^{-} - v_{ai})^2} \tag{2.8}$$

where

da^{+} distance for each action to the ideal solution;

da^{-} distance for each action to the anti–ideal solution;

v_i – best or worst weighted value of criteria.

Then relative closeness coefficient of each alternative is calculated using Eq. (2.9):

$$C_a = \frac{d_a^{-}}{d_a^{+} + d_a^{-}} \tag{2.9}$$

where C_a relative closeness to the ideal solution $0 \leq Ca \leq 1$, $i = 1,2,\ldots,m$.

The closeness coefficient is always between 0 and 1, where 1 is preferred action.

2.2 Describing problem

There are many ways to remove HM from contaminated water. However, the latest global trend is the ever–tightening of environmental standards. In today's world, technological application and affordability are critical factors in the choice of adsorbents for the treatment of contaminated wastewater. Heavy metal contamination has recently led to an increase in research into new and cheaper ways to remove metals. (Tabatabaee et al., 2014).

Although chemical precipitation, coagulation, ion exchange, filtration, membranes, and other methods have been extensively studied for this purpose, most methods have some drawbacks. For example, requiring reprocessing, some of them are less efficient or require high capital costs. As a result, many scientists have begun new research using organic waste to remove Pb (II) ions from aqueous solutions (M. Ahmad et al., 2012; Babel and Kurniawan, 2003; Park et al., 2007).

Nevertheless, sustainable, environmentally sound water treatment technology should have the following key features:

- keep the cost of water treatment as low as possible;
- not to require large investments;
- use low energy and do not require high operating pressures;
- to allow the recovery of most of the treated water and
- to keep the impact on the environment to a minimum, ie to use as many renewable, recyclable and environmentally friendly materials as possible (Bolisetty et al., 2019).

2.3 Describing lead removal alternatives

Application of TOPSIS method was used to solve the water treatment method selection problem. Alternatives chosen for this MCDA are provided in Table 2.2.

Table 2.2. Alternatives of water treatment methods

Alternative	Alternative definition
a_1	Reverse Osmosis
a_2	Nanofiltration
a_3	Adsorption
a_4	Ion exchange
a_5	Electrochemical treatment (Electrodyalisis)

2.4 Describing methodology criteria

The main criteria were established on the basis of the detailed results of experiments and studies already carried out and the opinion of experts. Using the experience of the staff of Vilnius Gediminas Technical University, special recommendations on specific criteria were received. Finally, six criteria have been chosen and provided in Table 2.3.

Table 2.3. Criteria for lead removal from contaminated water methods

Criteria	Criteria definition	Desired properties	Units
c_1	Total costs	Lower is better	EUR/1mln. L of treated water
c_2	Removal efficiency	Higher is better	%
c_3	Operating flux	Higher is better	m^3
c_4	Operating cost	Lower is better	EUR/m^3
c_5	Required power	Lower is better	kW h /m^3
c_6	Water recovery efficiency	Higher is better	%

According to the first step of the TOPSIS procedure, the decision matrix was created (Table 2.4). The data was collected from studies of Bolisetty et al., (2019) and Nemati et al., (2017). Collected data was optimized – average values provided in studies were used in MCDA matrix.

Goal – choose most suitable method to remove lead ions from contaminated water.

Table 2.4. Multicriteria decision analysis matrix

Criteria	Alternatives				
	a_1	a_2	a_3	a_4	a_5
c_1	197.4	174.0	84.0	105.0	174.0
c_2	98.0	99.8	99.9	99.7	99.9
c_3	28450	3700	3050	3050	1270
c_4	0.4	0.2	$3.00E^{-05}$	$4.00E^{-04}$	0.8
c_5	3.6	0.5	0.1	0.4	0.5
c_6	50	65	100	98	85

After this, the normalization of the decision matrix was performed and a normalized matrix was created (Table 2.5).

Distributive normalization of criteria data requires that the values would be divided by the square root of the sum of the squares of each value in the column.

Table 2.5. Normalized matrix

Alternatives/ Criteria	a_1	a_2	a_3	a_4	a_5
c_1	0.58	0.51	0.24	0.31	0.51
c_2	0.44	0.45	0.45	0.45	0.45
c_3	0.98	0.13	0.11	0.11	0.04
c_4	0.48	0.17	$3.00E^{-05}$	$4.00E^{-04}$	0.86
c_5	0.97	0.14	0.02	0.11	0.14
c_6	0.27	0.35	0.55	0.54	0.46

2.5 Describing gained criteria weights

Determining the weights (importance) of criteria is a biased assessment because it is individual to each person who is influenced by personal feelings, experiences, and opinions. An expert survey was conducted to obtain more objective information. The data obtained were statistically processed and the means of the values were used to determine the weights of the criteria (shown in Table 2.6).

Table 2.6. AHP comparison matrix

Criteria	c_1	c_2	c_3	c_4	c_5	c_6
c_1	1.00	2.00	8.00	5.00	8.00	3.00
c_2	0.50	1.00	5.00	0.50	6.00	3.00
c_3	0.13	0.20	1.00	0.50	3.00	0.14
c_4	0.20	2.00	2.00	1.00	8.00	2.00
c_5	0.13	0.17	0.33	0.13	1.00	0.17
c_6	0.33	0.33	7.00	0.50	6.00	0.25
$\sum c_i$	2.28	5.70	23.33	7.63	32.00	8.56

The survey data were processed and the weighting of the criteria was determined on the basis of the survey results. Each element in the matrix was divided by its column total to generate a normalized pairwise matrix. Also, the sum of the normalized column of matrix was divided by the number of criteria used to generate priority vectors (priority vectors are used as criteria weights in the TOPSIS method). Obtained results are given in Table 2.7.

Table 2.7. Normalized criteria weight matrix

Criteria	c_1	c_2	c_3	c_4	c_5	c_6	Priority vector
c_1	0.44	0.35	0.34	0.66	0.25	0.35	0.40
c_2	0.22	0.18	0.21	0.07	0.19	0.35	0.20
c_3	0.05	0.04	0.04	0.07	0.09	0.02	0.05
c_4	0.09	0.35	0.09	0.13	0.25	0.23	0.19
c_5	0.05	0.03	0.01	0.02	0.03	0.02	0.03
c_6	0.15	0.06	0.30	0.07	0.19	0.03	0.13

The selected weights for each criterion are shown in Fig. 2.1.

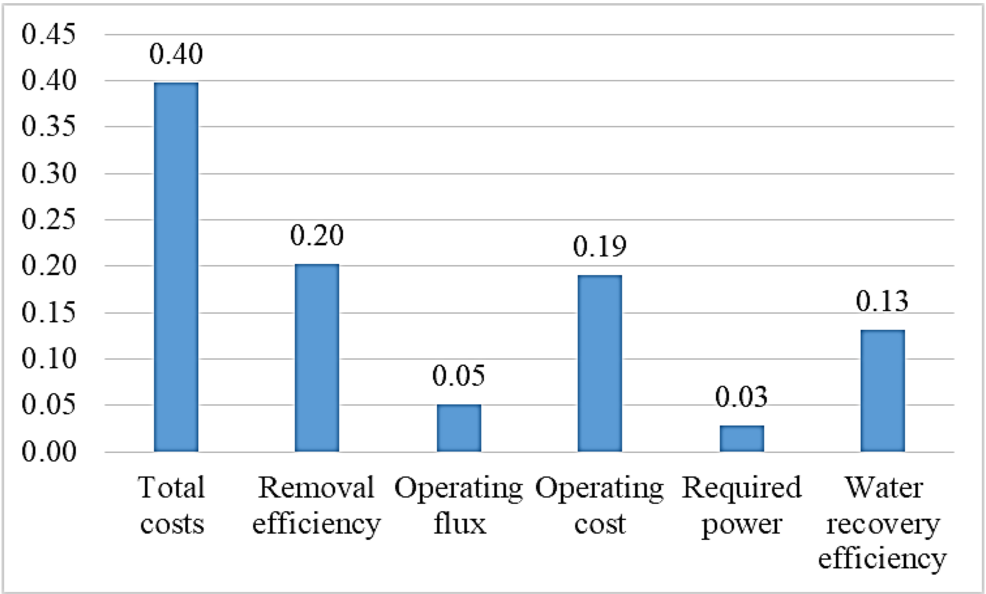

Fig. 2.1. Criteria weights

After processing the data, it is clear that two criteria have become priorities: total costs (40 %) and removal efficiency (20 %).

Then, weighted normalized matrix was obtained, and the best and worst alternatives were found (Table 2.8).

Table 2.8 Weighted normalized decision matrix

	a_1	a_2	a_3	a_4	a_5	Ideal solution	Anti–ideal solution
c_1	0.23	0.20	0.10	0.12	0.20	0.10	0.23
c_2	0.08	0.08	0.08	0.08	0.08	0.08	0.08
c_3	0.04	0.01	$4.59E^{-03}$	$4.59E^{-03}$	$1.91E^{-03}$	0.04	0
c_4	0.11	0.04	$1.00E^{-05}$	$1.00E^{-04}$	0.19	0	0.19
c_5	0.03	$3.84E^{-03}$	$6.10E^{-04}$	$2.88E^{-03}$	$3.80E^{-03}$	0	0.03
c_6	0.03	0.04	0.07	0.07	0.06	0.07	0.03

2.6 Ideal and anti–ideal option and calculation of relative closeness

The distance between alternatives and the positive ideal solution and the distance between alternatives and the negative ideal solution were calculated (Table 2.9) and determination of relative closeness coefficient was conducted (Table 2.10).

Table 2.9. Separation measures

Alternatives		Criteria					
		c_1	c_2	c_3	c_4	c_5	c_6
Distance for each alternative to the ideal solution	a_1	0.02	0	0	0.01	$1.00E^{-03}$	$1.00E^{-03}$
	a_2	0.01	0	$1.00E^{-03}$	$1.00E^{-03}$	0	$1.00E^{-03}$
	a_3	0	0	$1.00E^{-03}$	0	0	0
	a_4	$1.00E^{-03}$	0	$1.00E^{-03}$	0	0	0
	a_5	0.01	0	$2.00E^{-03}$	0.04	0	0
Distance for each alternative to the anti–ideal solution	a_1	0	0	$2.00E^{-03}$	0.01	0	0
	a_2	$1.00E^{-03}$	0	0	0.02	0	0
	a_3	0.02	0	0	0.04	$1.00E^{-03}$	$1.00E^{-03}$
	a_4	0.01	0	0	0.04	$1.00E^{-03}$	$1.00E^{-03}$
	a_5	$1.00E^{-03}$	0	0	0	0	$1.00E^{-03}$

The relative closeness coefficient is always between 0 and 1, where 1 is preferred action.

Table 2.10. Determination of relative closeness coefficient

Alternatives:	a_1	a_2	a_3	a_4	a_5
Distance for each alternative to the ideal solution	0.031	0.014	0.001	0.002	0.050
Distance for each alternative to the anti–ideal solution	0.009	0.026	0.057	0.051	0.002
Relative closeness coefficient	0.230	0.640	0.970	0.960	0.030

From the Fig. 2.2 it is visible, that the best method for lead removal according MCDA is adsorption (0.96), second would be Ion exchange method (0.94), third – Nanofiltration, forth – Reverse osmosis and lastly – Electrochemical method.

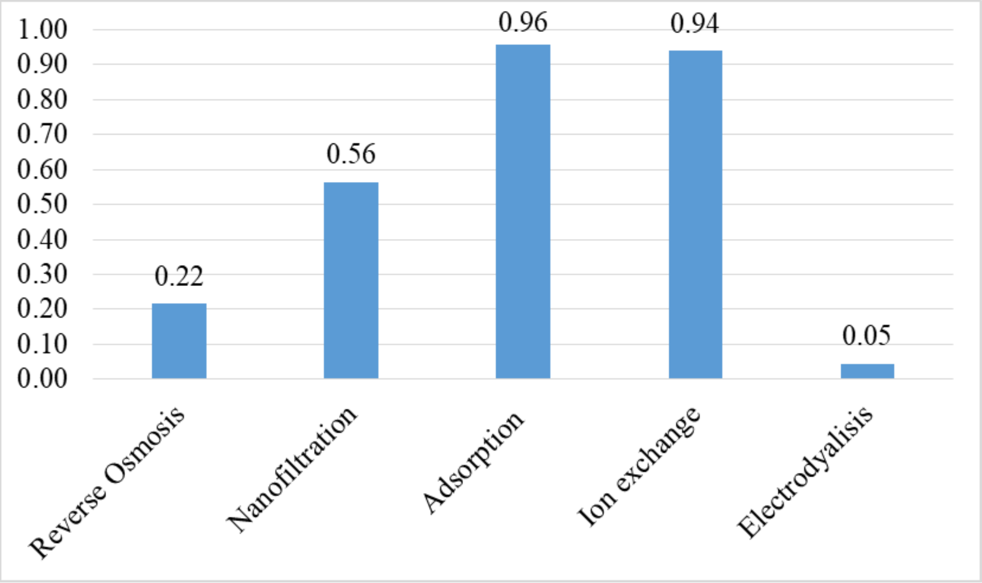

Fig. 2.2. Relative distances to choice of the ideal solution

The distance to the best solution of nanofiltration, reverse osmosis and electrodyalisis are significantly low compared with the remaining two alternatives and it is because of high total costs of the methods.

The multicriteria analysis showed that there is no big gap between the first and second place in preference order, and this shows the sensitivity of results – even a small change in total costs or removal efficiency could influence the rearrange in results.

Conclusions of the second chapter

1. The main criteria for this multicriteria analysis were: total costs, removal efficiency, operating flux, operating cost, required power and water recovery efficiency. The AHP revealed, that total costs and removal efficiency are the key criteria in this TOPSIS analysis.
2. MCDA has shown that the adsorption method is the most favorable method for the treatment of water contaminated with lead ions compared to reverse osmosis, nanofiltration, ion–exchange and electrodyalisis methods.
3. Multicriteria analysis showed that there is no significant difference between first and second place in order of priority, and this indicates the sensitivity of the results – even a small change in the overall cost or lead ion removal efficiency can affect the conversion of the results.

3. METHODOLOGY FOR EXPERIMENTAL INVESTIGATION OF SORPTION PROCESSES USING EGG SHELL WASTE

The objective of the experiments on adsorption parameters is to determine the capability of the ES to adsorb lead ions from contaminated aqueous solution. Evaluation of adsorption capacity effectiveness is performed by assessing the value of pH of the solutions, initial Pb (II) ion concentration in the experimental solution and the duration of adsorption contact time. Batch experiments are performed according to a standard operating procedure (Mashangwa et al., 2017).

The porosity of the eggshell makes it an important substance as a potential adsorbent (Koumanova et al., 2002). The structure of the eggshell is usually made of ceramic material. The shell consists of three main layers - the membrane in the outer layer, the sponge structure layer and the inner membrane layer. The eggshell is an effective adsorbent due to its structure, the eggshell layers are formed so that there are many pores for adsorbate absorption (Mashangwa et al., 2017).

Numerous calcium supplements and other nutritional sources derived from eggshell albumin, membranes, and matrices that have been processed by crushing and grinding to produce fine particles began as early as the 1970s. Thus, attempts have been made to use eggshell waste at that time, and these studies are expected to lead to a more useful and unprofitable method of managing this waste stream (Mashangwa, 2016).

3.1 Adsorbent collection and preparation

Before experimental studies on lead adsorption, an egg shell waste analysis and a heavy metal – Pb (II) content analysis must be carried out. All solutions included in this study have been diluted in deionized water as required. Chicken egg shells are collected from household use. After thorough cleaning with tap water, ES are partially separated from egg shell membrane (ESM). After drying in room temperature ES are washed several times with deionized water to remove any residual dirt particles.

Fig. 3.1 Drying cabinet „SNOL 3,5“ (Гомельский завод измерительных… 2020)

Following methodology of (R. Ahmad et al., 2012) egg shells are dried to constant weight in an oven (shown in Fig. 3.1) at 100 °C and after, allowed to cool to 22 °C (ambient temperature). Then dried egg shells are grounded into small particles using a grinder and sieved well in fraction of 300 – 900 µm mesh size particles (Fig. 3.2). After sieving the grounded ES, the adsorbent is placed in closed, sterilized containers for use as a test adsorbent material in further steps.

Fig. 3.2 Grounded and sieved egg shell adsorbent

For further experiments samples of 0.5 g, 1.0 and 2.0 g of adsorbent is weighed and stored in closed individual containers. Each container is labelled. This is done to prevent adsorbent from adsorbing ambient humidity and for optimizing time to prepare for experiments (Badrealam et al., 2018).

3.2 Adsorbate solution preparation

Standard solution of Pb (II) is prepared by dissolving lead standard solution (Pb $(NO_3)_2$ in HNO_3, 1000 mg/L Pb) in deionized water. Deionized water is artificially contaminated with Pb (II); initial concentration of lead – 1 mg/L. This concentration was chosen according to the maximum permitted concentrations (MPC) in the sewage collection system, which is 0,5 mg/L.

The reference value was chosen from the Lithuania wastewater management regulation as it was the nearest official standard that specifies the permissible concentrations of pollution that are appropriate for this experiment. The chemicals used in these experiments, including the NaOH and HCl used in the pH adjustment process, are of analytical reagent quality and are used in assays without further purification (Mashangwa, 2016).

3.3 Determining the Adsorption Capacity of Egg Shell Adsorbent

The effectiveness of the sorption process is influenced by the main 4 parameters:

1. Effect of pH on Pb (II)adsorption
2. Effect of contact time on Pb (II)adsorption
3. Effect of adsorbent dose on Pb (II) adsorption
4. Effect of initial metal concentration on Pb (II) adsorption

The initial influence of metal concentration and adsorbent content on the sample is determined using different concentrations of metals (for Pb: 500, 1000, 1500, 2500 and

5000 µg/l) and 3 different masses (0.5 g, 1.0 g, 2 g) of adsorbent. Blank samples are analyzed for analytical parameters to control the quality of deionized water and eliminate the influence of impurities in deionized water and chemical reagents. In order to increase the reliability of the experimental results obtained, samples shall be taken twice and each sample measured 3 times and the statistical parameters (mean, standard deviation, confidence interval) calculated. Further methodology is provided below (Dambudzo Mashangwa, 2016).

3.3.1 Effect of pH on Pb (II) adsorption

The effect of pH on the adsorption of Pb (II) ions on the eggshell is investigated using constant 1,0 g of adsorbent with 100 mL of a 1 mg/L solution of individual Pb (II) ions adsorbate at different pH values from 2 to 3.5, 5, 6.5 and 8 at 22ºC (room) temperature.

The variable pH is adjusted with 0.1 M NaOH and 0.1 M HCl and measured with a pH meter. The pH of the solutions is measured with a pH–meter "Mettler Toledo" with a glass electrode (Fig. 3.3).

Fig. 3.3. "Mettler Toledo" pH meter

Before each measurement, the pH–meter glass electrode is washed with distilled water, dried and immersed in the prepared suspension.

After preparing different pH solutions, the mixtures are then put into rotating drum shaker "Labos Shake–Gerhardt" for 90 minutes (Fig. 3.4).

The solutions are then filtered through Whatman filter ("Frisenette" Grade 202, medium filtration speed, diameter 150 mm, retention 5–8 µm) then the filtrate is studied for remaining metal concentration.

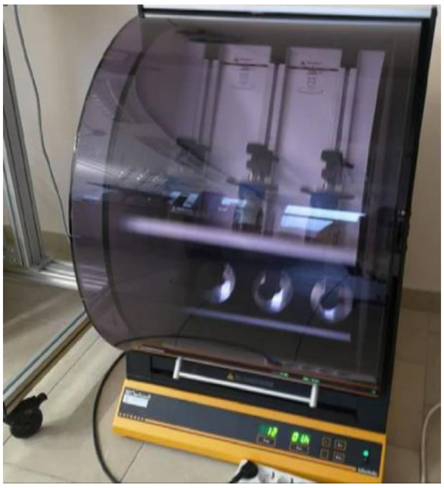

Fig. 3.4. Rotating drum shaker “Labos Shake–Gerhardt”

Using „Buck Scientific 210 VGP“ Atomic Absorption Spectrometer (AAS) final concentration of Pb (II) is measured. Nitric acid is added after adsorption to stop the process, otherwise lead precipitation may occur.

3.3.2 Effect of adsorbent dose on Pb (II) adsorption

The effect of the adsorbent dose on the adsorption of Pb (II) ions is investigated using 3 different eggshell adsorbent masses from 0.5 to 2.0 g. The eggshell dose is mixed with 100 ml of a 1 mg/L Pb concentration of each adsorbate solution at room temperature and with the optimum pH of the lead ion solution (Mashangwa, 2016). The individual ion mixtures are then taken to rotating drum shaker “Labos Shake–Gerhardt” for 90 min. The solutions are then filtered through “Frisenette” paper filters and analyzed with AAS.

3.3.3 Effect of initial metal concentration on Pb (II) adsorption

The effect of initial Pb (II) ions concentration on adsorption is studied by mixing 0.5, 1.0 and 2.0 grams of adsorbent with 100 mL of the individual adsorbate solution in varied concentrations of Pb (II): 500, 1000, 1500, 2500 and 5000 µg/L at ambient temperature and optimal pH.

Fig. 3.5 Adsorbent filtering process

The solutions are then shaken in rotating drum shaker for 90 minutes and then filtered through paper filters (process of filtering is shown in Fig. 3.5) and analyzed with AAS.

3.3.4 Effect of contact time on Pb (II) adsorption

The effect of contact time on the adsorption of Pb (II) ions is investigated for three different quantities of the adsorbent 0.5 g (and 1.0 g, 2.0 g) and 100 mL of each 1 mg/L individual adsorbate solution. Six different contact times are studied, ranging between 5, 10, 15, 30, 60, 90 minutes at room temperature and optimal pH. The solutions are then filtered through filter paper and the remaining concentration of Pb (II) in the filtrate is measured with „Buck Scientific 210 VGP“ Atomic Absorption Spectrometer (Mashangwa et al., 2017).

3.3.5 Equilibrium studies

The effect of the adsorption time was determined by placing three different masses (0.5 g, 1.0 g and 2.0 g) of egg shell adsorbent in 100 mL of initial 1 mg/L concentration lead Pb (II) solution for 90 min at ambient temperature 24 °C and initial Pb (II) solution pH 4.

3.3.6 Metal concentration determination

Atomic Absorption Spectrometer (AAS) Buck Scientific 210 VGP with a graphite furnace was used to investigate the concentration of metals in different samples prepared by varying various adsorption parameters (Fig. 3.6).

Fig. 3.6. Atomic absorption spectrometer (AAS) „Buck Scientific 210 VGP“

Atomic absorption graphite furnace spectrometry (GFAAS) is a type of spectrometry in which an aqueous sample of a solution is evaporated using a graphite–coated furnace (in this case a graphite cell). This technique is explained by the fact that free atoms absorb light at frequencies or wavelengths specific to the element under study (in this case lead). Within certain limits, the amount of light absorbed can be directly related to the concentration of the analyte being tested. Concentrations of free atoms in many elements can be obtained from samples using high temperatures. GFAAS samples are injected with a syringe into a small graphite or pyrolytic carbon–coated graphite tube, which is then heated to evaporate and decompose the analytes (Borges and Holcombe, 2017; Buck Scientific, 2019).

A blank and a set of standards of Pb: 0.02; 0.05; and 0.1 mg/L of metal solutions are prepared in standard graduated flasks (25 mL) using standard metal solutions and distilled water. Three different standard solutions of lead ions are introduced into the graphite cuvette by syringe in ascending order of concentration. After generating the data, the absorbance of each solution and plot a standard calibration curve is determined using analytical software. The lead ion adsorption sample solution is then taken with a syringe and introduced into a graphite cuvette and the absorbence reading of the solution is then monitored. Using the analytical program, the amount of metal in each sample is calculated using a standard calibration curve. (Buck Scientific, 2019).

The quantity of metal adsorbed onto one gram of adsorbent is calculated according to a mass balance on the Pb (II) concentration using Eq. (3.1):

$$q = \frac{(C_I - C_F) \cdot V}{w} \tag{3.1}$$

where

C_I – Initial lead concentration, (mg/L);

C_F – Final lead concentration after adsorption, (mg/L);

V – is the volume of lead ion solution, (L);

w – is the mass of egg shell adsorbent added to the solution, (g).

The adsorption efficiency (E) is calculated as:

$$E = \frac{(C_I - C_F)}{C_I} \cdot 100\,\% \tag{3.2}$$

The quality of the results is assured by using blank sample, each test is repeated 3 times, arithmetic mean of the results, dispersion and other quality parameters are calculated (He et al., 2019).

3.4 Statistical processing of results

After the experiments and numerical values of the results, they need to be mathematically processed. The main statistical indicators are calculated as follows (American Public… 1999):

1. Arithmetic mean $\underline{x}$:

$$\underline{x} = \frac{\sum_{i=1}^{n} x_i}{n} \tag{3.3}$$

where

x_i – the result of a separate measurement;

n – number of results.

2. Dispersion s^2:

$$s^2 = \frac{\sum_{i=1}^{n} (x_i - \underline{x})^2}{n-1} \tag{3.4}$$

where $x_i - \underline{x}$ – deviation of the individual result from the arithmetic mean.

3. Average square deviation s:

$$s = \sqrt{\frac{\sum_{i=1}^{n} (x_i - \underline{x})^2}{n-1}} \tag{3.5}$$

4. Coincidental error of measurement result Δ:

$$\Delta = t_{P,n} \cdot \frac{s}{\sqrt{n}} \tag{3.6}$$

where $t_{P,n}$ – Student coefficient at n–1 degree of freedom (in our case n is the number of measurements) and P at confidence level (in engineering its usually P = 0,95). Therefore $t_{P,n}$ is equal to 2.353.

5. Confidence interval I_β:

$$I_P = \left(\underline{x} - \Delta;\ \underline{x} + \Delta\right) \quad (3.7)$$

Confidence interval defines the accuracy of the results. The smaller the confidence interval, the better.

6. Relative random error δ_{ats}:,

$$\delta_{ats} = \frac{\Delta}{\underline{x}} \cdot 100\ \% \quad (3.8)$$

When relative error δ_b smaller or equal to 5 % the results obtained are considered to be sufficiently accurate, when δ_b, is equal to 5 to 10 % – the accuracy of the results is satisfactory; when δ_b >10 % – accuracy is not satisfactory.

Statistical data (average, confidence interval, standard deviation and ect.) is calculated with Microsof Office Excel 2016 program.

Conclusions of the third chapter

1. Batch experiments were performed according to a standard operating procedure. To evaluate the process of lead ion adsorption, parameters affecting adsorption, in this case pH, primary contaminant concentration, adsorbent dose, and time, were investigated in these experiments.
2. Influence of pH on the adsorption of Pb (II) elements in the eggshell is studied by way of mixing each individual adsorbate solution with 5 different pH values from 2 to 8 (every 1.5 pH).
3. The effect of the initial concentration of lead ions in the sample is determined using five different concentrations of the solutions (Pb: 500, 1000, 1500, 2500 and 5000 µg/l).
4. The effect of the adsorbent dose on the adsorption of the analyzed lead ions is investigated by way of combining different quantities of eggshell adsorbent alternating from 0.5 to 2.0 g at an ambient temperature of 22 ^oC and an optimal pH.
5. The effect of contact time on the adsorption of Pb (II) ions is investigated by mixing three different masses of adsorbent (0.5 – 2.0 g) with a solution contaminated with 1 mg/L lead ions with different contact times of 5, 10, 15, 30, 60 and 90 minutes.
6. The final concentration of Pb (II) ions is measured using a Buck Scientific 210 VGP atomic absorption spectrometer.
7. The quality of the results is ensured by using a blank sample, repeating each test 3 times and performing statistical processing of the results.

4. ANALYSIS OF ADSORPTION EXPERIMENTS RESULTS

The experimental research on the removal of the lead from the aqueous solutions was carried out in the scientific laboratory of the Department of Environmental Protection of the Vilnius Gediminas Technical University.

4.1 Calibration curve of lead

Calibration curve which shows optical density dependence on initial lead concentration was composed based on three times measuring of different concentration solutions. Every time the AAS is used calibration curve with standard lead concentrations (blank, 0.02 mg/L, 0.05 mg/L and 0.1 mg/L) must be made, to ensure accuracy of measurements made with this device. It is recommended to check the middle concentration value of standard Pb solution to check if spectrometer calibration curve has not changed if experiments take longer time. In Fig. 4.1 one of the curves used in experiments is presented.

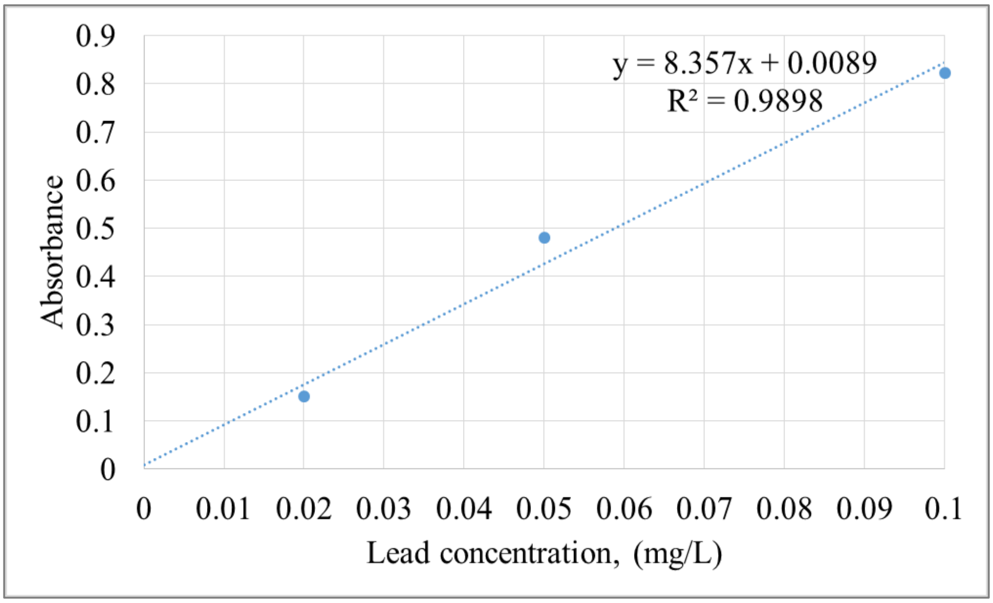

Fig. 4.1. Lead concentration calibration curve

It is good practice to store this data, because if the curve is changing drastically it could indicate that the graphite cuvette has worn out and must be changed.

4.2 Evaluation of the influence of pH on Lead adsorption

Three samples are prepared for each case (corresponding lead ion concentration and corresponding adsorbent content). 100 mL of the appropriate concentration of the Pb (II) solution was added to the screw–top vessels, then 1 g of adsorbent was added. The dishes are tightly screwed and placed in a Labos Shake–Gerhardt rotary drum shaker. After a fixed contact time, the contents of the vessels are filtered through 5–8 μm paper filters to stop adsorption. The effect of pH on adsorption efficiency was investigated at ambient temperature (22 °C). The effectiveness of Pb (II) ion removal from water–based solutions was estimated by residual lead (II) ion concentration, where the concentrations of lead prior to contact with the adsorbent in the test solutions were 1 mg/L.

The pH of the test solution has a strong effect on the adsorption capacity of metal ions, as it can affect several process criteria. The pH of the test solution may affect the release of metal ions in solution, the chemical state of the reactive adsorbent, and affect the adsorption of target metal ions. In order for adsorbents to remove heavy metal ions from a contaminated solution, it is necessary to know the pH at which the metals are removed most efficiently. Also, in order to avoid the formation of Pb (II) ion hydroxide deposits, the initial pH of the solution should be in the range of 2.0–6, otherwise it would be difficult to assess which processes actually cause the removal of metals (Zhan et al., 2018). After all, pH 8 value is also in the experiments, and the process of precipitation of Pb (II) is observed. In Table 4.1 it is visible that when pH was increased from 6.5 residual concentration of lead started to drop significantly (0.38 mg/L), but this was because adsorption process was affected by chemical precipitation process, too. Therefore with pH 8 value is not appropriate to assess ES adsorption further.

Table 4.1. Experimental results of pH influence on concentration and adsorption uptake

		Residual Pb (II) ion concentration, (mg/L)	Egg shell adsorption, (mg/g)
Experimental pH values	2	0.89 ± 0.05	0.01
	3.5	0.34 ± 0.05	0.07
	4	0.31 ± 0.05	0.07
	4.5	0.37 ± 0.05	0.06
	5	0.70 ± 0.05	0.03
	6.5	0.54 ± 0.05	0.05
	8	0.38 ± 0.05	0.06

In the Fig. 4.2 the affiliation between primary solution pH and contaminants exclusion is showed. The results suggest that solution pH affected the performance of ES adsorbent, with acidic pH 2 resulting in significant reduction in the lead removal (about 10 %). As the pH of the solution is gradually increased (especially above 3.5), it is observed that the adsorption efficiency begins to increase sharply (above 66 %) and then tends to stabilize.

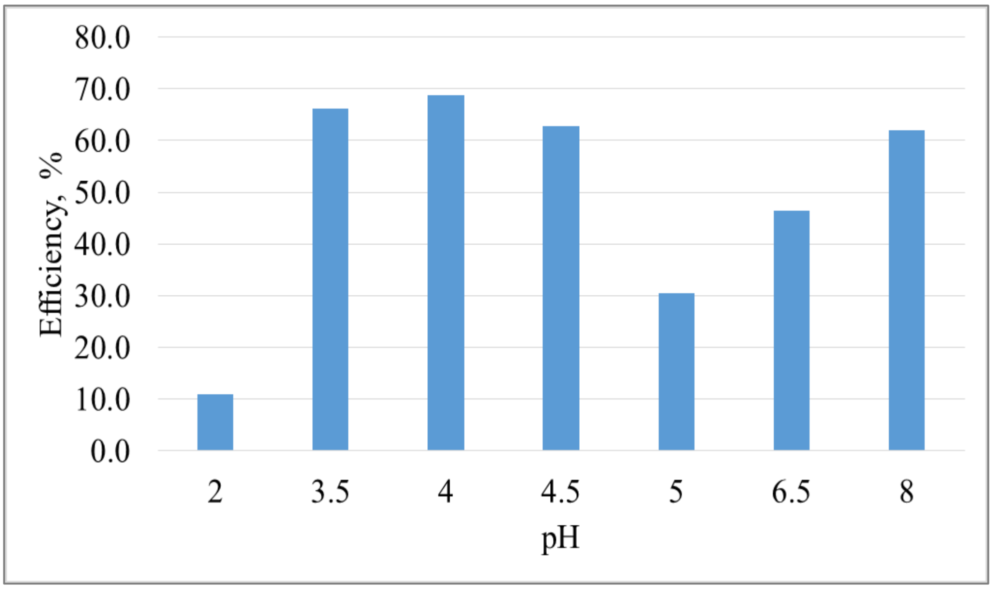

Fig. 4.2. Pb (II) ion adsorption efficiency relation with solution initial pH

The experimental results obtained can be explained by the specific structure of the eggshell adsorbent. The properties of the acids and alkalis of the reactive groups are affected by their chemical environment in solution. This means that at pH < than 3.5, most carboxylate groups are less responsive to metal ion binding, and at pH > 3.5, carboxylate groups are more conducive to metal ion bond formation (Zhan et al., 2018).

After determining initial five pH values (2; 3.5; 5; 6.5 and 8) two further intermediate values between 3.5 and 5 were tested. In Fig. 4.2 it is visible, that efficiency of adsorption is nearly stabile in pH range of 3.5–4.5 and after that efficiency starts to decrease again.

Experimental studies have shown that the optimal pH of lead ion adsorption is in the range of 3.5–4.5. It is assumed that all other adsorption experiments were performed at the initial pH of the solution at level 4, which is the optimal pH value of the experiments in this final work.

4.3 Evaluation of the influence of lead concentration on adsorption

In subsequent experiments, pH is the primary condition for the assay (the optimum pH for the first assay is 4). Variable conditions include lead concentrations ranging from 0.5–5 mg/L and adsorbent doses ranging from 0.5–2.0 g (Note: The error of the analytical weights is ±0.05). Change in Pb (II) ion concentration after adsorption is depicted in Fig. 4.3.

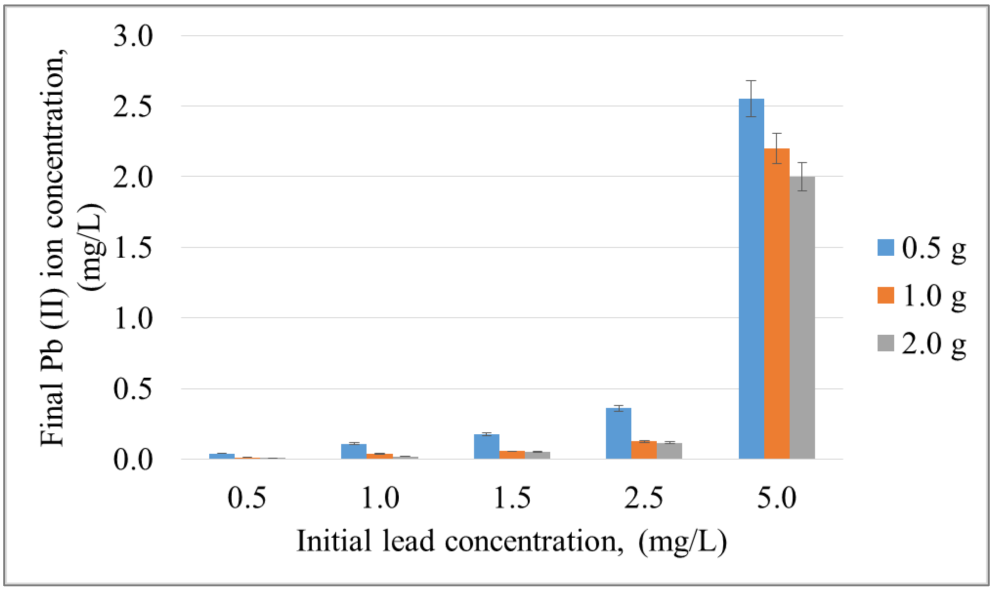

Fig. 4.3. Residual Pb (II) ion concentration dependence on different initial concentration Pb (II) solutions

The adsorption uptake of the adsorbent increased significantly with the growth of initial concentration even though there is decrease in the adsorption efficiency.

Decrease of adsorption efficiency and the change in adsorption uptake is depicted in Fig. 4.4 and 4.5 respectively.

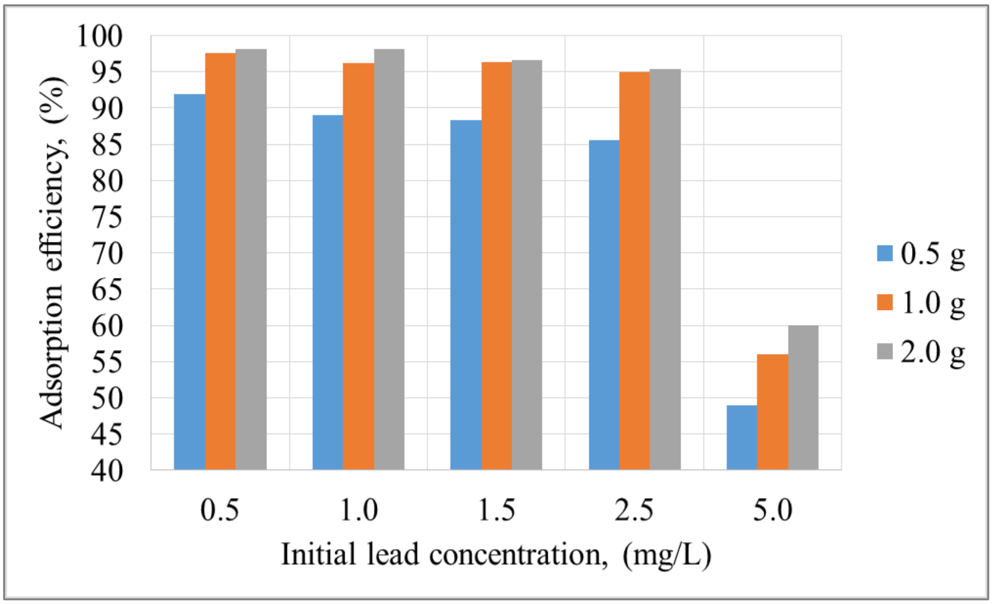

Fig. 4.4. Pb (II) ion adsorption efficiency relation with solution initial concentration

The increase of adsorption can be due to growth of concentration gradient, which causes an increase in the number of lead Pb (II) ions coming in contact with the adsorbent. On the other hand, the number of existing adsorption sites in the adsorbent is the same for all initial concentrations. Therefore, as the initial concentration increases, more ions has to compete for the same adsorption site. This may cause many lead ions to be left without being adsorbed, thus decreasing the efficiency of the removal upon increasing the concentration of Pb (II) ions (Khan et al., 2015).

At low concentrations of lead ions, the solution contains less lead ions compared to the number of available adsorption sites in the adsorbent. However, at higher ion concentrations, the potential number of adsorption sites decreases. Therefore, it is observed that the removal of lead ions depends on the initial concentration and the adsorbent sites (the more porous the adsorbent, or the larger the surface area of the adsorbent, the more potential adsorption sites are available) (Jeyakumar and Chandrasekaran, 2014).

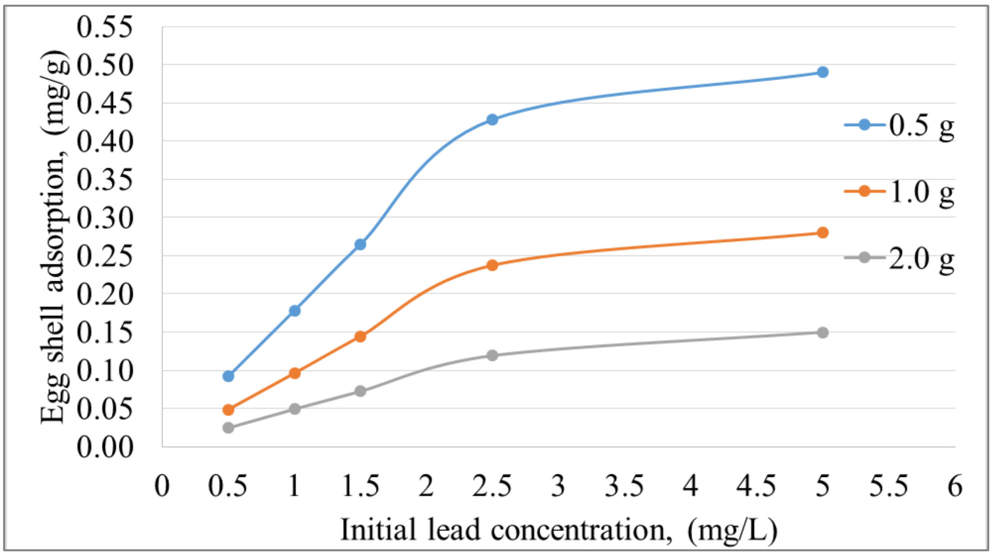

Fig. 4.5. Initial lead ion concentration effect on adsorption

The maximum adsorption uptake (about 0.5 mg/g) of Pb (II) is achieved at 5 mg/L of lead solution, but from Fig. 4.5 it is visible, that adsorption uptake is only increasing, which means, that egg shell adsorbent could be used in higher concentration lead solutions.

4.4 Evaluation of the influence of time on adsorption

The influence of adsorption contact time on the amount of lead ions adsorbed by eggshell (ES) adsorbent was investigated with 6 different time values (range 5 to 90 min). Tests were performed using 100 mL of 1 mg/L Pb (II) containing 0.5 to 2.0 g of EU adsorbent at pH 4 at room temperature. The outcomes are shown in Fig.4.6. It is evident that ES was found to absorb approximately ≈ 0.140 mg/g of total absorbable lead solution within the first 15 minutes with an adsorbent content of 0.5 g, and the maximum absorbance of lead (0.161 mg/g) in this study was reached after 90 minutes. Additionally, it is visible from the Fig.4.6 that adsorption starts so settle down within 30 min, when the adsorbent dose is 2.0 g. Also, with this dose of ES adsorbent at 90 min. efficiency of 98 % of Pb (II) removal was reached (see Fig. 4.7).

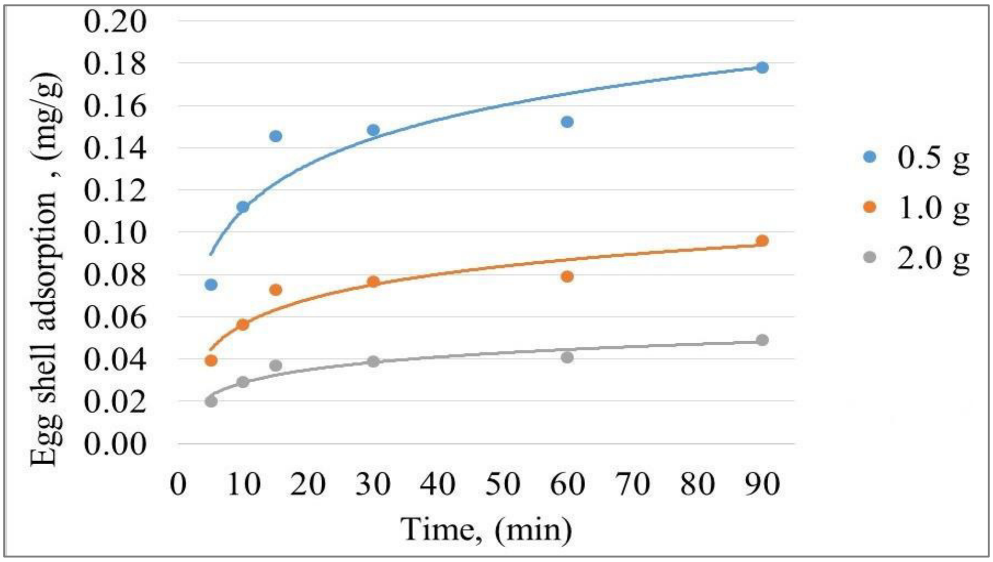

Fig. 4.6. Impact of time on adsorption of egg shell adsorbent

With 0.5 and 1.0 g doses it is speculated, that the equilibrium was reached within 90 min, but further studies should be held to confirm this.

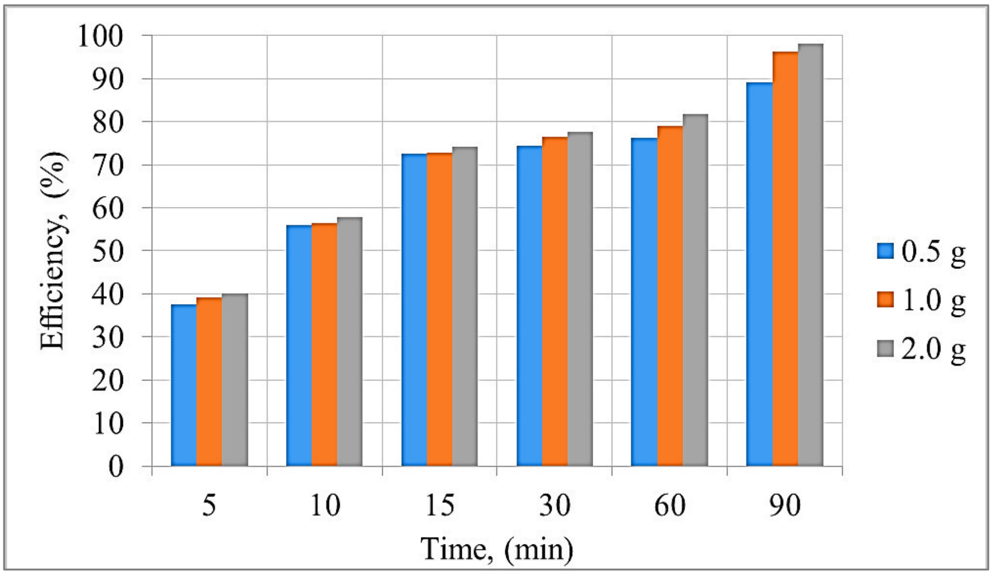

Fig. 4.7. Impact of time on Pb (II) ion removal efficiency of egg shell adsorbent

These results indicate that from the outset, adsorption occurs at a rapid rate on the outer surface of the adsorbent. This is followed by a slower internal diffusion process, which may be a determinant of the overall adsorption rate. This trend of lead adsorption ions suggests that the bond between the adsorbent and lead ions depends on the interaction with functional groups on the ES surface. Based on the obtained results, it is confirmed that the maximum contact time is required for the most efficient absorption of metal ions by the ES adsorbent. (Khan et al., 2015).

4.5 Adsorption isotherm studies

Adsorption isotherms provide information on how adsorption system proceeds and indicate how efficiently adsorbent interacts with the adsorbate (Bayuo et al., 2018). The ability of hen ES to adsorb Pb (II) ions from aqueous solution is analyzed and evaluated from the shape of the adsorption isotherm plots. In this study, equilibrium isotherm data were applied to one one–parameter (Henry) and two two–parameter (Langmuir, Freundlich) adsorption models. The regression results of the linear isotherm model were used to find the best model. The linear form of the various isotherm models are presented in Eq. (4.1) to (4.3) while, their correlation coefficients (R^2) and constants are presented in Table 4.3.

Henry's isotherm (Bayuo et al., 2018):

$$q_e = K_{HE} \cdot C_e \tag{4.1}$$

where

q_e – Amount of metal ions adsorbed at equilibrium, (mg/g);

K_i – Constants characteristic of the system, where indexes – HE, L and F are for each Henry, Langmuir and Freundlich isotherms accordingly;

C_e – Concentration of metal ions at equilibrium (mg/L)

Model linear expression of Langmuir isotherm (Nagy, 2019):

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m \cdot K_L} \tag{4.2}$$

where q_m – maximum adsorption capacity of metal ion uptake (mg/g).

And linear form of Freundlich isotherm is expressed in Eq. (4.3) (Boparai et al., 2011):

$$\text{Log } q_e = \log K_F + \left(\frac{1}{n}\right) \log C_{eq} \qquad (4.3)$$

where n – Freundlich constant which indicates the intensity of the adsorption process.

The final concentrations (C_e) of lead, are plotted as q_e versus C_e for the Henry model, C_e/q_e versus C_e for the Langmuir model, and log q_e versus log C_e for the Freundlich model, and values of the constants for each type of ES are determined after linearizing the equations through linear regression analysis (Arunlertaree et al., 2007).

Data for adsorption isotherm plotting is provided in Table 4.2.

Table 4.2. Adsorption isotherm data matrix

Dose of egg shell, (g)	Final Conc. (mg/L) Ce	Solute Adsorbed (mg)	Adsorption capacity (mg/g) Qe	Ce/Qe	Log Ce	Log Qe
0.5	0.109	0.089	0.178	0.612	-0.963	-0.749
1.0	0.038	0.096	0.096	0.395	-1.420	-1.017
2.0	0.018	0.098	0.049	0.367	-1.745	-1.309

In Fig. 4.8, it is found that the equilibrium results fitted the one–parameter isotherm model (Henry) with correlation coefficient (R^2) of 0.842. The value of K_{HE} (1.756 L/g) is relatively high which confirmed the fitness of the Henry adsorption isotherm model.

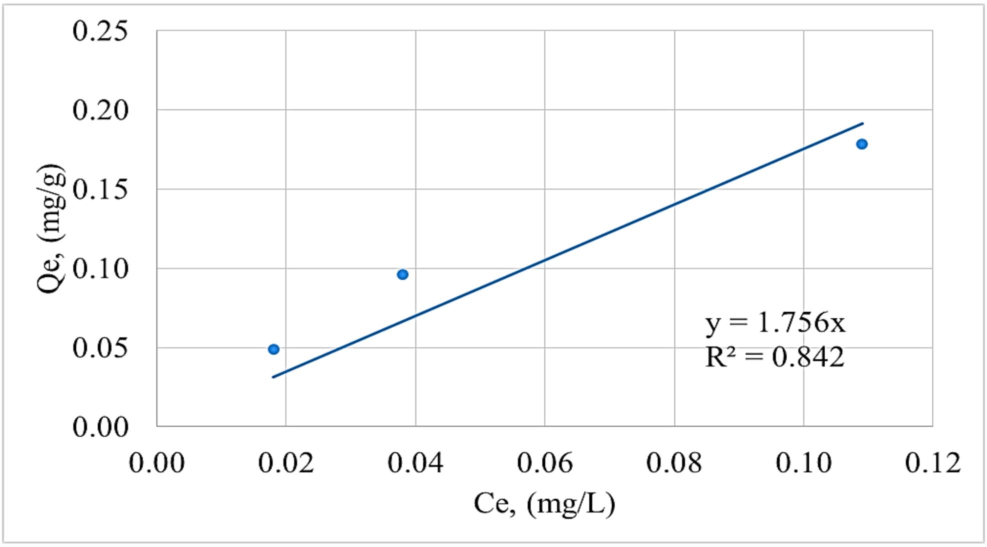

Fig. 4.8. Henry adsorption isotherm

Analysis of two–parameter adsorption models revealed that the Langmuir isothermal model characterized the adsorption of Pb (II) ions by ES from aqueous solution as indicated by a high correlation coefficient (R^2) of 0.989 (as shown in Fig. 4.9).

The Langmuir parameters are also used to predict the affinity of the adsorbent surfaces towards the metal ions by using dimensionless constant called equilibrium parameter R_L, which is expressed according to the literature (Jeyakumar and Chandrasekaran, 2014) in Eq. (4.4):

$$R_L = \frac{1}{1 + K_L \cdot C_o} \qquad (4.4)$$

where C_o is the initial amount of adsorbate, in this case 1.0 (mg/L).

The shape of isotherm is described in terms of equilibrium parameter R_L:

- When $R_L > 1$ – adsorption process is unfavorable;
- When equilibrium parameter is equal to 1, adsorption is linear;
- When equilibrium parameter is $0<R_L<1$, the adsorption process is favorable;
- When R_L is equal to zero – adsorption is irreversible (Khan et al., 2015).

In this study R_L value is between 0 and 1 (0.098), which indicates the favorability of the adsorption process under the considered conditions.

The value of K_L (9.158 L/mg) is relatively high implying high surface energy in the process and consequently high bonding between metal ions and the ES. It was found that the Langmuir adsorption capacity (q_m) rate was equal to 0.359 mg/g, meaning high adsorption capacity effectiveness of the ES adsorbent.

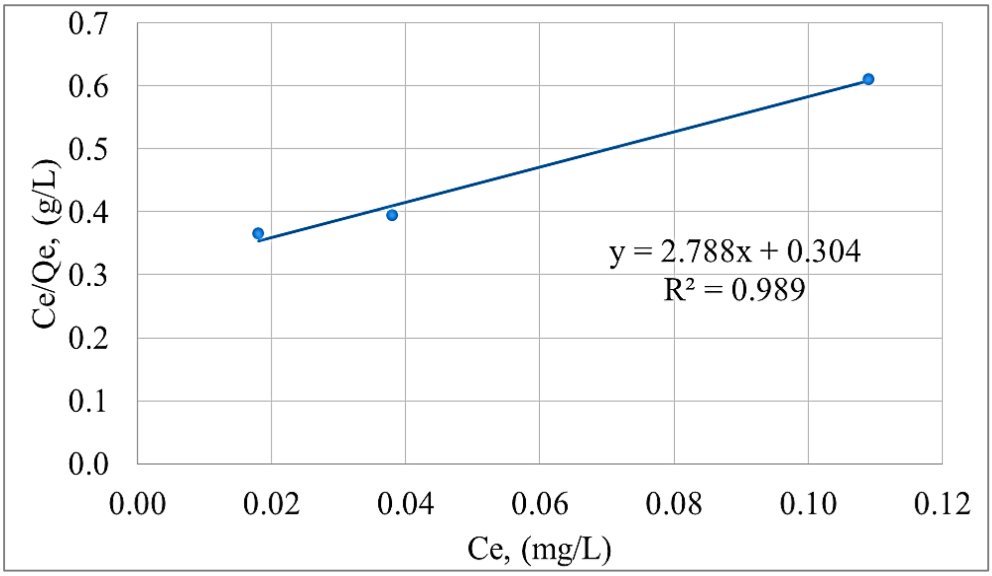

Fig. 4.9. Langmuir adsorption isotherm

From the linear isotherm shown in Fig. 4.10, it was found that the Freundlich isotherm model is also consistent with the experimental data.

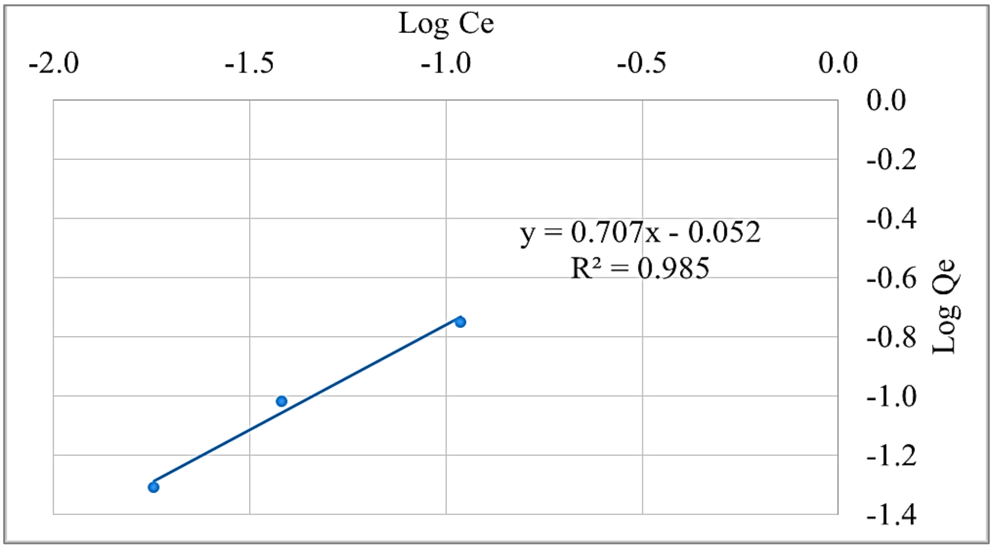

Fig. 4.10. Freundlich adsorption isotherm

The Freundlich isotherm correlation coefficient of 0.985 also confirms the high validity of the model. The K_F value found is 0.887 mg/g, which means that lead ions are poorly absorbed on the adsorbent surface. The value of 1/n is found to be 1.414. 1/n values of > 1 are typical of S–type isotherms. These situations are relatively rare but are often observed at low concentration ranges for compounds. Studies by other researchers has shown that, at low concentrations, such compounds are in competition with water for adsorption sites (Ecetoc, 2020).

After analysis of all three isothermal models, it was observed that the equilibrium data fit well with all three models. But in this study results of ES adsorption tended to be described by the Langmuir model, because the correlation coefficient (highest R^2 value) obtained from linear Langmuir curve fitted the best.

Table 4.3. Analyzed isotherm correlation coefficients (R^2) and constants

Henry	K_{HE} (L/g)			R^2
	1.756			0.842
Langmuir	K_L, (L/mg)	q_m, (mg/g)	R_L	R^2
	9.158	0.359	0.098	0.989
Freundlich	K_F, (mg/g)	n	1/n	R^2
	0.887	0.707	1.414	0.985

The results suggest that the adsorption of Pb (II) ions can be assessed by considering the formation of a solid layer of lead ions on the surface of the adsorbents. The highest adsorption, which is derived from the Langmuir equation, may be useful in evaluating potential adsorption capacity for ES adsorbent. Based on the Langmuir isotherm, ES has relatively high sorption affinity. These findings indicate that the adsorption of Pb (II) onto the surface of ES is likely due to the complexation – ion exchange reaction (M. Ahmad et al., 2012).

4.6 MCDA regarding adsorption efficiency

The list of alternatives and criteria was created according to the different adsorption efficiencies and adsorption factors affecting it (shown in Table 4.4).

The main goal of this multicriteria analysis is to determine the impact of pH, initial lead concentration in solution, adsorbent dose and adsorption time influence on efficiency of ES adsorption. Data for decision matrix have been obtained in accordance with the important properties of adsorption which have been experimentally investigated in this paper.

Table 4.4. Decision making matrix

Efficiency, %	pH	Initial Lead concentration, mg/L	Adsorbent doses, g	Time, min
	C_1	C_2	C_3	C_4
10	2.0	8.0	0	0
30	5.0	6.0	0.5	5.0
50	6.5	5.0	0.5	10
70	3.5	4.0	1.0	30
90	4.0	0.5	2.0	90

Impact factor was calculated using method derived from experiment where efficiency index was calculated using 3 main steps.

1)Data normalization. Data normalization is used to scale data set, so it becomes comparable. In this case, instead of indicators there are adsorption conditions C_x, that are expressed with different values of measurement and resulting adsorption efficiency.

Each of the conditions that affects the reaction has different values of measurement. In order to assess the impact of each condition on the results and compare them, data needs to be converted to unified scale. Min–Max Feature scaling is a well–known data normalization method from statistics field and was adopted for this step.

$$X' = \frac{X - X_{min}}{X_{max} - X_{min}} \tag{4.5}$$

where:
X' –normalized value;
X– original value;
X_{min} – minimal value for the condition C_i (where i=1,…,4);
X_{max} – maximal value for the condition C_i (where i=1,…,4).

2)Data adjustment in accordance with weight factors. Weight factors are added to adjust the preference for desired outcome (higher efficiency).

Source data contains information of reaction conditions and the resulting efficiency. It is adjusted to account for the preference for higher efficiency using Eq. 4.6:

$$X_w = X' \cdot w \tag{4.6}$$

where
Xw – normalised weighted value;
w – weight factor.

Identifying weights is a non–objective measurement as it is subjective for each person affected by personal emotion, experience and opinion. A survey of experts was therefore formed in order to obtain more reliable knowledge. The survey data were processed and the weighting of the criteria was determined on the basis of the survey results. For each criteria, the selected weights are shown in Table 4.5:

Table 4.5. Criteria weights

Efficiency, %	Weight
10	0.05
30	0.10
50	0.15
70	0.30
90	0.40

3)Calculation of impact factor. Normalized weighted values are summed for each adsorption condition to see, which has higher overall impact.

Impact factor for each condition was calculating as a sum of its normalised weighted values:

$$I_i = \sum X_{w,ci} \qquad (4.7)$$

where

I_i – impact factor for each condition C_i;

$X_{w,ci}$ – normalised weighted values of condition C_i.

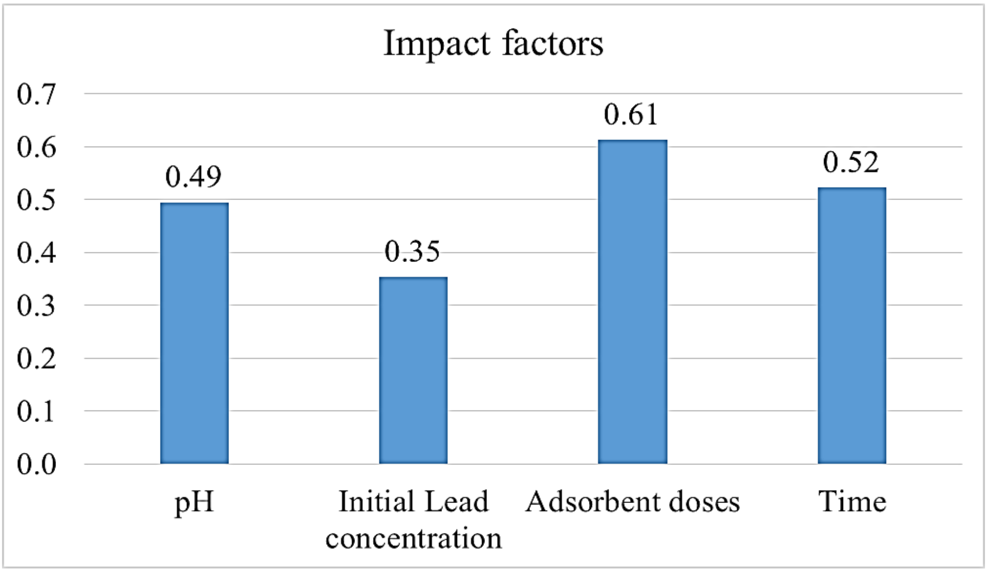

Fig. 4.11. Impact factors of adsorption properties affecting efficiency

Depending on the impact factors, adsorbent doses tend to have the greatest impact on adsorption efficiency (with indicator factor equal to 0.61) as shown in Fig. 4.11. Time and pH are the following at having the biggest impact to lead removal efficiency.

Conclusions of the forth chapter

1. It has been established that the ES has an acceptable adsorption uptake toward the Pb (II) ions. It has been observed that the adsorption capacity to adsorb lead ions is significantly affected by the concentration and pH of the solution. The optimal initial pH of the solution for adsorption of lead ions is between 3.5 and 4.5 pH. After accepting this range, the optimal starting pH of 4 for the solution was chosen for further experiments.
2. The maximum adsorption uptake (about 0.5 mg/g) of Pb (II) is achieved at 5 mg/L of lead solution, but from obtained results it is clear that adsorption uptake is only increasing, which means, that egg shell adsorbent could be used in higher concentration lead solutions
3. Egg shell contact time of 90 minutes showed that the eggs shell could remove about 98 % of Pb (II) ions from the aqueous solution, when initial lead concentration was 1 mg/L.
4. In adsorption isotherm studies it was concluded from correlation coefficients that the applicability of models distributed as follows: Langmuir (0.989)> Freundlich (0.985)> Henry (0.842). These findings indicate that the sorption of Pb (II) can be considered by a monolayer formation of the lead ion on the surface of the adsorbents. Also, adsorption of Pb (II) onto the surface of egg shell is likely due to the ion exchange/complexation reaction.
5. Multi–criteria decision–analysis was used to solve the problem of the decision on which adsorption parameter impacts the removal efficiency most. The results of the analysis showed that the adsorbent dose has the greatest impact on adsorption efficiency.

CONCLUSIONS

1. The main sources of heavy metals in the environment of anthropogenic origin are industrial wastewater, agri–culture, energy and electronics production and waste sector. HM are hazardous to the environment, therefore many different techniques for removing heavy metals from wastewaters are used (chemical precipitation, membrane filtration, sorption, etc.).
2. Egg shell waste was considered as possible adsorbent material for this research due to its availability – according to the data of the Department of Statistics of Lithuania, egg shell wastes amounted to about 5895 tons in 2018 alone.
3. Total costs, removal efficiency, operating flux, operating cost, required power and water recovery efficiency were chosen as the main criteria for this multicriteria analysis. The AHP revealed, that total costs and removal efficiency are the key criteria in this TOPSIS analysis. MCDA has shown that the adsorption method is the most favorable method for the treatment of water contaminated with lead ions compared to reverse osmosis, nanofiltration, ion–exchange and electrodyalisis methods.
4. Eggshell was found to adequately absorb lead (II) ions. Experimental studies have shown that the concentration and pH of the solution have a significant effect on the efficiency of the adsorption capacity. The most favorable pH value for the adsorption of the target metal ions was found to be between pH 3.5 and 4.5, so the optimal initial pH of 4 for the solution was chosen for further experiments.
5. Egg shell adsorption contact time of 90 minutes and the smallest dosage of adsorbent material (0.5 g) showed that the eggs shell could remove about 98 % of Pb (II) ions from the aqueous solution, when initial lead concentration was 1 mg/L.
6. The analysis of adsorption isotherms showed the following correspondence of adsorption isotherm models: Langmuir (0.989)> Freundlich (0.985)> Henry (0.842). These findings indicate that the sorption of Pb (II) can be considered by a monolayer formation of the lead ion on the surface of the adsorbents and that the adsorption of Pb (II) onto the surface of egg shell is likely due to the ion exchange reaction.
7. Multi–criteria decision–analysis used for the the problem of the decision on which adsorption parameter impacts the removal efficiency most. The results of the analysis showed that the adsorbent dose has the greatest impact on adsorption efficiency.

RECOMMENDATIONS

1. Further experiments on evaluation of the influence of contact time on Pb (II) ion adsorption and initial Pb (II) ion concentrations should be conducted to conclude at which point adsorption equilibrium is reached.
2. Experiments on effects of modified eggshell Pb (II) ion adsorption from polluted water should be conducted to confirm if modification of adsorbent could increase efficiency of heavy metal ion removal efficiency.
3. Regeneration of eggshell adsorbent should be studied, to increase cost–effectiveness of eggshell adsorbent and to prevent the process from secondary pollution.
4. To determine the functional groups of the adsorbent, to confirm on chemical level, what functional groups could affect the Pb (II) ion adsorption process.
5. To adapt obtained results for possible lead ion removal technologies in real life situations, such as additional water treatment section in industries with small lead ion concentration effluents.

REFERENCES

Ahmad, M., Usman, A.R.A., Lee, S.S., Kim, S.C., Joo, J.H., Yang, J.E., Ok, Y.S. 2012. Eggshell and coral wastes as low cost sorbents for the removal of Pb $^{2+}$, Cd $^{2+}$ and Cu $^{2+}$ from aqueous solutions. *J. Ind. Eng. Chem.* (18), pp. 198–204.

Ahmad, R., Kumar, R., Haseeb, S. 2012. Adsorption of Cu $^{2+}$ from aqueous solution onto iron oxide coated eggshell powder: Evaluation of equilibrium, isotherms, kinetics, and regeneration capacity. *Arab. J. Chem.* (5), pp. 353–359.

Akpor, O.B., Muchie, M. 2010. Remediation of heavy metals in drinking water and wastewater treatment systems: Processes and applications. *Int. J. Phys. Sci.* (5), pp. 1807–1817.

Akpor, O.B., Ohiobor, G.O., Olaolu, T.D. 2014. Heavy Metal Pollutants in Wastewater Effluents: Sources, Effects and Remediation. *Adv. Biosci. Bioeng.* (2), pp. 37–43.

Anwar, J., Shafique, U., Waheed-uz-Zaman, Salman, M., Dar, A., Anwar, S. 2010. Removal of Pb (II) and Cd (II) from water by adsorption on peels of banana. *Bioresour. Technol.* (101), pp. 1752–1755.

Aquarden Technologies 2019. *Coagulation & flocculation.* [Online]. Available at: https://aquarden.com/technologies/coagulation-flocculation/ [Accessed 17 June 2019].

Arunlertaree, C., Kaewsomboon, W., Kumsopa, A., Pokethitiyook, P., Panyawathanakit, P. 2007. Removal of lead from battery manufacturing wastewater by egg shell. *J. Sci. Technol.* (29), pp. 857–868.

Ayawei, N., Ebelegi, A.N., Wankasi, D. 2017. Modelling and Interpretation of Adsorption Isotherms. *J. Chem.* (2017), pp. 1–11.

Ayawei, N., Ekubo, A.T., Wankasi, D., Dikio, E.D. 2015. Adsorption of Congo Red by Ni/Al-CO_3: Equilibrium, Thermodynamic and Kinetic Studies. Orient. *J. Chem.* (31), pp. 1307–1318.

Aziz, H.A., Adlan, M.N., Ariffin, K.S. 2008. Heavy metals (Cd, Pb, Zn, Ni, Cu and Cr(III)) removal from water in Malaysia: Post treatment by high quality limestone. *Bioresour. Technol.* (99), pp. 1578–1583.

Babel, S., Kurniawan, T.A. 2003. Low-cost adsorbents for heavy metals uptake from contaminated water: A review. *J. Hazard. Mater.* (97), pp. 219–243.

Badrealam, S., Roslan, F.S., Dollah, Z., Bakar, A.A.A., Handan, R. 2018. *Exploring the eggshell from household waste as alternative adsorbent for heavy metal removal from wastewater*. In: AIP Conference Proceedings. American Institute of Physics Inc., pp. 020077–1–020077–6.

Balioti, V., Tzimopoulos, C., Evangelides, C. 2018. Multi-Criteria Decision Making Using TOPSIS Method Under Fuzzy Environment. Application in Spillway Selection. In: Insights on the Water-Energy-Food Nexus. Greece: MDPI AG, p. 637.

Banerjee, A., Panda, S., Sidhantha, M., Chakrabarti, S., Chaudhuri, B., Bhattacharjee, S. 2010. Utilisation of eggshell membrane as an adsorbent for carbon dioxide. *Int. J. Glob. Warm.* (2), pp. 252–261.

Bayuo, J., Pelig-ba, K.B., Abukari, M.A. 2018. Isotherm Modeling Of Lead (II) Adsorption From Aqueous Solution Using Groundnut Shell As A Low-Cost Adsorbent. *IOSR J. Appl. Chem.* (11), pp. 18–23.

Bhaumik, R., Mondal, N.K., Das, B., Roy, P., Pal, K.C., Das, C., Baneerjee, A., Datta, J. 2012. Eggshell Powder as an Adsorbent for Removal of Fluoride from Aqueous Solution: Equilibrium, Kinetic and Thermodynamic Studies. *E-Journal Chem.* (9), pp. 1457–1480.

Bilal, M., Shah, J.A., Ashfaq, T., Gardazi, S.M.H., Tahir, A.A., Pervez, A., Haroon, H., Mahmood, Q. 2013. Waste biomass adsorbents for copper removal from industrial wastewater-A review. *J. Hazard. Mater.* (263), pp. 322–333.

Bolisetty, S., Peydayesh, M., Mezzenga, R. 2019. Sustainable technologies for water purification from heavy metals: review and analysis. *Chem. Soc. Rev.* (48), pp. 463–487.

Bonilla-Petriciolet, A., Mendoza-Castillo, D.I., Reynel-Ávila, H.E. (Eds.) 2017. *Adsorption processes for water treatment and purification*, 1st ed, Mexico: Springer International Publishing.

Boparai, H.K., Joseph, M., O’Carroll, D.M. 2011. Kinetics and thermodynamics of cadmium ion removal by adsorption onto nano zerovalent iron particles. *J. Hazard. Mater.* (186), pp. 458–465.

Borges, D.L.G., Holcombe, J.A. 2017. Graphite Furnace Atomic Absorption Spectrometry. In: Encyclopedia of Analytical Chemistry. Chichester, UK: John Wiley & Sons, Ltd, pp. 1–20.

Borhade, A. V., Kale, A.S. 2017. Calcined eggshell as a cost effective material for removal of dyes from aqueous solution. *Appl. Water Sci.* (7), pp. 4255–4268.

Buck Scientific 2019. *Graphite Furnace Atomic Absorption spectrometer (GFAAS) Package.* [Online]. Available at: https://www.bucksci.com/products/220gf-atomic-absorption-graphite-furnace-package [Accessed 10 May 2019].

Carvalho, J., Araujo, J., Castro, F. 2011. Alternative low-cost adsorbent for water and wastewater decontamination derived from eggshell waste: An overview. *Waste and Biomass Valorization* (2), pp. 157–167.

Choi, H.J., Lee, S.M. 2015. Heavy metal removal from acid mine drainage by calcined eggshell and microalgae hybrid system. *Environ. Sci. Pollut. Res.* (22), pp. 13404–13411.

Crini, G., Lichtfouse, E., Wilson, L.D., Morin-Crini, N. 2018. *Adsorption-Oriented Processes Using Conventional and Non-conventional Adsorbents for Wastewater Treat*ment. Springer: Cham, pp. 23–71.

Debabrata, P. 2013. *Removal of lead from polluted water using waste eggshell*. MSc Dissertation, Deemed University.

Ecetoc 2020. *Freundlich isotherms*. [Online]. Available at: http://www.ecetoc.org/report/measured-partitioning-property-data/adsorption-desorption-distribution-kd-and-organic-carbon-water-partition-koc-coefficients/freundlich-isotherms/ [Accessed 30 April 2020].

Feng, N., Guo, X., Liang, S., Zhu, Y., Liu, J. 2011. Biosorption of heavy metals from aqueous solutions by chemically modified orange peel. *J. Hazard. Mater.* (185), pp. 49–54.

Foktas, P. 2014. *Determination of heavy metals concentrations in different ways prepared herbal raw material of St. John's Wort (Hypericum perforatum L.)*. MSc Thesis, Lithuanian University of Health Sciences.

Foo, K.Y., Hameed, B.H. 2010. Insights into the modeling of adsorption isotherm systems. *Chem. Eng. J.* (156), pp. 2–10.

Fu, F., Wang, Q. 2011. Removal of heavy metal ions from wastewaters: a review. *J. Environ. Manage.* (92), pp. 407–18.

Gunatilake, S.K. 2015. Methods of Removing Heavy Metals from Industrial Wastewater. *J. Multidiscip. Eng. Sci. Stud. Ind. Wastewater* (1), pp. 13–18.

Hamidpour, M., Hosseini, N., Mozafari, V., Heshmati Rafsanjani, M. 2018. Removal of Cd (II) and Pb (II) from aqueous solutions by pistachio hull waste. *Rev. Int. Contam. Ambient*. (34), pp. 307–316.

He, Yayuan, Wu, P., Xiao, W., Li, G., Yi, J., He, Yafei, Chen, C., Ding, P., Duan, Y. 2019. Efficient removal of Pb(II) from aqueous solution by a novel ion imprinted magnetic biosorbent: Adsorption kinetics and mechanisms. *PLoS One* (14), pp. 1–17.

Hincke, M.T., Nys, Y., Gautron, J., Mann, K., Rodriguez-Navarro, A.B., McKee, M.D. 2012. The eggshell: structure, composition and mineralization. *Front. Biosci*. (17), pp. 1266–80.

Hu, X., Zhao, M., Song, G., Huang, H. 2011. Modification of pineapple peel fibre with succinic anhydride for Cu^{2+}, Cd^{2+} and Pb^{2+} removal from aqueous solutions. *Environ. Technol.* (32), pp. 739–746.

Hubicki, Z., Koodynsk, D. 2012. *Selective Removal of Heavy Metal Ions from Waters and Waste Waters Using Ion Exchange Methods*. In: Kilislioğlu, A. (Ed.), Ion Exchange Technologies.

Hwang, C.L., Yoon, K. 1981. *Multiple Attribute Decision Making.* A state-of-the-art study. New York: Springer Berlin Heidelberg.

Ikram, M., Rehman, A.U., Ali, Sharafat, Ali, Sher, Hasnain Bakhtiar, S.U., Alam, S. 2016. The adsorptive potential of chicken egg shells for the removal of oxalic acid from wastewater. *J. Biomed. Eng. Informatics* (2), pp. 118–131.

Jeyakumar, R.P.S., Chandrasekaran, V. 2014. Adsorption of lead (II) ions by activated carbons prepared from marine green algae: equilibrium and kinetics studies. *Int. J. Ind. Chem.* (5), pp. 1–9.

Kalyani, G., Rao, H.J., Kumar, T.A., Mariadas, K., Vijetha, P., Kumar, Y.P., Kumaraswamy, K., Pallavi, P., Sumalatha, B. 2010. Biosorption of Lead from Aqueous Solutions using Egg Shell Powder as Biosorbent : Equilibrium. *Int. J. Biotechnol. Biochem.* (6), pp. 911–920.

Khan, M.A., Alemayehu, A., Duraisamy, R., Berekete, A.K. 2015. ISSN 2348 - 2710 Original Article Removal of Lead ion from aqueous solution by Bamboo activated Carbon. *Int. J. Water Res.* (5), pp. 33–46.

Khulbe, K.C., Matsuura, T. 2018. Removal of heavy metals and pollutants by membrane adsorption techniques. *Appl. Water Sci.* (8), pp. 1–30.

Koumanova, B., Peeva, P., Allen, S.J., Gallagher, K.A., Healy, M.G. 2002. Biosorption from aqueous solutions by eggshell membranes and Rhizopus oryzae: Equilibrium and kinetic studies. *J. Chem. Technol. Biotechnol.* (77), pp. 539–545.

Ladshaw, A., Yiacoumi, S., Tsouris, C., DePaoli, D. 2015. Generalized gas-solid adsorption modeling: Single-component equilibria. *Fluid Phase Equilib.* (388), pp. 169–181.

Łatuszyńska, A. 2014. Multiple-Criteria Decision Analysis Using Topsis Method For Interval Data In Research Into The Level Of Information Society Development. *Folia Oeconomica Stetin.* (13), pp. 63–76.

López-Mesas, M., Navarrete, E.R., Carrillo, F., Palet, C. 2011. Bioseparation of Pb(II) and Cd(II) from aqueous solution using cork waste biomass. Modeling and optimization of the parameters of the biosorption step. *Chem. Eng. J.* (174), pp. 9–17.

Mahmood-ul-Hassan, M., Suthor, V., Rafique, E., Yasin, M. 2015. Removal of Cd, Cr, and Pb from aqueous solution by unmodified and modified agricultural wastes. *Environ. Monit. Assess.* (187), pp. 1–8.

Martín-Lara, M.A., Blázquez, G., Calero, M., Almendros, A.I., Ronda, A. 2016. Binary biosorption of copper and lead onto pine cone shell in batch reactors and in fixed bed columns. *Int. J. Miner. Process.* (148), pp. 72–82.

Martín, M.I., López, F.A., Pérez, C., López-Delgado, A., Alguacil, F.J. 2005. Adsorption of heavy metals from aqueous solutions with by-products of the steelmaking industry. *J. Chem. Technol. Biotechnol.* (80), pp. 1223–1229.

Mashangwa, T.D. 2016. *An Investigation Into the Efficacy of Eggshells As a Low Cost Adsorbent for the Removal of Potentially Toxic Inorganic Elements From Aqueous Solutions*. MSc Dissertation, University of South Africa.

Mashangwa, T.D., Tekere, M., Sibanda, T. 2017. Determination of the Efficacy of Eggshell as a Low-Cost Adsorbent for the Treatment of Metal Laden Effluents. *Int. J. Environ. Res.* (11), pp. 175–188.

Maurya, N.S., Mittal, A.K. 2006. Applicability of equilibrium isotherm models for the biosorptive uptakes in comparison to activated carbon-based adsorption. *J. Environ. Eng.* (132), pp. 1589–1599.

Meade, R.H. (Ed.) 1995. *Contaminants in the Mississippi River, 1987-92*, U.S. Geological Survey Circular: 1133.

Minister of Environment of the Republic of Lithuania 2006. *Wastewater Management Regulation*. State news, Lithuania.

Mittal, A., Teotia, M., Soni, R.K., Mittal, J. 2016. Applications of egg shell and egg shell membrane as adsorbents: A review. *J. Mol. Liq.* (223), pp. 376–387.

Nagy, E. 2019. *Mass Transport Through a Membrane Layer*. In: Basic Equations of Mass Transport through a Membrane Layer. Veszprém: Elsevier, pp. 21–68.

Nemati, M., Hosseini, S.M., Shabanian, M. 2017. Novel electrodialysis cation exchange membrane prepared by 2-acrylamido-2-methylpropane sulfonic acid; heavy metal ions removal. *J. Hazard. Mater.* (337), pp. 90–104.

Nguyen, K.M., Nguyen, B.Q., Nguyen, H.T., Nguyen, H.T.H. 2019. Adsorption of arsenic and heavy metals from solutions by unmodified iron-ore sludge. *Appl. Sci.* (9), pp. 619.

OSP 2020. *Indicators database - Oficialiosios statistikos portalas*. [Online]. Available at: https://osp.stat.gov.lt/statistiniu-rodikliu-analize#/ [Accessed 30 April 2020].

Park, H.J., Jeong, S.W., Yang, J.K., Kim, B.G., Lee, S.M. 2007. Removal of heavy metals using waste eggshell. *J. Environ. Sci.* (19), pp. 1436–1441.

Patil, N., Puttaiah, E.T. 2013. Evaluation of Heavy Metal Accumulation in Soil around Bhadravathi Taluk Shimoga District Karnataka. *International Journal of Life Sciences* (2), pp. 124–129.

Reliance Home Comfort 2019. *What is Reverse Osmosis (RO) and How You can Benefit From It*. [Online]. Available at: https://reliancehomecomfort.com/ro-benefits/ [Accessed 17 June 2019].

Roy, A. 2014. *Nanotechnology in Industrial Wastewater Treatment, Water Intelligence Online*. London: IWA Publishing.

Sauliutė, G. 2013. *Experimental investigation of heavy metals accumulation tissues of salmon Salmo salar L.* MSc Thesis, Vilnius Gediminas Technical University.

Tabatabaee, Azam, Dastgoshadeh, F., Tabatabaee, Akram 2014. Biosorption of heavy metals by low cost adsorbents. *Int. J. Environtmental Ecol. Eng*. (8), pp. 699–704.

Tchounwou, P.B., Yedjou, C.G., Patlolla, A.K., Sutton, D.J. 2012. *Heavy metal toxicity and the environment*. In: Experientia Supplementum. Basel: Springer, pp. 133–164.

Tzeng, G.-H., Huang, J.-J. 2011. *Multiple Attribute Decision Making Methods and Applications*, 1st Edition. ed, Multiple Attribute Decision Making. New York: Chapman and Hall/CRC.

Vilniaus Aplinkos Informacinė Svetainė 2019. *Sunkiųjų metalų poveikis sveikatai [eng. Health effects of heavy metals]*. [Online]. Available at: https://aplinka.vilnius.lt/wp-content/uploads/2013/03/ SM_poveikis_sveikatai.pdf [Accessed 01 May 2020].

Volesky, B. 2003. *Biosorption process simulation tools*. In: Hydrometallurgy. pp. 179–190.

Wang, J., Chen, C. 2009. Biosorbents for heavy metals removal and their future. *Biotechnol. Adv. (*27), pp. 195–226.

Wuana, R.A., Okieimen, F.E. 2011. Heavy Metals in Contaminated Soils: A Review of Sources, Chemistry, Risks and Best Available Strategies for Remediation. *ISRN Ecol.* (2011), pp. 1–20.

Yuan, X.Z., Meng, Y.T., Zeng, G.M., Fang, Y.Y., Shi, J.G. 2008. Evaluation of tea-derived biosurfactant on removing heavy metal ions from dilute wastewater by ion flotation. *Colloids Surfaces A Physicochem. Eng. Asp*. (317), pp. 256–261.

Žadeikytė, M. 2013. *Heavy metal removal from contaminated aqueous solutions using synthetic zeolite*. MSc Thesis, Aleksandro Stulginskio Universitetas.

Zhan, W., Xu, C., Qian, G., Huang, G., Tang, X., Lin, B. 2018. Adsorption of Cu(II), Zn(II), and Pb(II) from aqueous single and binary metal solutions by regenerated cellulose and sodium alginate chemically modified with polyethyleneimine. *RSC Adv.* (8), pp. 18723–18733.

Zhao, M., Xu, Y., Zhang, C., Rong, H., Zeng, G. 2016. New trends in removing heavy metals from wastewater. *Appl. Microbiol. Biotechnol*. (100), pp. 6509–6518.

Гомельский завод измерительных приборов 2020. *Шкаф сушильный СНОЛ | Гомельский завод измерительных приборов.* [Online]. Available at: http://www.zipgomel.by/ru/snol [Accessed 22 May 2020].

LIST OF AUTHOR'S PUBLICATIONS

Dervinytė, R., Blumberga, D., Paliulis, D. 2020. Application of egg shells to the removal of lead from contaminated water. *Environmental and Climate Technologies*. --- In review

LIST OF AUTHOR'S PRESENTATIONS

Poster presentation at 22th Conference of Lithuanian junior researchers, Science – Future of Lithuania in Vilnius Gediminas Technical University, 20-03-2020 on topic "Literature review on application of egg shells to the removal of heavy metals from contaminated water".

Poster presentation at 23th Conference of Lithuanian junior researchers, Science – Future of Lithuania in Vilnius Gediminas Technical University, 08-05-2020 on topic "Application of egg shells to the removal of heavy metals from contaminated water".

Poster presentation at CONECT conference in Riga Technical University, 2020-05-14 on topic "Application of egg shells to the removal of lead from contaminated water".

APPENDICES