Removal of Lead and Nickel from Polluted water using L-Cysteine and L-Methionine Modified Silica gel

Etembet Desta Tona

A Thesis Submitted to the Department of Applied Chemistry

School of Applied Natural Science

Presented in Partial Fulfillment of the Requirements for the Degree of

Master of Science in Chemistry (Industrial Chemistry)

Office of Graduate Studies

Adama Science and Technology University

December, 2021

Adama, Ethiopia

Removal of Lead and Nickel from Polluted water using L-Cysteine and L-Methionine Modified Silica gel

Etembet Desta Tona

Major -Advisor: Dereje Tsegaye (PhD)

Co-Advisor: Fedlu Kedir (PhD)

A Thesis Submitted to the Department of Applied Chemistry

School of Applied Natural Science

Presented in Partial Fulfillment of the Requirements for the Degree of

Master of Science in Chemistry (Industrial Chemistry)

Office of Graduate Studies

Adama Science and Technology University

December, 2021

Adama, Ethiopia

APPROVAL SHEET

We, the advisors of the thesis entitled "**Removal of Lead and Nickel from Polluted water using L-Cysteine and L-Methionine Modified Silica gel**" and developed by **Etembet Desta Tona**; hereby certify that the recommendation and suggestions made by the board of examiners are appropriately incorporated into the final version of the thesis.

_____	_____	_____
Major Supervisor	Signature	Date
_____	_____	_____
Co-supervisor	Signature	Date

We, the undersigned, members of the Board of Examiners of the thesis by **Etembet Desta Tona** have read and evaluated the thesis entitled "**Removal of Lead and Nickel from Polluted water using L-Cysteine and L-Methionine Modified Silica gel**" and examined the candidate during the open defense. This is, therefore, to certify that the thesis is accepted for partial fulfillment of the requirement of the degree of Master of Science in Applied Chemistry (Specialization in Industrial Chemistry).

_____	_____	_____
Chairperson	Signature	Date
_____	_____	_____
Internal Examiner	Signature	Date
_____	_____	_____
External Examiner	Signature	Date

Finally, approval and acceptance of the thesis are contingent upon submission of its final copy to the Office of Postgraduate Studies (OPGS) through the candidate's Department Graduate Council (DGC) and School Graduate Committee (SGC).

_____	_____	_____
Department Head	Signature	Date
_____	_____	_____
School Dean	Signature	Date
_____	_____	_____
Office of Postgraduate Studies, Dean	Signature	Date

DECLARATION

I hereby declare that this Master Thesis entitled "**Removal of Lead and Nickel from Polluted water using L-Cysteine and L-Methionine Modified Silica gel** " is my original work. That is, it has not been submitted for the award of any academic degree, diploma or certificate in any other university. All sources of materials that are used for this thesis have been duly acknowledged through citation.

_____	_____	_____
Name of the studen	Signature	Date

RECOMMENDATION

We, the advisors of this thesis, hereby certify that we have read the revised version of the thesis entitled **"Removal of Lead (Pb) and Nickel (Ni) from polluted water by Modification of Silica gel with L-Cysteine and L-Methionine"** prepared under our guidance by **Etembet Desta Tona** submitted in partial fulfillment of the requirements for the degree of Master of Science in Chemistry (Industrial Chemistry). Therefore, we recommend the submission of revised version of the thesis to the department following the applicable procedures.

Dereje Tsegaye (PhD)

_____	_____	_____
Major Advisor	Signature	Date

Fedlu Kedir (PhD)

_____	_____	_____
Co-advisor	Signature	Date

DEDICATION

This M.Sc thesis is dedicated to my beloved families, especially to my Mother Zenebech Abera, and to all my sisters and brothers, whose advice, support, prayers, and cherish helped me all along the right way made me who I am today. They will always be in my heart until the end of time.

ACKNOWLEDGEMENTS

To begin with and preeminent, I would like to thank St. Mary's Son all-powerful God, the embodiment of intelligence Who gives wellbeing, strength, and accurate understanding into reality to his divine intervention during my research work.

Although this thesis work eventually represents my achievements, I have profited significantly from many people that I would like to recognize. First and foremost, I am thankful to my hard-working advisors: Dr. Dereje Tsegaye and Dr. Fedlu Kedir, for their excellent supervision and scientific input in this research work. I am lucky to be guided by them, and it is an incredible benefit and honor for me to be advised by them. Their brotherly and humble approach makes me successful. I would like to thanks Prof. Neeraj K. for his scientific input in this research. In addition, I would like to thanks Dr. Aschalew Tadesse (the department head of Applied Chemistry) for his necessary support and adevice during this thesis work.

Then I would like to express my genuine appreciation to Eastern Industry Zone Factories for giving me all the necessary help to conduct my research work. I never forgot their incredible contribution.

I greatly acknowledge Ato Tilahun and Ermias from Hawassa University (HU) for FAAS characterization and Alebel Abebaw from Bahir Dar University (BDU) for FT-IR and BET, and Demeke Tesfaye from Adama Science and Technology University (ASTU), Department of Materials Engineering, for his assistance in XRD characterization and Eticha Abdisa from ASTU, Department of Applied Biology for SEM characterization. And also Dr. Lema Teshome, Aklilu Guale and Dehennet Getachew for their necessary help to conduct this thesis, finally, I would like to thank greatly Dire Dawa University (DDU) for giving me the opportunity to join this postgraduate program.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS AND ACRONYMS

AC……..…Activated Carbons

ASG…….…..Activated silica gel

BET……..….Brunauer-Emmett-Teller

CAA……..Commercial Activated Aluminas

CAC……..…….Commercial Activated Carbons

COD……...…..……..…….. Chemical Oxygen Demand

COPs…….....Covalent organic polymers

DW…….….....Distilled water

EIZ……...….....Eastern Industrial Zone

EPS…….....Extracellular Polymeric Substances

FAAS……...…..Flame Atomic Absorption Spectroscopy

FT-IR……..Fourier Transform Infrared Spectroscopy

IUPAC…….....……..……..International Union of Pure and Applied Chemistry

L-Cys…….....…L-Cysteine

L-Meth……..…L-Methionine

MBRs …….Membrane Bioreactors

NMPs…….....Nano-Magnetic Polymers

rpm…….…….. Revolution per minute

SEM……...Scanning Electron Microscope

SG……..Silica gel

SiO_2-(L-Cys + L-Meth)……..…SiO_2-(L-Cysteine + L-Methionine)

SiO_2-Cys……..…..SiO_2-(L-Cysteine)

SiO_2-Meth……..SiO_2-(L-Methionine)

SPE……..…..Solid-Phase Extraction

TDS……Total Dissolved Solid

TEOS ……Tetraethyl OrthoSilicate

TMOS……Tetra-Methoxy Silane

TSS…….Total Suspended solid

US EPA……..United States Environmental Protection Agency

VOCs…….Volatile Organic Compounds

WHO…….....World Health Organization

XRD……...X-Ray Diffraction

ABSTRACT

Heavy metals are inorganic pollutants of water that cause a health risk if taken at above-recommended levels. The objective of this study was to use activated silica gel (SiO_2), modified activated silica gel with L-cysteine (SiO_2-Cys), L-methionine (SiO_2-Meth), and a mixture of L-cysteine and L-methionine (SiO_2-(L-Cys + L-Meth)) for adsorptions of lead and nickel ions from aqueous solution. Activated silica gel and its modified forms were prepared and characterized by Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), Scanning electron microscopy (SEM), and Brunauer-emmett-teller method (BET). It was observed that increasing in surface area form BET result of SiO_2-(L-Cys + L-Meth) (772.816 m²/g) and SiO_2-meth (730.710 m²/g) than SiO_2(629.425 m²/g) and it was also supported by SEM result. Pb (II) and Ni (II) removal efficiency of SiO_2, SiO_2-Cys, SiO_2-Meth, and SiO_2-(L-Cys + L-Meth), were investigated using a batch adsorption technique. Experimental parameters such as pH of the solution, contact time, initial Pb and Ni ions concentration in solutions, and adsorbent dosage were also studied carefully. Those maximum removal efficiencies showed that 97.15 % observed at pH 6, 90 min contact time, 0.8 g/L of adsorbent dose, and 2 mg/L initial concentration for lead ion removal while 100% removal of 0.645 mg/L Pb^{+2} from wastewater taken from Eastern industry zone (EIZ). The highest removal efficiency of Ni (II), 99.35 % was observed at pH 5, 60 min contact time, 0.4 g/L of adsorbent dose, and 2 mg/L initial concentration using SiO_2-(L-Cys + L-Meth) adsorbent. Through this optimum condition, kinetic and isotherm of the adsorption process were studied using different models. The result revealed that the kinetics of the process fitted well with the Pseudo-second-order kinetic model for lead and nickel ions. From the tested isotherm model, the Langmuir isotherm model was found to be the best fit for Pb (II), and the Freundlich model was found to be the best fit for Ni (II). From the results notably, the adsorbent SiO_2-(L-Cys + L-Meth) can be regenerated continuously without affecting its extraction percentage. The removal efficiency of SiO_2-(L-Cys + L-Meth) decreased as the cycles increased was observed. Removals of Pb (II) and Ni (II) ions are improved using modified ASG with a mixture of L-cysteine and L-methionine (SiO_2-(L-Cys + L-Meth)).

Keywords: Activated Silica gel, Modification, Methionine, Cysteine, Lead (II), Nickel (II), Adsorption

CHAPTER ONE

1. INTRODUCTION

1.1. Background of the study

Safe water is significant for all that have life because, without water, no life exists (Issakhov et al., 2021). However, Water pollution is currently a threat to humans (Mokarram et al., 2020). The growing number of different industries and the wastewater released from these various industries have several pollutants that become the main reason for pollution. The wastewater pollutants are categorized under organic, inorganic, biological, and microscopic contaminants (Briffa et al., 2020; Masindi & Muedi, 2018). Among these water contaminants, heavy metals are mentioned under inorganic contaminants (P. Sharma et al., 2021). Most industries have been discharging wastes irresponsibly to the natural environment without any treatments, or partial treatment that has become a big concern for the community in developing countries like Ethiopia (Amare, 2019).

Even though there is confusion about the definition of heavy metals in most literature, heavy metals are defined as metals and some metalloids with high atomic weight and density compared to the density of water. In addition, the term heavy metals have been used for toxic and carcinogenic metals and metalloids. But not all heavy metals are poisonous and carcinogenic, and there are also essential heavy metals for a biological system such as cobalt (Co), copper (Cu), chromium (Cr), iron (Fe), magnesium (Mg), manganese (Mn), molybdenum (Mo), nickel (Ni), selenium (Se), and zinc (Zn). However toxic heavy metals such as cadmium, mercury, lead, and arsenic are very poisonous and carcinogenic chemicals even in small amounts, they are hazardous for humans and animals (Briffa et al., 2020; Duffus, 2002; Ibrahim et al., 2020; Koller & Saleh, 2018; Tchounwou et al., 2012). Therefore, toxic heavy metals need more attention than other pollutants, due to their three characteristic features are environmental persistence, bioaccumulation nature, and toxicity nature. So, heavy metals tend to accumulate in the environment for a long time and affect humans (Ali, H., Khan, E., & Ilahi, 2019; Sheet et al., 2014). Heavy metals enter the natural water system in dry and wet forms. The two main sources are the anthropogenic sources (mining and smelting, industry combustion fossil fuel, phosphate

fertilizer, and Metallo-pesticide, etc). and natural sources (volcanic eruption and weathering of metal contaminated rockers). Thus heavy metals after discharge from either of the two sources accumulate upon cumulative exposure, and cannot be easily decayed, and threatening human health by the entire food chain (Ali, H., Khan, E., & Ilahi, 2019; Briffa et al., 2020; Rasheed et al., 2020). Therefore, it is significant to remove these toxic heavy metals by treating industrial wastewater before released into the natural aquatic environment. Several conventional techniques are available for the treatment of heavy metals from wastewater. These are chemical precipitation, ion exchange, coagulation-flocculation, membrane, and adsorption. However, adsorption is a preferred technique for heavy metal treatment because of its low energy consumption, ease of operation, and high removal efficiency than other techniques due to, some limitations such as low removal efficiency, high working cost, and mud production. Due to these properties, the adsorption process has been gaining a great deal of attention from researchers in the treatment of industrial wastewater contaminated with heavy metal ions (Bolisetty et al., 2019; Chakraborty et al., 2020; Rasheed et al., 2020).

There are different physicochemical parameters, i.e., temperature, pH, etc., that affect the mechanism of the adsorption process. For adsorption purposes, there are many solid materials have been used. Among the many types of solid materials used in adsorption silica gel are the most common, due to its advantageous characteristics of low cost, commonly available, no swelling, high surface area, uniform pore structure, high pore volume, and extraordinarily wide possibilities for functionalization, thermal and mechanical stability (Dakova et al., 2011; Svraka I., Memić M., Sulejmanović J., 2014). Many solid-phase extractions are based on silica gel modified with different chelating agents, due to the high selectivity and binding affinity exhibited by N- and S- donor groups towards heavy metals (Alghanmi, 2012; Svraka I., Memić M., Sulejmanović J., 2014). Further, because the abundant hydroxyl groups on the silica gel surface tend to agglomerate so, a modification to produce a hydrophobic surface is necessary to improve the dispersion and compatibility of silica gel (SiO_2) (Ismail, Khalili, & Abu Orabi, 2020). The thiol and amine-functionalized adsorbents have been used for the removal of heavy metals from aqueous solution (Alghanmi, 2012; Petrova et al., 2018). Recently, several researchers targeted the sorption of amino acids by silica gel. The suggested mechanisms for adsorption are electrostatic interactions, hydrogen bond formation, ion exchange, and

ligand exchange through carboxyl and amino groups on the amino acides and the hydroxyl on the activated silica gel (Ismail, Khalili, & Abu Orabi, 2020; Petrova et al., 2017a). Recently, Dakova et al. (Dakova1 & , P. Vasileva 2, 2011) used cysteine functionalized silica gel as an effective adsorbent for preconcentration of Cd (II) and Pb (II), Petrova et al. (Petrova et al., 2017b) prepared and studied sorbent based on methionine and cystine modified silica gel for solid-phase extraction of Au (III). Mladenova et al. (Mladenova et al., 2012) used cysteine modified silica gel as a sorbent for preconcentration and separation of noble metals Au(III), Pd(II), Pt(II), and Pt(IV). They were reported as fast and quantitative retention of metal ions using amino acid modified silica gel. However, the limitation of these studies is: uses of various organic and inorganic solvents, the adsorption takes place in acidic media, and reported for very low concentration of metal ions. Further, Ismail et al. (Ismail, Khalili, & Orabi, 2020) studied on modification of silica nanoparticles with cysteine or methionine as effective removal of U(VI) from aqueous solution. This method of removal even though achieved quantitative removal for U(VI) but, the silica gel modification method took time for drying of the adsorbent at room temperature and also the removal % reported for a higher concentration of U(VI).

The purpose of this study is to prepare activated silica gel adsorbent and physically impregnate with amino acids, namely L-cysteine (SiO_2-Cys) and L-methionine (SiO_2-Meth); which were already published by another researcher for removal of metal ions. However, in this study, the method of modification of activated silica gel is changed using a simple and time-saving method of modification, and no need for any organic and inorganic solvents for silica gel modification except distilled water. Furthermore, the preparation of a mixture of L-methionine and L-cysteine as modifiers for activated silica gel and used as an efficient adsorbent for extraction of Pb and Ni ions from aqueous solution and Pb ion from real sample are studied. In the previous workes adsorption of metal ions on the silica gel modified with a mixture of L-methionine and L-cysteine have not been reported.

1.2. Statement of the problem

Currently, in Ethiopia, there is establishing and spread out of industries, increasing of population and urbanization as well as migration to urban area. Such trend has resulted in rising market demand for urban agriculture to occur as a mechanism to reduce the level of lack and deliver adequate and regular access to food like fruits and vegetable supplies

(Gashaye, 2020; Girmaye, 2014; Yeshiwas & Tadele, 2017), however the primary sources of irrigation water in the city are heavily polluted and untreated wastewater that contains different pollutants like heavy metals (Dickin et al., 2016; Gashaye, 2020). Studies (Bahiru et al., 2019; Bekele Bahiru & Yegrem, 2021) showed that vegetables and other food crops consumed in Ethiopia are polluted by heavy metals. These are associated with adverse health issues such as cancer, which is currently serious in Ethiopia. Lead has no biological function in the human body; a lower concentration of lead exposure is not considered safe. The neurological and behavioral effects of lead exposure are irreversible. Complete control and prevention over lead exposure are still far from being achieved. Similarly, exposure to a higher level of nickel (II) can cause several adverse health effects on animals, plants, and humans (Yadessa Chibssa, 2015). A study reported (Dagne, 2020) that the concentration of Pb(II) in wastewater sample taken from Eastern Industrial Zone (EIZ) located in Dukem, Ethiopia, was beyond the permissible limit set by WHO and USEPA for irrigation. And literature reported value of the concentration of nickel in wastewater sample taken from Modjo Tannery Share Company exceed the WHO and USEPA, standard (Mengistie*, 2013). Therefore, heavy metals need superior attention because they are very persistent in the environment (Debebe, D., Behulu, F., & Getaneh, 2020). It is an urgent need to develop cost-effective and efficient heavy metals removal technology. So this study is intended to use an environmentally friendly and simple preparation method of adsorbent called modified activated silica gel with amino acid performed by understanding the above interest and aim to achieve an effective and efficient method. The main advantage of the silica gel over other solid inorganic supports is low cost (great abundance on earth), relative activity, large adsorption capacity, thermal and mechanical stability, no swelling, easy preparation of its different types with different pore sizes, and total surface area under standard conditions. Chelating agents like amino acids (L-Cysteine & L- methionine) containing N-and S- groups are highly efficient for the metals and could be used for physical modification of silica gel (Dakova1 & , P. Vasileva 2, 2011; Ismail, Khalili, & Orabi, 2020; Petrova et al., 2017c, 2018).

1.3. Objectives of the study

1.3.1. General objective

The general objective of this study is to prepare activated silica gel modified with sulfur-containing amino acids L-cysteine and L-methionine for Lead(II) and Nickel(II) removal from a polluted water sample.

1.3.2. Specific objectives

- To prepare activated silica gel
- To prepare L-cysteine and/or L-methionine modified activated silica gel.
- To investigate the activated silica gel and its modified forms using; Fourier transforms infrared spectroscopy (FT-IR), X-ray diffraction (XRD), Scanning electron microscopy (SEM)**,** and Brunauer-emmett teller method (BET).
- To study effects of different variables, equilibrium adsorption isotherm, and kinetics for adsorption of Pb(II) and Ni(II) on SiO_2-(L-Cys + L-Meth).
- To investigate and compare the adsorption efficiency of unmodified and modified activated silica gel towards the removal of Pb(II) and Ni(II) ions from aqueous solution.
- To investigate the Pb(II) removal efficiency of SiO_2-(L-Cys +L-Meth) on real sample.

1.4. Significance of the study

This study is expected to provide a method to remove non-biodegradable contaminants that pose serious health and environmental hazard using a simple, cost-effective, and environmentally friendly adsorption method. It can be applicable and useful in different industries for heavy metals, especially for Pb (II) and Ni (II), removal from wastewater before discharge to the environment. For researchers, it is important to do further study by expanding this investigation. It has also been significant for fruits and vegetable consumers because of the market supply of heavy metal-free fruits and vegetables.

1.5. Scope of the study

This thesis is limited to the preparation of modified activated silica gel with L-cysteine, L-methionine, and a mixture of L-cysteine and L-methionine for removals of Pb(II) and Ni(II) metal ions from aqueous solution by adsorption technique. And the characterization techniques for this study were limited to XRD, FT-IR, SEM, BET, and FAAS techniques.

CHAPTER TWO

2. LITERATURE REVIEW

2.1. Waster pollution and wastewater

Industrialization, in any society, is the primary initiator of development and urbanization. But, it has been identified as a higher risk to the environment because it discharges different poisonous chemicals, gases, solid wastes as well as microbes of various kinds into our immediate environment: land, air, and water (Inyinbor Adejumoke A., Adebesin Babatunde O., Oluyori Abimbola P., Adelani-Akande Tabitha A., 2018). Water pollution happens when harmful substances often, chemicals or microbes contaminate a stream, river, lake, ocean, aquifer, or other body of water, degrading water quality and rendering it poisonous to people or the environment. Wastewater (untreated, partially treated, or diluted) is any polluted water and mixture of liquid wastes discharged by domestic households, farms, institutions, and commercial and industrial formations finally mixed with natural water bodies.Therefore, generally causes of water pollution are urbanization, deforestation, industrial effluents, fertilizers and agricultural**.** It contains pathogens, organic particles, inorganic particles, pesticides and other toxins ((FAO), 2 C.E.; Arega, 2020; Gashaye, 2020; Intizar Hussain, Liqa Raschid, Munir A. Hanjra, 2020; Ungureanu et al., 2020). The reuse of wastewater for irrigation has been a global issue. However, in developed countries much of wastewater is treated before use for irrigation, but most developing countries use partially treated or untreated wastewater for irrigation(Dickin et al., 2016; Intizar Hussain, Liqa Raschid, Munir A. Hanjra, 2020). The reuse of wastewater has advantages for farmers by increasing the yield of crops; minimize the shortage of water for irrigation, and lowering the necessity of fertilizer. However, the crops irrigated by untreated wastewater cause for numerous health effects on humans because wastewater contains pollutants that have a bioaccumulation nature like heavy metals (Dickin et al., 2016; Keraita et al., 2008; Kesari et al., 2021; Narain-Ford et al., 2020). Generally, the reuse of untreated wastewater has been a negative impact on humans and ecological systems, which need to be recognized and assessed.

2.2. Heavy metals contamination

Heavy metals are among the most examined environmental contaminants and are a quickly growing problem in natural water bodies. In the modern age, heavy metal contamination has occurred historically and worldwide with the industrial revolution (Briffa et al., 2020; Masindi & Muedi, 2018; Oljira, 2016; Ozaki et al., 2019). Heavy metals are hazardous substances due to their persistence, toxic and bioaccumulative nature (Figure 2.1). Nowadays, heavy metal contamination is a major environmental worry that threatens plant, animal and human health and the quality of the environment (Ali, H., Khan, E., & Ilahi, 2019; Briffa et al., 2020; Issakhov et al., 2021; Jaishankar et al., 2014; Srivastava et al., 2017). The most common heavy metal contaminants and associated with environmental, plant, animal, or human health problems are Cr, Mn, Ni, Cu, Zn, Cd, Pb Fe, Co, Hg, V, Ni, Mo, Ag, Sn, As, and Se (Ali, H., Khan, E., & Ilahi, 2019; Masindi & Muedi, 2018; Oljira, 2016). However, any heavy metal and metalloid are potentially toxic to biota depending upon the dose and duration of exposure (Ozaki et al., 2019; Rasheed et al., 2020; Tchounwou et al., 2012). The primary source of heavy metals is anthropogenic activities like metal mining, smelting, foundries, and other metal-based industries. The secondary source of heavy metals includes pesticides, insecticides, fertilizers, and more in agricultural sectors. Therefore, wastewater containing heavy metals released from the above sources by any means ends up in one of the natural environmental systems like water bodies (Ali, H., Khan, E., & Ilahi, 2019; Briffa et al., 2020; Mahboob et al., 2014; Masindi & Muedi, 2018; Oljira, 2016; Ozaki et al., 2019; Srivastava et al., 2017).

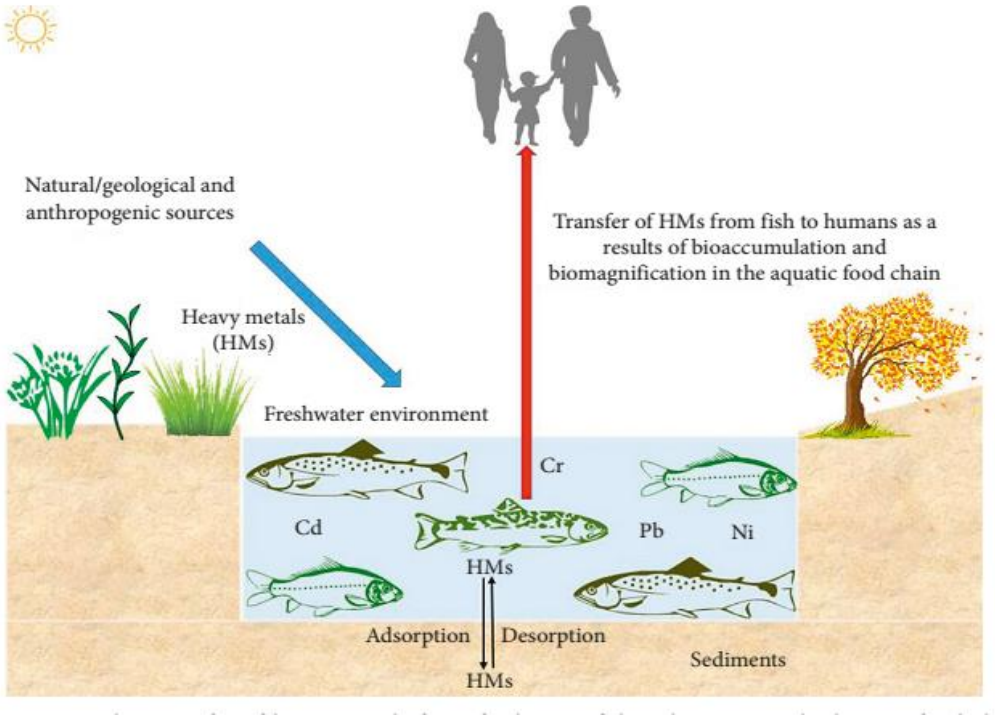


Figure 2.1. Trophic transfer of heavy metals from freshwater fish to humans (Ali, H., Khan, E., & Ilahi, 2019).

2.3. Health effects of heavy metals

Heavy metals comprise essential and non-essential. Both have an environmental impact when they exist in higher concentrations. However, non-essential heavy metals are toxic to plants, animals, and humans even at very low concentrations (Masindi & Muedi, 2018),(Ali, H., Khan, E., & Ilahi, 2019; Zelalem KA1 and Chandravanshi BS, 2015). Heavy metal toxicity has numerous health effects which can either be acute or chronic after long-term exposure and which can lead to many disorders in the functioning of organs such as the brain, kidney, lungs, liver, and blood (Figure 2.2). The long time exposure of toxic heavy metals leads to failure of muscular, physical, and neurological processes and some heavy metals may cause cancer (Al-Lami et al., 2020; Ametepey et al., 2018; Engwa et al., 2019; Jaishankar et al., 2014; Sankhla, 2019; Reena Singh et al., 2011).

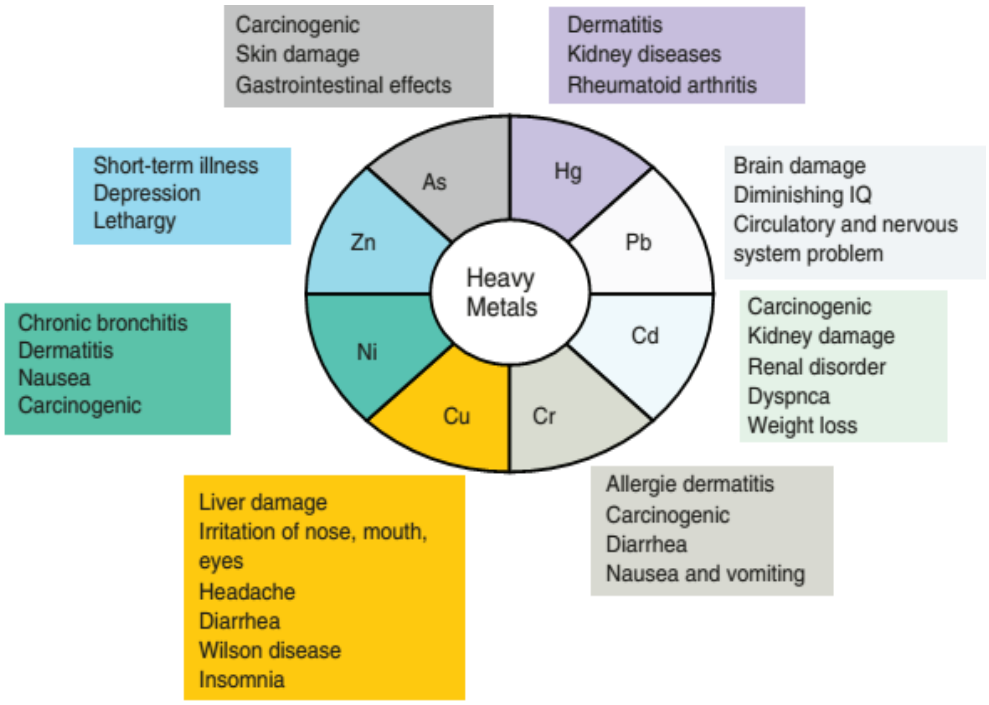


Figure 2.2. Human health hazards associated with exposure to toxic heavy metals (Maharana et al., 2021).

2.4. Lead (II) and Nickel (II) heavy metals

Lead is a bluish-white metal that exists naturally in earth's crust in small amount, and anthropogenic activities such as fossil fuels burning, mining, and manufacturing also contribute to the release of high concentrations. While lead has many applications in different sectors like industrial, agricultural, and domestic, it can be toxic to humans and animals, causing health effects (Duressa, n.d.; Jaishankar et al., 2014; Kaur et al., 2019; Tchounwou et al., 2012). No level of lead exposure can be safe because lead, unlike other heavy metals such as Cu, Zn, and Mn, has a biological role in the body (Duressa, n.d.; Jaishankar et al., 2014; Obasi & Akudinobi, 2020). Lead poisoning occurs mainly through inhalation of lead-contaminated dust particles or aerosols and ingestion of food, water, and paints contaminated with lead. In the human body, lead affects several organs such as the kidneys, liver, central nervous system, hematopoietic system, cardiovascular system, endocrine system, and reproductive system (Assi et al., 2016; Tchounwou et al., 2012; Wani et al., 2015). Children and fetuses are more subject toward lead poisoning; in children, it can affect central nervous system disease. And it can be the reason for learning and concentration difficulties (Angevine et al., 2006). Plants with a high level of lead

concentration cause lipid membrane damage because of the fast production of reactive oxygen species (ROS) (Ali & Nas, 2018; Sytar et al., 2013).

Nickel is a commonly used heavy metal with some essential roles in animals and humans, and it is an essential micronutrient for higher plants. In addition, it has broad industrial applications; for example, used in stainless steel through electroplating. However, nickel is harmful to animals, humans, and plants when present in excess (Genchi et al., 2020).

Some effects of nickel on humans are lung fibrosis, kidney and cardiovascular diseases and cancer of the respiratory tract, (Masindi & Muedi, 2018), (Genchi et al., 2020; Harasim & Filipek, 2015). Literature reported that the effect of excess nickel concentration in plants, for example adverse effects on fruit yield, interference with other essential metal, induction of oxidative stress, quality reductions, altering the normal metabolism, and causing cellular injuries in plant. Substantial levels of nickel have emerged into the environment via volcanic and anthropogenic activities. Nickel is naturally available in all soil types, sediments, and waters. Its toxicity comes from anthropogenic activities like burning of fossil fuels, application of phosphatic fertilizers, smelting, sludge water, electroplating industries, vehicle emissions, chemical industries, rubber and plastic industries, nickel-cadmium battery industries, mining, refining, paints, and ink formulation units (Chakraborty et al., 2020; Das et al., 2018; Harasim & Filipek, 2015; U.S Geological Survey, 1997). The extensive use of nickel in various industries or its occupational exposure is a matter of serious impact on human health. Heavy metals like nickel can produce free radicals from the diatomic molecule. Once nickel is released into the environment from human manufacturing waste, nickel, as Ni (II), can assume both soluble and insoluble forms. In aquatic environments, particulate nickel remains close to the source of contamination, but soluble nickel is mobile and easily entered into soils and sediments at greater distances. The wastewater generated from nickel processing still contains a substantial amount of nickel that should be treated before the final discharge to the environment (Briffa et al., 2020; Chakraborty et al., 2020; Das et al., 2018; Kane et al., 2016). In the environment, nickel is principally bound with oxygen or sulfur and forms oxides or sulfides in the earth's crust. Industrial uses of nickel during its production, recycling, and disposal have led to widespread environmental pollution. Nickel (Ni) is one of 23 metal contaminants, and it is seriously threatening our ecosystem and human health

(M. S. A. Ahmad & Ashraf, 2011). The U.S. EPA has set the permissible level of nickel for drinking water as 0.015 mg/L (Chakraborty et al., 2020).

2.5. Wastewater treatment

Wastewater treatment is a process of removal of physical, chemical (like heavy metals), and biological contaminants from water that has been used or polluted by anthropogenic activity or nature (Aghalari et al., 2020; Crini & Lichtfouse, 2019; Edokpayi et al., 2017; Englande et al., 2015). Mainly there are two purposes for wastewater treatment, the first to protect human health and prevent environmental contamination by disposal of safe domestic and industrial wastewater. The second is to gain energy, nutrients, water, and other valuable resources from wastewater during purification steps. The recycling of wastewater has been important for reuse in irrigation, thereby preserving water resources, which is rare in dry and semiarid regions of the world (Englande et al., 2015; Ince & Kaplan Ince, 2020; Jasim, 2020; Samer, 2015). Wastewater treatment methods are classified into three-stages, which are pretreatment /primary treatment stage, Secondary treatment stage, and Tertiary treatment stage (Crini & Lichtfouse, 2019; Englande et al., 2015; Ince & Kaplan Ince, 2020; Oljira, 2016).

2.5.1. Pre-treatment / Primary water treatment method

The pre-treatment method is the stage to purify the wastewater suitable and compatible to subsequent treatment processes. Typically processes include equalization, neutralization, oil and grease separation by physical and mechanical operations (Crini & Lichtfouse, 2019; Englande et al., 2015; Ince & Kaplan Ince, 2020). Primary treatment is a preliminary water purification process to remove about 25% of organic matter; and large suspended solids from wastewater by physical and chemical operation often consist of screening and microfiltration, centrifugation, sedimentation, chemical precipitation, coagulation, gravity, and flocculation methods (Bolisetty et al., 2019; Crini & Lichtfouse, 2019; Englande et al., 2015; Ince & Kaplan Ince, 2020; Jasim, 2020; Oljira, 2016; Samer, 2015).

2.5.2. Secondary water treatment method

Primary treatment has defined as the preparation for a biological treatment called secondary treatment. This treatment stage helps to break down and eliminate organic matter in the presence of microorganisms (bacteria), oxygen, and nutrients. Bacteria consume organic matter as food and converting it to carbon dioxide, water, and energy for

their growth. The secondary treatment stage has two main categories these are anaerobic and aerobic treatments. This stage can remove about 85% of the suspended solids and organic matter (Bolisetty et al., 2019; Crini & Lichtfouse, 2019; Ince & Kaplan Ince, 2020; Jasim, 2020; Kesari et al., 2021; Oljira, 2016). There are many stages to design a way for the biological wastewater treatment process, but the two most commonly used are the activated sludge and the trickling filtration process (Englande et al., 2015; Jasim, 2020; Naidoo & Olaniran, 2013). A secondary treatment stage does not remove pollutants like heavy metals because they are non-degradable substances. Therefore tertiary treatment method is important and should be applied to wastewater (Englande et al., 2015; Jasim, 2020; Kesari et al., 2021; Oljira, 2016).

2.5.3. Advanced (tertiary) water treatment method

Advanced wastewater treatment is employed when contaminants like toxic organics, volatile organic compounds (VOCs), phosphorus, nitrogen, heavy metals, refractory organics, and difficult-to-remove pathogens such as giardia lamblia have not significantly removed after the secondary treatment processes. Tertiary treatment is including techniques like ion exchange, nitrification, filtration, denitrification, membrane processes, air stripping, adsorption, chemical oxidation, and chemical precipitation of phosphorus. Usually, the tertiary treatment stage has used different disinfectants like chlorine, ozonation, and ultraviolet radiation to treat wastewater, and also nearly 99% of all impurities are removed from wastewater (Englande et al., 2015; Ince & Kaplan Ince, 2020; Jasim, 2020; Kesari et al., 2021; Naidoo & Olaniran, 2013; Oljira, 2016).

2.6. Conventional methods of heavy metal removal from wastewater

It is significant to remove heavy metals from contaminated water through conventional techniques. So far, various technologies have been available for heavy metals removal from wastewater, such as ion exchange, chemical precipitation, coagulation, membrane separation, electro-coagulation, reverse osmosis, and adsorption. These different techniques consist of physical, chemical or biological methods and all have its individual advantages and disadvantages (Ali, H., Khan, E., & Ilahi, 2019; Bazrafshan et al., 2015; Chakraborty et al., 2020; Kanamarlapudi et al., 2018; Khulbe & Matsuura, 2018; Lakherwal, 2014; Qasem et al., 2021; Tang et al., 2016) .

2.6.1. Chemical precipitation

Chemical precipitation is one of the physicochemical methods used for heavy metal removal by the addition of chemicals such as alum, lime, iron salts, and other organic polymers and are used for metals to precipitate out via the formation of metal hydroxides, sulfides, carbonates, and phosphates. Generally, chemical precipitation is a two-step process first, addition of coagulants chemicals like alum, lime, iron salts, and other organic polymers. Next separation of precipitated solids is achieved from cleaned water (Chakraborty et al., 2020; Ince & Kaplan Ince, 2020; Kanamarlapudi et al., 2018; Lakherwal, 2014; Oljira, 2016). The main drawbacks of the chemical precipitation technique are its requirement of an excess amount of chemical reagents and produced a large amount of sludge containing toxic compounds (Chakraborty et al., 2020; Oljira, 2016).

2.6.2. Ion-exchange

The ion exchange technique is a physicochemical and reversible process where ions present in the solution; are exchanged with ions on the solid surface. There are two types of ion exchangers, which are cation (Figure 2.3) and anion exchangers. Natural and synthetic clays, zeolites, and synthetic resins are commonly used with high cation exchange capacity for the uptake of heavy metals and release counter-ions of a similar charge in a chemically equivalent amount from and to wastewater (Ince & Kaplan Ince, 2020; Jiang et al., 2015; Kanamarlapudi et al., 2018; Oljira, 2016). The drawback of this technique is; it is affected by the pH of the solution. In addition, synthetic resins are expensive, high labor, and it is limited in small concentrations of metals in the solution (Chakraborty et al., 2020; Masindi & Muedi, 2018).

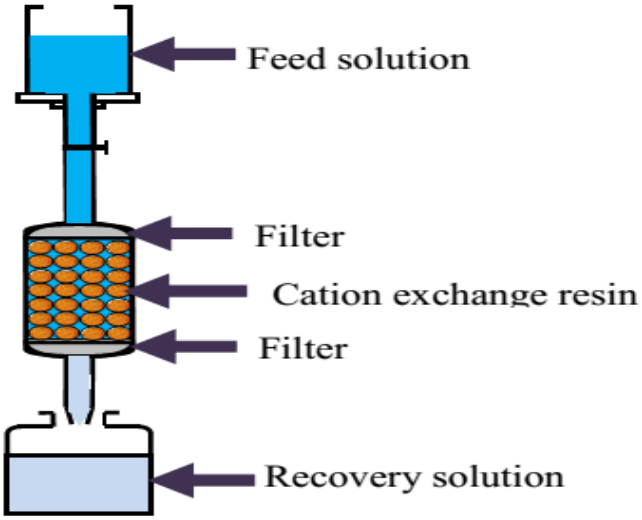


Figure 2.3. Schematic diagram showing ion exchange method (Lalmi et al., 2018).

2.6.3. Coagulation–flocculation

Coagulation-flocculation is a commonly used technique for drinking water as well as wastewater treatment. In this technique, the chemical reaction is occurred after the addition of coagulants like ferric/alum salts to remove colloidal materials, some soluble compounds, and very small solid suspensions initially present in the wastewater. The purposes of the coagulants are to destabilize, neutralize, and combine the colloidal particle into small aggregates called flocs. Flocculation is the process of gently mixing water to help the flocs to produce and grow in size as well so the flocs can settle down simply and leaving pure water behind (Borchate et al., 2014; Johnson et al., 2008; Kweinor Tetteh & Rathilal, 2020; Lakherwal, 2014; Pang et al., 2009). The drawbacks of this method are the requirement of high operational cost; and the high volume of toxic sludge generated (Chakraborty et al., 2020; Naidoo & Olaniran, 2013; Oljira, 2016) (Figure 2.4).

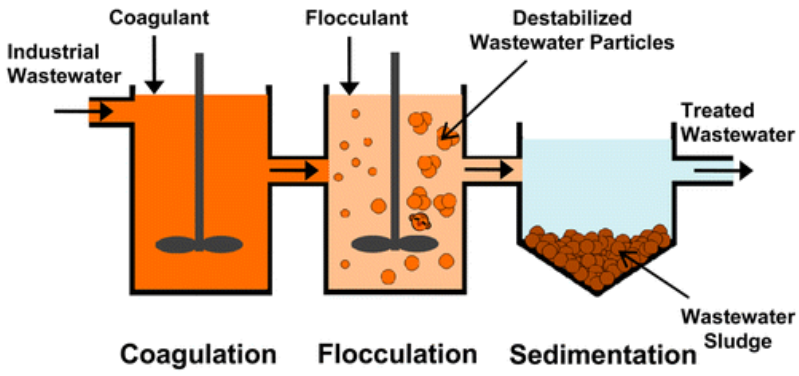


Figure 2.4. Coagulation, flocculation and sedimentation (Teh et al., 2016).

2.6.4. Membrane filtration

More recently, membrane filtration has been known for seawater pretreatment and treatment of industrial effluent. It is capable of eliminating suspended solids, organic compounds, and inorganic contaminants such as heavy metals. Several techniques of membrane filtration techniques are microfiltration, ultra-filtration, nanofiltration, electrodialysis, and reverse osmosis. The drawback of these methods is high maintenance and operational cost (Chakraborty et al., 2020; Jeong et al., 2017; Oljira, 2016). Reverse osmosis is the opposite of the natural osmosis process of water. It is also called hyper-filtration and pressure-driven membrane filtration process used for contaminants removal like heavy metals from wastewater by using a semi-permeable membrane (Chakraborty et al., 2020; Ince & Kaplan Ince, 2020; Kanamarlapudi et al., 2018; Lakherwal, 2014; Mokarram et al., 2020) (Figure 2.5).

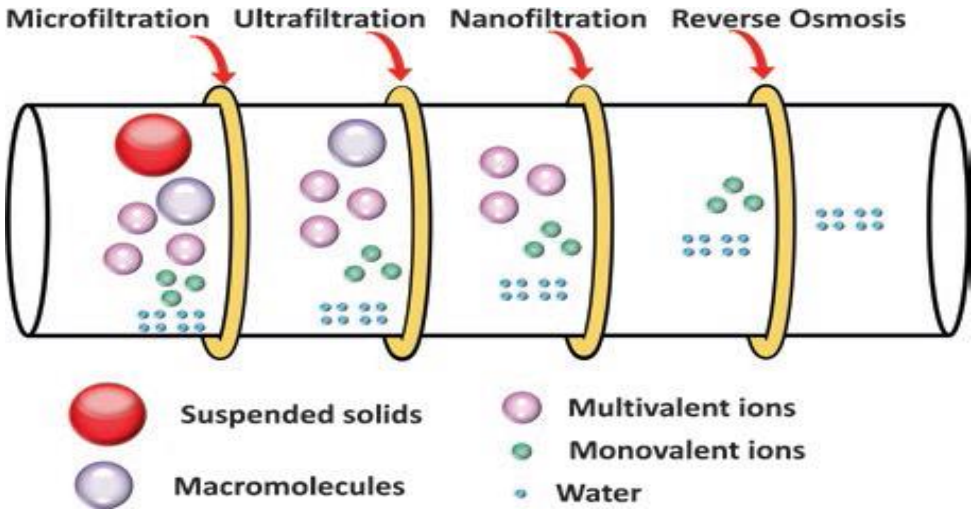


Figure 2.5. Different kinds of membranes filitration (Lichtfouse, 2021).

(Microfiltration retains suspended solids, ultrafiltration retains macromolecules, and nanofiltration retains multivalent ions and reverses osmosis monovalent ions)

2.6.5. Adsorption

Adsorption is the accumulation of particles (adsorbate) at a surface (adsorbent or substrate). The reverse process is called desorption.Currently, adsorption becomes an advisable technique because of its simplicity, efficiency, low cost, and flexibility to concentrate and allow removal and recovery of the harmful contaminants from wastewater. Adsorption is a process of accumulation of ions or atoms species of solid, liquid, or gas to surface and bound by physical or chemical interactions. Thus this process creates a layer of

the adsorbate (metal ion) on the surface of the adsorbent. The molecular species or substance, which accumulates at the surface of the adsorbent is called adsorbate, and adsorbent is the material at which adsorption takes place (Ariffin et al., 2017; Diana Iruretagoyena Ferrer, 2016; Ince & Kaplan Ince, 2020; Khulbe & Matsuura, 2018; Lakherwal, 2014; Patel, 2019) (Figure 2.6). Even though several heavy metal ions removal methods exist; these methods have many disadvantages such as high cost, production of a higher amount of toxic sludge and disposal problem, high energy consumption, and requirement of an excess amount of chemicals. So it is significant to develop an appropriate and environmentally friendly wastewater treatment method that is the adsorption method. The adsorption method has many advantages, and one is generating clean water that is free from heavy metals. The drawback of this method is the chemical requirement for regeneration and the cost for adsorbent preparation (Chakraborty et al., 2020; Grégorio Crini, Eric Lichtfouse, Lee Wilson, 2018; Khulbe & Matsuura, 2018; Oljira, 2016).

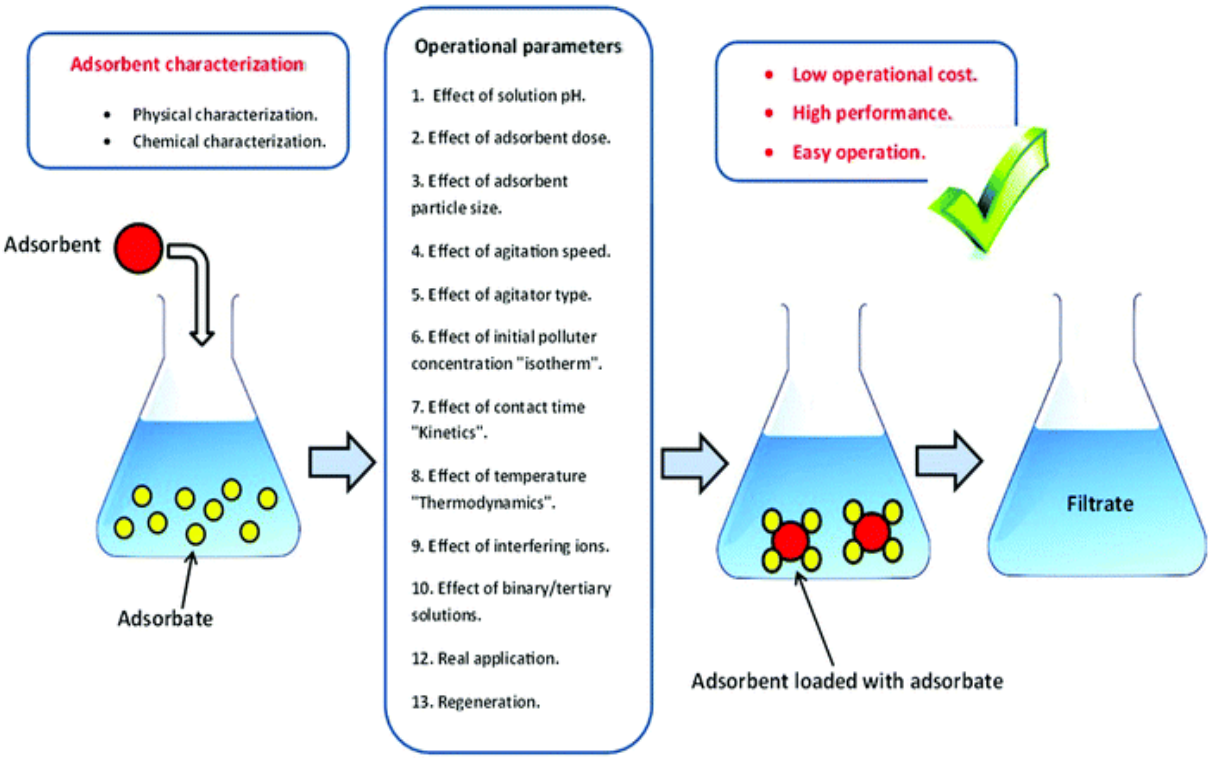


Figure 2.6. Schematic diagram of batch adsorption (Khalid Z. Elwakeel, Ahmed M. Elgarahy, Ziya A. Khan, Muath S. Almughamisi, 2020).

3.6.5.1. Type of adsorption

In the adsorption technique, the adsorbents and adsorbate interact physically (Physisorption) or chemically (Chemisorption) that are different interaction mechanisms (Figure 2.7). Physical adsorption is an important surface phenomenon caused by the intermolecular force of attraction called van der Waals forces. It has a low enthalpy of adsorption (20–40 kJ mol^{-1}) value than chemical adsorption and reversible reaction. Therefore, no activation energy is required because the energy of interaction between the adsorbate and adsorbent has the same order of magnitudes, and the interaction occurs at a lower temperature. In addition, the adsorbate can form a multilayer in physical adsorption mechanisms to provide high adsorption capacity. But, chemical adsorption is irreversible and is referred to as activated adsorption. It is mainly involved in catalysis so, the energy of chemical adsorption is considered similar to a chemical reaction, and the process may be exothermic or endothermic. This adsorption process requires activation energy. In chemical adsorption, the adsorbate is forming a monolayer adsorption process that provides high adsorption capacity. Generally, chemical adsorption is more popular for heavy metal removal because it has stronger interactions and higher adsorption capacity. Chemical adsorption is occurring by ion exchange, complexation including coordination, and chelation. It has high enthalpy of sorption (200 kJ mol^{-1}) than physical sorption (Grégorio Crini, Eric Lichtfouse, Lee Wilson, 2018; Khulbe & Matsuura, 2018; Knippenberg et al., 2006; Rudi et al., 2020).

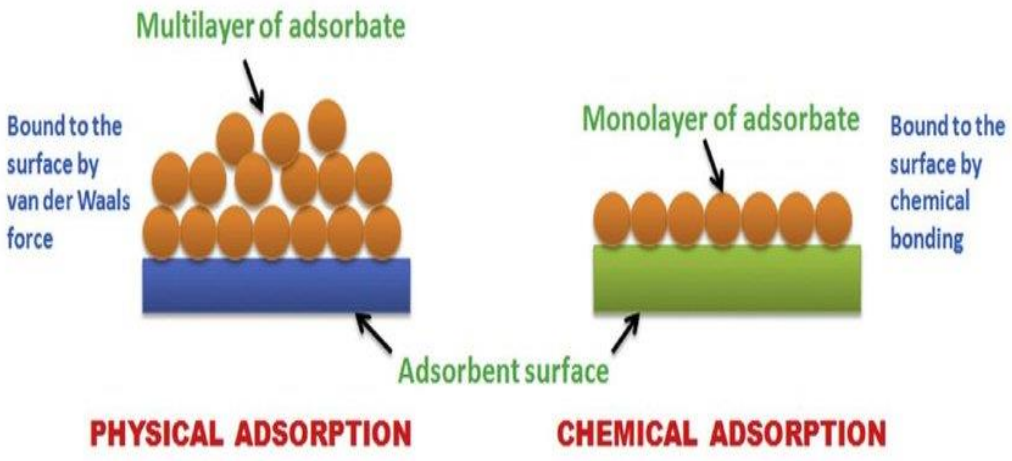


Figure 2.7. Physically and chemically adsorption (Sarkar & Paul, 2016).

2.6.5.1. Adsorbents classification

There are numerous solid materials used for adsorption purposes. Adsorbents are materials that can take a broad range of chemical arrangements and different geometrical surface structures. Generally, adsorbents are classified as conventional and non-conventional used for the removal of contaminants from wastewater. The conventional adsorbents include commercial activated carbons (CAC), commercial ion-exchange resins (polymeric organic resins), and inorganic materials such as commercial activated aluminas (CAA), silica gel, zeolites, and molecular sieves. While non-conventional adsorbents encompasses activated carbons (AC) obtained from agricultural solid waste and industrial by-products, natural materials such as clays, industrial by-products such as red mud, biosorbents such as chitosan, and various adsorbents such as alginates(Canosa et al., 2019; Gabelman, 2017; Grégorio Crini, Eric Lichtfouse, Lee Wilson, 2018; Quintero-Jaramillo et al., 2021; Tripathi & Rawat Ranjan, 2015) (Figure 2.8).

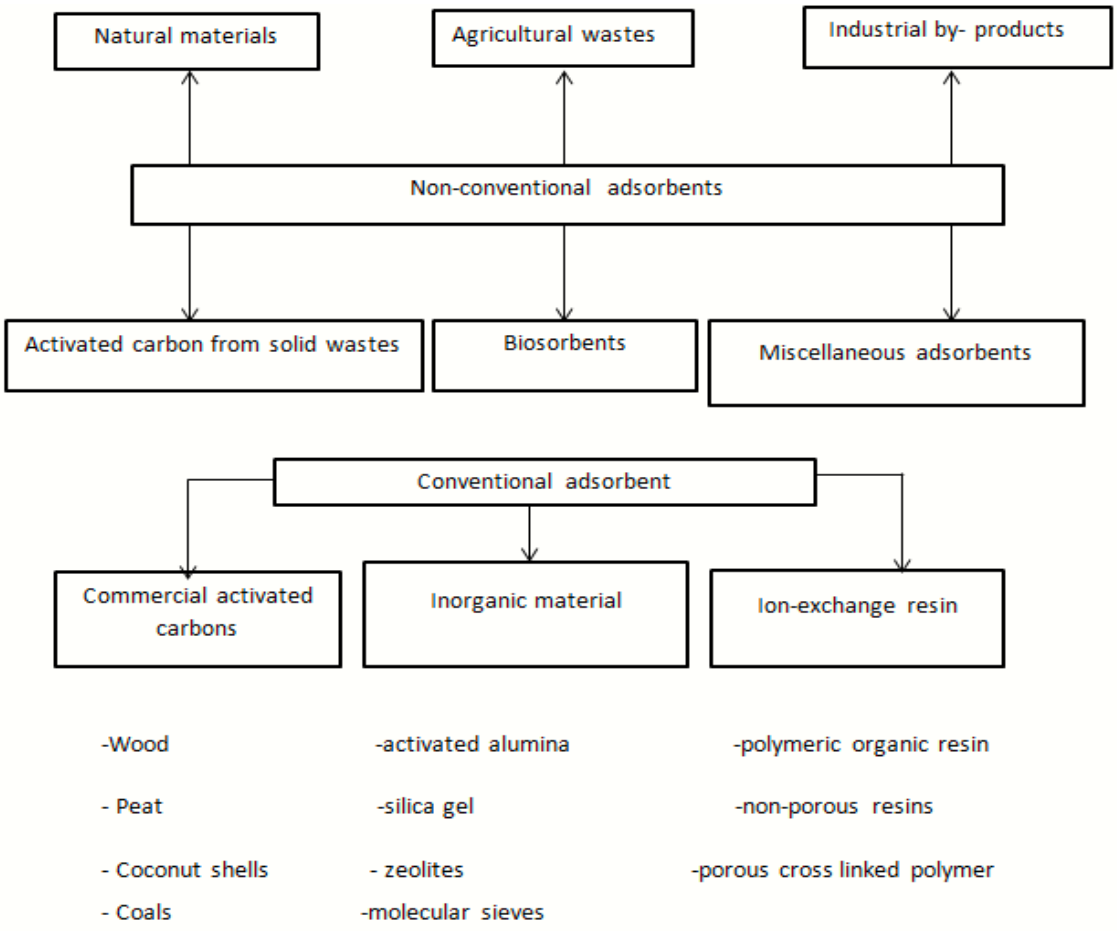


Figure 2.8. Conventional and non–conventional adsorbents (Crini et al., 2018).

2.6.5.2. Common types of adsorbents

Currently, for wastewater treatment, various types of adsorbents have been used. Thus researchers have used these various adsorbents to study their efficiencies to remove toxic pollutants like heavy metals. Zeolites, activated carbon, activated alumina (Al_2O_3), silica gel (SiO_2), and polymeric adsorbents are the most commonly used adsorbents. Activated carbon and some zeolites are manufactured from naturally existing materials, but the remaining can be synthetically manufactured. Activated carbon can be applied to adsorb a wide variety of compounds. Silica gel has an affinity for water adsorption and is often used to control humidity. Zeolites have very uniform pores and can adsorb molecules based on their size. Polymeric adsorbent covers a range of cross-linked resins that can be tailored for specific applications (Canosa et al., 2019; Gabelman, 2017; Grégorio Crini, Eric Lichtfouse, Lee Wilson, 2018; Quintero-Jaramillo et al., 2021; Renu et al., 2017).

2.6.5.2.1. Zeolites

The naturally occurring zeolites can be defined as crystalline aluminosilicates with a three-dimensional structure formed by repeating units of silicon-oxygen (SiO_4) and aluminum-oxygen (AlO_4) tetrahedral. They are also recognized as “molecular sieves” because of their capability to accept and reject molecules based on their size (A. Ahmad & Azam, 2019; Ghasemi et al., 2018; Shi et al., 2017; S. Singh et al., 2020). The natural zeolites have uniform pore-sized, hydrated minerals and the pore is formed by a combination of different tetrahedrons. Zeolites have ion exchanging capacities and defined porous size so, this property leads to removing heavy metal from wastewater. The adsorption mechanism is by the cations (alkaline and alkaline earth) inside the pore and the network of the negatively charged aluminosilicate structure can be substituted by another cation. The disadvantages of zeolite adsorbents are the adsorption properties depend on the different materials because it has more than 60 natural species (Canosa et al., 2019; Grégorio Crini, Eric Lichtfouse, Lee Wilson, 2018; Morante-Carballo et al., 2021; Shi et al., 2017; Tripathi & Rawat Ranjan, 2015).

2.6.5.2.2. Activated Carbons

Activated carbons are one of the oldest and most commonly used adsorbents in gas treatment and water purification. The materials which have high carbon contents like coals material, industrial by-products, and lignocellulose biomass can be sources for producing activated carbon adsorbents (A. Ahmad & Azam, 2019; Bamdad et al., 2018; Grégorio

Crini, Eric Lichtfouse, Lee Wilson, 2018; Renu et al., 2017). Many kinds of literature (Abdulrazak et al., 2017; Herdyastuti et al., 2019; Karnib et al., 2014; Ullah et al., 2020) reported that activated carbon has good potential for adsorbing heavy metals because of its greater surface area, microporous, and chemical complexity of its external area. However, the disadvantages of activated carbon are: dust can lead to blockages, component mixes may lead to early malfunction, risk of spontaneous combustion in the bed, polymerization risk for unsaturated hydrocarbons on the activated carbon, and expensive due to the depletion of coal-based source and especially for producing high quality activated carbon. The processes of removal of contaminants by activated carbon are often carried out in a batch mode, by adding activated carbon to a vessel containing the contaminated solution, or by feeding the solution continuously through a packed bed of carbon.

2.6.5.2.3. Activated alumina

Activated alumina (Al_2O_3) is a crystalline polar filter media made by treating aluminum ore. It is porous and highly adsorptive. It can also be described as a granulated form of aluminum oxide and used to remove impurities in wastewater. Activated alumina is much less likely to be used in water purification than activated carbons; however, it is used to remove inorganic contaminants such as fluorides, arsenic, selenium, and silicates. Among possible techniques, adsorption on activated alumina is extensively applied, as it is most effective for removing organic compounds such as surfactants, pesticides, dyes, aromatic molecules, and even heavy metals. There is much research on heavy metals adsorption using activated alumina. The economic viability of processes using adsorption is thus directly related to their efficiency in regenerating and recycling the activated alumina. Activated alumina has been used as an effective adsorbent, especially for point-of-use applications. The main disadvantage of activated alumina is that the highest adsorption efficiency is obtained only at low pH. In addition, the use of other treatment methods would be necessary to reduce levels of other contaminants of health concern (Canosa et al., 2019; Ghaedi & Mosallanejad, 2013; Rabia et al., 2018; Szatyłowicz & Skoczko, 2017).

2.6.5.2.4. Polymer-based adsorbents

Polymeric adsorbents are spherical synthetic polymers with defined pore structures and are highly tailorable materials that can be produced with a range of properties. They are typically composed of polar or nonpolar and can be hydrophobic or hydrophilic depending on the synthesis process groups in a rigid, cross-linked polymer network. This network

provides the materials with the high surface area needed to perform well as adsorbents. They are frequently used for gas chromatography columns, water treatment, and volatile organic compounds (VOCs) collection. Polymeric adsorbent includes nano-magnetic polymers (NMPs), polysaccharides, extracellular polymeric substances (EPS), and covalent organic polymers (COPs), which are established low-cost and readily available. NMP_S can quickly and accurately determine trace environmental pollutants like phenols and heavy metal ions. The advantages of polymeric adsorbents are high flexibility in design, physical stability, porosity, uniform pore size distribution, high surface area, and chemical stability towards acids and bases, feasible regeneration, and thermal durability. But, polymeric adsorbents have limitations this is because they are often very specific adsorbents (Alaba et al., 2018; Rahman et al., 2020; Separation, 2017; Shabkhizan & Mousazadeh, 2011).

2.6.5.2.5. Silica gel

Silica gel is a chemically inert inorganic porous form of silicon dioxide (silica), SiO_2. The chemical formula of silica gel is SiO_2 x H_2O. It is a solid, amorphous form of hydrous silicon dioxide distinguished by its microporosity and hydroxylated surface (Canosa et al., 2019; Ganokar et al., 2018; Khanvilkar, 2019; Natu et al., 1984; Series & Science, 2019). The structure of silica gel is sphere-shaped particles of colloidal silica. It is a continuous three-dimensional rigid network called micelles that can take on several properties or pore structures depending on the production process. In the structure of silica gel, both siloxane (-Si-O-Si-) and silanol (-Si-OH) bonds are present. The silica gel properties are a result of the silica, their state of aggregation, and the chemistry of the micelle surface. The hydrophilic characteristics of silica gel are due to the presence of silanol (Si-OH) functional groups in the silica gel. It is commonly used as a desiccant. It exhibits high surface area per unit mass, fully porous structure, high mechanical stability, a high tendency to adsorb inorganic impurities, and it is non-toxic and dimensionally stable. The surface area of silica gel range from 200 to 1000 m^2/g and 2–10 nm in diameter. Silica gels have been used commercially as an adsorbent since World War I (Acker et al., 1967; Bamdad et al., 2018; Briffa et al., 2020; Ganokar et al., 2018; Khanvilkar, 2019; Natu et al., 1984). As a result of its structural characteristics, the possibility of functionalization and modification with an impregnation medium or reagent, silica gel has been widely known and used polar adsorbent for gases, liquids, and metals. In addition, it is particularly

used in its deactivated form in chromatography and solid phase applications. Solid-phase extraction technique using a different kind of solid adsorbents ensures high enrichment factor, rapid phase separation, and the ability to combine with different detection techniques (Masindi & Muedi, 2018). Silica gel has characteristics of the controlled structure, composition, and morphology. The main advantage of the silica gel over other solid inorganic supports is low cost (great abundance on earth), relative activity, large adsorption capacity, easy preparation of its different types with different pore sizes, and total surface area under standard conditions. Because it is a polar material and so has an affinity for attracting water molecules. Many zeolites must be heated to temperatures exceeding 350 °C to remove water, while silica gel only requires heating to 150 °C (Canosa et al., 2019; Ismail, Khalili, & Orabi, 2020; S. Singh et al., 2020). There are various methods to synthesize silica gels. The most common one is by sol-gel method from suitable alkoxides like tetra-methoxy silane (TMOS) and tetraethyl orthosilicate (TEOS) which are the most common raw materials for silica gel production. In addition, silica gel are synthesized by acidifying an aqueous solution of sodium silicate which is a conventional method that has many benefits, such as a slow growth rate, low cost, possibility of particle surface modification, etc. (Acker et al., 1967; Baccile et al., 2017; Iman, n.d.; Kierys et al., 2015). However, silica gel can be also obtained from agricultural waste like rice husks ash. This kind of wastes is an inexpensive and high abundant source of adsorbent (Purwanto & Putri, 2017; Yu et al., 2016), Figure 2.9 shows the structure of silica gel.

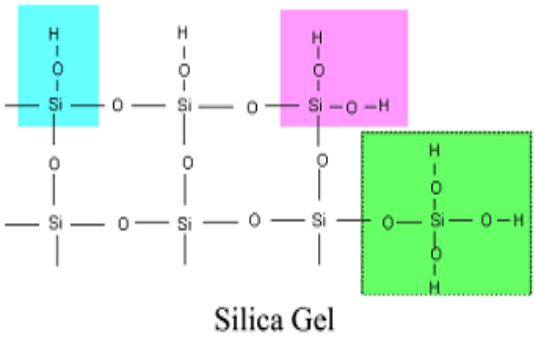


Figure 2.9. Structure of silica gel (Tigabu, 2017).

2.6.6. Silica gel functionalization for heavy metals removal

It is important stating that the key to the application of SPE is dependent on the properties of the adsorbents, including high capacity, selectivity, and resistibility. In the SPE the properties and structure of adsorbents are significant for effective retention of metals. Therefore SPE technique typical performance significantly can be improved by efficient selection of a suitable adsorbent (Jung et al., 2019),(Veronica B. Cashina, Daniel S. Eldridgea, 2017). There are various solid phase adsorbents available for preconcentration of heavy metals, specifically classified as modified silica gel, resins, nanomaterial, natural organisms, ion-imprinted polymers, etc., and these confirm high enrichment factor, rapid phase separation and the ability of combination with different detection techniques. Silica gel (SG) is considered to be one of the most appreciated solid supports, for its outstanding performance. Through physical and chemical modification with different chemical reagents or biosorbents the extraction efficiency and selectivity of silica gel has been improved. Usually introducing many ligands or fine particles onto the surface of SG are used for the preconcentration of heavy metal in environmental samples. The introduction of foreign functional groups to a silica gel surface is called functionalization and it can be categorized under two main strategies. The first of these strategies is the post-synthetic surface modification approach, in which silica materials are initially manufactured or obtained before a modifying agent with a particular functional group is attached to the surface. This attachment can be achieved by simple physical adsorption or chemical bonding via a chemical reaction. The process usually involves dissolution along with heating and stirring, however may also extend to advanced methods including spray-coating, molecular imprinting, or other surface deposition techniques. The outcome of this approach is an intact adsorbent featuring anew introduced surface moieties, possessing functional groups that can form stable links to the previously existing surface features of the adsorbent. Often, such post-synthetic functionalization is preceded by processes like activation, to improve the affinity of the modifying agent for the adsorbent surface. The second strategy for surface functionalization contains any bottom-up method that involves tailoring of the adsorbent synthesis, by incorporation of some precursor in the synthesis reaction(s). In this approach, a silane precursor is suspended in a polar solvent containing a mesostructure template, which when mixed and heated (such as refluxed), enables the recombination of hydrolyzed reactants to form the final product, which can then either be dried to a powder or left suspended in solution. Modifications to this approach often

involve the inclusion of an alternate structure-directing agent, a different silica source, or the addition of some other reagent to influence the final surface chemistry of the as-synthesized adsorbent (Veronica B. Cashina, Daniel S. Eldridgea, 2017). The modified SG is generally divided into ion-imprinted materials-modified SG, nanomaterials-modified SG, and organic-groups-functionalized SG. Thus to improve the removal efficiency of heavy metal from wastewater suitable functional groups have been chemically or physically bonded to the reactive sites on the silica surface (Petrova et al., 2018; Shabkhizan & Mousazadeh, 2011; Veronica B. Cashina, Daniel S. Eldridgea, 2017). Due to the abundance of hydroxyl groups on the SG surface, chemical modification of silica gel is the most commonly used strategy. The silanizing or chlorinating agents are commonly used as a bridge between organic substances and SG. Also, donor atoms such as O, N, and S atoms with chelating ability are attached to the surface of SG to form a functionalized silica gel (Zhan et al., 2019). So through introducing organic chelating molecules which have some active donor atoms or groups onto the skeleton of silica gel, the solid silica gel would possess many extraordinary adsorption properties for heavy metal treatments such as fast kinetics, solvent independent, easy to use, mechanically stable, thermally stable, controlled loading, easily scalable and flexible formats (Veronica B. Cashina, Daniel S. Eldridgea, 2017). Even though there exists many types of solid adsorbent used in SPE, silica gel functionalization by numerous organic chemicals that's used for a metal chelating agent to remove, extract, separate and preconcentrate heavy metal ions from different media like wastewater show high thermal, chemical and mechanical stability and is less susceptible to swelling, shrinking, and microbial and radiation decay. Thus selection of the modified silica gel mostly depends on the structure of the immobilized organic compound and generally it depends on the nature of the combined donor atoms (O, N, P and S), the positioning of the functional groups along the surface of the silica, and the steric requirements of the complex formed after uptake of the desired metal ion (Alghanmi, 2012; Petrova et al., 2018). Nowadays a silica gel surface has been modifying by variety of chelating ligands such as hydroxyl, carboxyl, thiol and amine groups containing chelating compounds are preferable for removal of most of heavy meals (Table 2.1). So functionalization of the surface of silica gel is done using an appropriate molecule designated as the precursor silylating agent. The silica gel surface and the silylating agent are bonded by covalent bond which yields a new modified silica surface with fixed functionality. It is then possible to immobilize new molecules with a variety of organic

functions, including chelating agents (Alghanmi, 2012). Inorganic solids surface-functionalized with various organic chelating groups are suitable for adsorption and preconcentration of metal ions. Silica functionalization with various organic compound or functionalizing agent is known as silica based inorganic–organic hybrid materials (Samiey et al., 2014). Silica gel generally contain high amount of internal siloxane groups (Si–O–Si) and silanol groups (Si–OH) that its active hydrogen atom is suitable for reaction with organosilyl containing groups to give some organic nature to the precursor inorganic support (Ghaedi et al., 2012; Jung et al., 2019). Therefore, it is valuable to construct a chelating matrix by introduction of multifunctional organic molecules onto the silica gel**.** Amino, thiol, and carboxyl functional groups could be simultaneously introduced onto silica gel by reacting with amino acids L-cysteine or L-methionine (Yu et al., 2016).

Table 2.1. Hydroxyl, carboxyl, amine and thiol functionalized silica adsorbents for pollutants.

Functionalizing agent	Functional group(s)	Inorganic pollutant(s) adsorbed	Efficiency	References
Amino penta-carboxylic acid	O = C – OH O – CH_3	Cu^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+}	2.40, 1.62, 0.85 and 0.3 mmol/g respectively.	(Radi et al., 2018)
Ethylenediaminetetraacetic acid modified silica and diethylenetriamine-Pentaacetic	O = C – OH -NH_2	Co^{2+}, Ni^{2+}, Cd^{2+} and Pb^{2+}	94.5, 80.6, 99.4, and 90.7 % 99.4, 94.5, 84.6, and 91.0%, respectively.	(Repo et al., 2017)
Diethylenetriaminepentaacetic acid	O = C – OH – NH – NR_3	Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}	0.26,0.29,0.06, 0.23,0.16 and 1.8 mmol/g, respectively.	(Repo et al., 2013)

p-dimethylamino-benzaldehyde	– CH_3 C = O N – R_3	Cr^{+3},Cu^{2+}, Ni^{2+}, $Pb^{2+}$and Zn^{2+}	89,51,31,77, and 245 µg/g, respectively.	(Cui et al., 2007)
Aminothioamido-anthraquinone	– SH – – NH_2 – NH – C = O	Pb^{2+}, Cu^{2+}, Ni^{2+}, $Co^{2+}$and Cd^{2+}	80, 85, 100, 98 and 97%, respectively.	(Ngeontae et al., 2007)
2-(benzo[d]thiazol-2-yl)-3,3-dimercapto acrylonitrile	-HS -CN	Hg^{+2} and Pb^{+2}	264–175 mg/g, respectively.	(Pranudta et al., 2021)
5-amino-1,3,4-thiadiazole-2-thiol	-SH -NH_2	Cd^{2+}, Co^{2+}, Cu^{2+},Fe^{+3},Hg^{2+} Ni^{2+}, $Pb^{2+}$and	0.35, 0.10, 0.15, 0.20, 0.46, 0.16, 0.13 and 0.15 mmol/g, respectively.	(De Magalhães Padilha et al., 1999)
L-Cysteine	-HS -COO^-	V^{+5},Cr^{+4}, Cu^{2+}, As^{+5}, Cd^{2+}, and Pb^{2+}	123, 100, 86, 106, 97, and 94%,. respectively.	(Liu et al., 2014)
	-SH	Pb^{2+}	234 mg / g, respectively.	(Ma et al., 2005)

L-Cysteine -COOH

2.6.7. Classification of selective adsorption for heavy metals

The selective adsorption of heavy metals in solution requires the preparation of specific adsorbents according to the nature of the separated materials or the creation of a specific adsorption environment. On the basis of literature about the selective adsorption of heavy metals, selective adsorption for heavy metals can be classified into three types. The first type: selective adsorption is based on the specific functional groups of adsorbent. When the adsorbents were modified with amine (-NH_2), carboxyl (COOH), and thiol (SH) functional groups, it can give priority to some heavy metals. Generally, this adsorption is achieved by complexation or chelation between metal ions and functional groups in a certain solution condition (Petrova et al., 2018; Renu et al., 2017; Veronica B. Cashina, Daniel S. Eldridgea, 2017). The second type: selective adsorption of heavy metals by adsorbents is based on ion-imprinting technique. The ion-imprinting polymers have a binding site similar to that of enzymes or receptors and they exhibit specific selectivity and recognition capability for imprinted heavy metal ions (Yasinzai et al., 2018). The third type: selective removal of heavy metals based on the ion-exchange principle as it is reported by Monica Pica (Pica, 2021) the affinity of zirconium phosphate-based materials for heavy metals lead and copper is generally significantly higher than for alkaline and alkaline earth metals.

2.6.8. Introduction of hydroxyl, carboxyl, amine and thiol groups on the silica

Most literature (Alghanmi, 2012; Veronica B. Cashina, Daniel S. Eldridgea, 2017) reported that the presence of hydroxyl, carboxyl, amine, and thiol group on the adsorbent surface related well with increases in adsorption capacity. The commercial silica gel possesses a low concentration of suitable surface silanol. Activation of silica gel is necessary for further modification by increasing the content of –OH groups at the surface of silica gel. It is often a one-step procedure in which a material is refluxed with an acid or a base. The introduction of oxygen-containing groups to a surface can provide additional sites for the successful adsorption of pollutants. The carboxylic functionality is also highly effective, as the two terminal oxygen atoms can present a highly electron-rich site for electrostatic attraction of pollutants (Alghanmi, 2012; Mokarram et al., 2020; Veronica B. Cashina, Daniel S. Eldridgea, 2017). The carboxylic functionality is also highly effective, as the two terminal oxygen atoms can present a highly electron-rich site for electrostatic attraction of

pollutants (Feinle et al., 2017; Veronica B. Cashina, Daniel S. Eldridgea, 2017). The functionalization of nitrogen atoms to the surface of silica gel most commonly occurs as amine groups. The capacity of amine groups at adsorbent surfaces has been efficient. Due to the lone pair of electrons and their affinity to undergo bond formation with cationic species; to examine the introduction of various amine groups to the surface of mesoporous and other types of silica has been reported by many studies (Aguado et al., 2009; Najafi et al., 2012; Veronica B. Cashina, Daniel S. Eldridgea, 2017). The thiol group that contains sulfur functionalization of silica has also attracted interest for adsorption applications similar to its periodic neighbor's nitrogen and oxygen. A substantial quantity of research has gone into the efficiency of thiol groups for the adsorption of heavy metals from the solution. Table 1 presents an insight into the hydroxyl, carboxyl, amine, and thiol groups on the functionalization of silica substrates. During the post-grafting functionalization process, the organic functional groups consisting of amine ($–NH_2$), carboxyl (–COOH), and thiol (–SH) could be covalently bonded to the silanol group (Si-OH) on the external or internal pore surface (Zaharudin et al., 2020).

2.6.9. Characterization of adsorbents

Fourier-transform infrared spectroscopy (FT-IR), x-ray diffraction (XRD), scanning electron microscope (SEM), and Brauer-Emmett teller (BET) are some of the analytical techniques used for the characterization of an adsorbent, and more generally available in adsorption research.

2.6.9.1. Fourier-transform infrared spectroscopy (FTIR)

FT-IR was used to show the spectra of organic functional groups in the adsorbent. Further FTIR analysis is important in order to establish the changes in the functional groups of adsorbents. Different peaks in the IR spectrum are interpreted for different functional groups in the formulations. The main information obtained from FT-IR is surface composition and ligand binding (Grégorio Crini, Eric Lichtfouse, Lee Wilson, 2018), (Bayu et al., 2019), (Mayssara A. Abo Hassanin Supervised, 2014).

2.6.9.2. X-ray diffraction (XRD)

The XRD is used to investigate the crystalline or amorphous nature of the adsorbent. The main information obtained from XRD is crystal structure and crystalline grain size (Grégorio Crini, Eric Lichtfouse, Lee Wilson, 2018).

2.6.9.3. Scanning electron microscope (SEM)

SEM is one of the most widely used surface identification methods. The main information obtained from SEM is the morphology and surface structure of adsorbent (Grégorio Crini, Eric Lichtfouse, Lee Wilson, 2018).

2.6.9.4. Brunauer-Emmett-Teller (BET)

The BET gas adsorption method has become the most widely used characterization method for the determination of the surface area of finely-divided and porous materials. Because adsorption is a surface phenomenon and as such the degree of adsorption is proportional to the specific surface area. So the amount of adsorption accomplished per unit weight of solid adsorbent is greater if the solid is more finely divided and more porous. Substances like silica gel are excellent adsorbents because they have a highly porous structure and hence have a large surface area, Pore volume, and pore diameter of adsorbents have been investigated using Brunauer-Emmett-Teller (Grégorio Crini, Eric Lichtfouse, Lee Wilson, 2018; K. Sing, 2001), (K. S. W. Sing, 1982).

2.6.10. Factors influencing adsorption process

2.6.10.1. Effect of pH

pH of the solution is another determinant factor in adsorption process. It exerts influence on the adsorptive uptake of adsorbate molecules, presumably due to its influence on the surface properties of the adsorbent and ionization/dissociation of the adsorbate molecule (Abbasi & Noorizadeh, 2017; Farrukh, Akram, Ghaffar, Oluz, et al., 2014). The acidity of a solution has two effects on metal adsorption. First, protons in an acidic solution can protonate the binding sites of the chelating molecules. Secondly, the hydroxide in a basic solution may form complex and precipitate with many metals. Therefore, the pH of a solution is the first parameter to be optimized (Alghanmi, 2012). The protonation/deprotonation of N- and S- containing functional groups is related to their pKa, which strongly depends on the pH of the solution. Consequently, the degree of metal sorption on amino acid modified silica gel sorbent should be strongly influenced by pH value of the sample solution; hence sorption experiments for optimization of the pH value should be performed (Petrova et al., 2018). (Dakova1 & , P. Vasileva 2, 2011; Liu et al., 2014; Moyo et al., 2013; Rimmy Singh & Bhateria, 2020).

2.6.10.2. Effect of contact time

In adsorption process contact time is one of the important factors to be optimized. The determination of the optimal contact time in adsorption process can be successfully used to determine the volume of solutions in adsorption processes, to design them, and also to effectively minimize the costs of the process (Tomasz Kalak 1,*, 2021). Each wastewater treatment alternatives should be effective economically and this parameter is important for the effective use of adsorbents in industry. In addition to this optimization of contact time is used to see the rate (kinetics) and the equilibrium of the adsorption process (i.e. the time of contact between the adsorbate and adsorbent) (Moyo et al., 2013; Tangjuank et al., 2009). So, studying the effect of contact time on adsorption experiment is very important for its practical applications.

2.6.10.3. Effect of initial metal ion concentration

The initial metal ions concentration is an important factor in adsorption to overcome all the mass transfer resistance between the solution and solid phases. A given mass of adsorbent material can only adsorb a fixed amount of metal ions. Several studies have shown that removal efficiency of heavy metal is concentration dependent and removal capacity of adsorbent will decrease with increase in initial metal ion concentration. This is because for a given mass of adsorbent material; the amount of ions that can be adsorbed is fixed there exist decreasing trend if further increase in initial concentration (Bilgiç, 2019; Kanamarlapudi et al., 2018; Rudi et al., 2020),(Ariffin et al., 2017).

2.6.10.4. Effect of dosage of adsorbent

Adsorbent dosage is an important parameter because adsorbents provide the binding sites for metal adsorption. Therefore, adsorbent dosages determine the capacity of an adsorbent for a given initial concentration, separation cost and consequently the overall water treatment cost (Kanamarlapudi et al., 2018),(Ariffin et al., 2017; Ouazene & Sahmoune, 2010),. Generally, increase in the adsorbent dose at a given initial metal concentration increases the adsorption of metal ions due to greater surface area which in turn increases the number of available binding sites. High adsorbent dosage provides more active exchangeable adsorption sites. At lower concentrations of adsorbent, the amount of metal adsorbed per unit weight of the adsorbent is high. On the other hand, at high concentration of the adsorbent, the quantity of metal ion adsorbed per unit weight decreases. This is because of lower adsorbate to binding site ratio due to the insufficient amount of solute

present for complete distribution onto the available binding sites and possible interaction between binding sites (Iftekhar et al., 2018; Rudi et al., 2020).

2.6.11. Adsorption mechanism

From all of the remediation techniques, the adsorption-supported technique is a very simple and commercial approach to adopt for the removal of heavy metal from wastewater. Adsorption mechanisms studies of various water polluters allow the assessment of their operational efficiency, which is critical to and useful for optimization of conditions of the removal process. So far, many studies have focused on evaluating the possible interaction mechanism of different water polluters on as-used biosorbents. High adsorption efficiency plays a vital role in characterizing a biosorbent for the removal of different water polluters effectively. Generally, the process of adsorption realizes the physicochemical features of the biosorbent, i.e., molecular size, solubility, chemical composition, surface charge, reactivity, and hydrophobicity. The structural components variable characters attributed to the existence of several functional groups, with varying degrees, on its surface, i.e., amino, hydroxyl, carboxyl, thiol, phosphate, etc., which facilities water polluters sorption onto the biosorbent via various sorption mechanisms. There are several interactions between contaminants and biosorbent surfaces, commonly, may occur through complexation/chelation, electrostatic interaction, ion exchange, oxidation, and reduction(Figure 2.10). The silica gel is one of the adsorbent solid surfaces therefore, any biosorbents containing several functional groups such as amide, hydroxide, phosphate, carboxylate, and thiols, which can form chemical bonds with the silanol(Si-OH) surface of the silica either by physical or chemical adsorption mechanisms as well as metal ions (Khalid Z. Elwakeel, Ahmed M. Elgarahy, Ziya A. Khan, Muath S. Almughamisi, 2020; Veronica B. Cashina, Daniel S. Eldridgea, 2017).

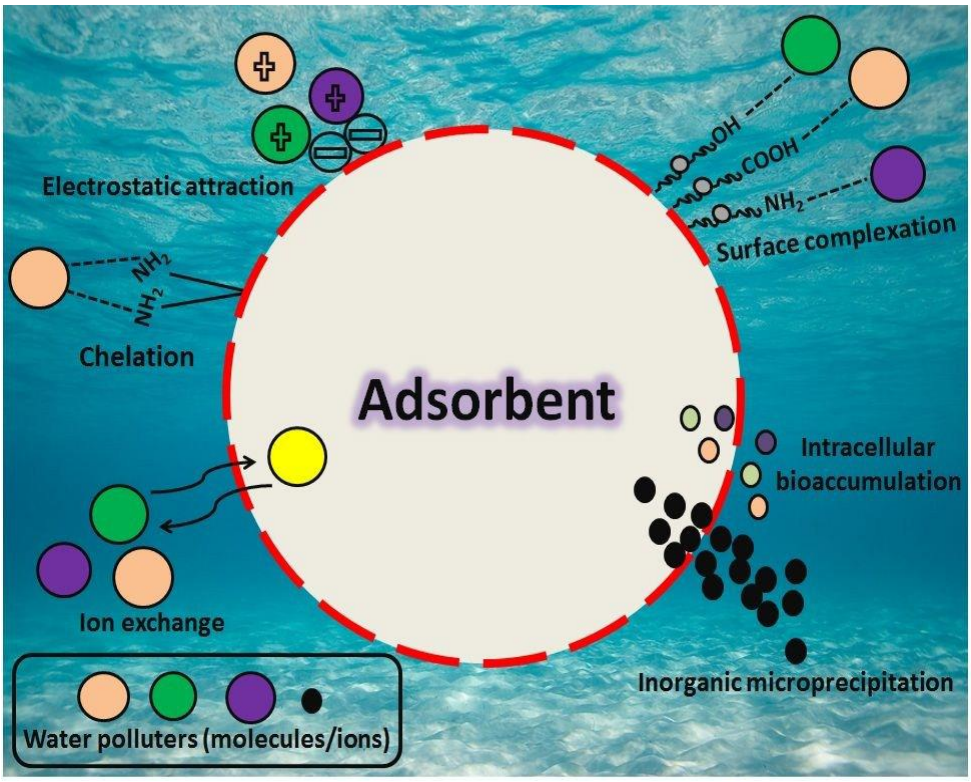


Figure 2.10. Various mechanisms occurring in the adsorption process (Khalid Z. Elwakeel, Ahmed M. Elgarahy, Ziya A. Khan, Muath S. Almughamisi, 2020).

2.6.12. Adsorption isotherms

The most suitable way to evaluate the adsorption process is called the adsorption isotherm. It is important to understand the interrelation between the amounts of adsorbate on the adsorbent surface to its concentration (Bilgiç, 2019; Farrukh, Akram, Ghaffar, Tuncel, et al., 2014). The adsorption isotherm models are used to describe the phenomenon governing the retention (or release) or agility of a substance from the aqueous porous media or aquatic environments to a solid phase at a constant temperature and pH (Aynekugnem, 2015). Langmuir and Freundlich isotherm models are most often employed for assessing the adsorption behavior of the adsorbents.

2.6.12.1. Langmuir adsorption isotherm

The Langmuir adsorption isotherm shows the equilibrium distribution of the metal ions between the solid and liquid phases. This model has been successfully applied to many real adsorption processes. It is based on the following assumptions:

- The adsorbate forms a monolayer on the adsorbent surface.
- The energy of adsorption is constant.

- ❖ The active sites are the same.
- ❖ The presence of interactions between the molecules that are being adsorbed.
- ❖ The adsorbent has a limited adsorption capacity (q_{max}).
- ❖ There is no migration of adsorbate molecules in the surface plane (Aynekugnem, 2015; Bilgiç, 2019; Natu et al., 1984). The equation for Langmuir Adsorption Isotherm can be described as:-Type equation here.

$$\frac{1}{qe} = \left(\frac{1}{ce} x \frac{1}{k_l q_{max}}\right) + \frac{1}{q_{max}} \quad \text{..... (2. 1)}$$

Where, Ce = the equilibrium concentration of metal in the solution (mg/L), qe = the amount of metal adsorbed per gram of the adsorbent at equilibrium (mg/g), q_{max} = maximum monolayer coverage capacity (mg/g), and K_L = langmuir isotherm constant (L/mg).

2.6.12.2. Freundlich adsorption isotherm

It is one of the oldest models which is extensively used, it was developed by Freundlich in 1932**.** The Freundlich adsorption isotherm model is an empirical model expressed by Equations 2.2 and 2.3 and usually interprets the non-ideal and multilayer adsorption. It is an empirical equation employed to describe heterogeneous systems. In this model, it is described that during the adsorption process different sites of the adsorbent are involved with several adsorption energy (Aynekugnem, 2015; Bilgiç, 2019; Natu et al., 1984).

$$qe = k_f ce^{1/n} \text{..... (2.2)}$$

Where qe is the amount of adsorbate per unit weight of adsorbent in equilibrium with a solution concentration Ce in mg/L., Kf and 1/n are Freundlich constants and the characteristics of the system.

$$\log q_e = \log k_f + \frac{1}{n} \log c_e \quad \text{..... (2. 3)}$$

2.6.13. Adsorption kinetics

To estimate the operational efficiency of adsorbents understanding the rate of adsorption is significant. Adsorption kinetics facilitates in analyzing the rate of adsorption, adsorption mechanism, and rate-limiting steps (Farrukh, Akram, Ghaffar, Tuncel, et al., 2014). To determine the rate-limiting step during the adsorption process different kinetic models have

been used to analyze the experimental data. These models include first-order and pseudo-second-order (Uddin et al., 2016).

2.6.13.1. Pseudo first order model

The first-order model is believed to be the earliest model and it was developed by Lagragren in 1898 (Qiu et al., 2009). To describe the kinetic process of liquid-solid phase adsorption he presented the first-order model as:-

$$\frac{dqt}{dt} = K_{p1}(q_e - q_t) \quad \text{..... (2. 4)}$$

Where q_e and qt (mg/g) are the adsorption capacities at equilibrium and time t (min), respectively, K_{p1} (min^{-1}) is the pseudo first order rate constant for the kinetic model. Integrating, Equation 2. 4 with the boundary conditions of qt=0 at t=0 and qt = qt at t=t, gives, $\ln\left(\frac{q_e}{q_e - q_t}\right) = k_{p1}t$ ..... (2. 5)

That can be rearranged to:-

$$\log(q_e - q_t) = \log q_e - \frac{k_{p1}}{2.303}t \quad \text{..... (2. 6)}$$

2.6.13.2. Pseudo-second-order mode

Currently, the pseudo-second-order (PSO) rate equation, popularized by Ho and McKay (Aurich et al., 2017), is probably the most widely used model for adsorption kinetics (Bullen et al., 2021; Ho, 2006). Most of the time this equation is used when the first-order model fails and the equation for this model is written as:-

$$\frac{dq_t}{d_t} = K_2(q_e - q_t)^2 \quad \text{.....,..... (2. 7)}$$

Integrating the equation for the boundary conditions t = 0 to t = t and $q_t = 0$ to $q_t = q_t$, gives:

$$\frac{1}{(qe - qt)} = \frac{1}{qe} + K_2 t \quad \text{..... (2. 8)}$$

q_e is the amount of ions sorbed at equilibrium, mg/ g ; k is the equilibrium rate constant of pseudo-second order sorption, g /mg min.

$$\frac{t}{q_t} = \frac{1}{K_2\, q_{e^2}} + \frac{1}{q_e}t \quad \text{.....(2.9)}$$

And, $h = Kq_{e^2}$ .....(2.10)

Where, h is the initial sorption rate, mg/g min.

2.7. Amino acids and sulfur containg amino acids

Amino acids form stable chelates with various metal ions through the amine, carboxylate, and thiol functional groups (Boles et al., 2021; Shimazaki et al., 2009). Moreover, the twenty common amino acids have characteristic side chains, which vary in size, shape, charge, hydrogen-bonding capacity, and chemical reactivity. This side chain is also an additional metal-binding site and thus can form metal complexes with a variety of structures. Indeed, the metal-binding groups on the side chain, such as imidazole group of histidine, carboxylate group of aspartate and glutamate, phenyl ring of tyrosine, and thiol group of cysteine, serve as metal-binding sites in proteins (Shimazaki et al., 2009; Ulrich & Jakob, 2019; Vandenbossche et al., 2015; Yamauchi et al., 2002). Amino acids can be classified according to their reactive side chain. Amino acids may exist either as uncharged molecules (H_2N-CHR-COOH) or as zwitterions ($^{+}H_3N$-CHR-COO^{-}) depending on the pH of the solution and the isoelectric point (Ismail, Khalili, & Orabi, 2020). Some amino acids have a chemical group that can interact with heavy metals. Sulfur amino acids (SAAs) are a kind of amino acids which contain sulfhydryl, and they play a crucial role in protein structure, metabolism, immunity, and oxidation. Among the SAAs, methionine, and cysteine are considered the primary SAAs. Methionine is an essential amino acid in mammals as it cannot be synthesized in amounts sufficient to maintain the normal growth of mammals. However, cysteine is a semi-essential amino acid in mammals, because cysteine can be produced through the transsulfuration pathway from methionine degradation (Khalil et al., 2001). Therefore, the content of methionine and cysteine is considered to represent the requirement of SAAs in the diet of mammals (Bin et al., 2017). In living organisms, cysteine plays important roles such as protein folding or antioxidant activity depending on the sulfur moiety it contains (Alcock et al., 2018; Guevara-Flores et al., 2017).

2.7.1. L-cysteine (L-Cys)

L-Cysteines are unique among naturally occurring amino acids because of their thiol-containing side chain, which leads to undergoing a variety of different nucleophilic reactions. Because cysteine contains a thiol functional group, it is best to coordinate with cations like heavy metal ions (Ulrich & Jakob, 2019) (Poole, 2015). L-cysteine has a chemical formula of [HO_2CCH (NH_2) CH_2SH] and has three functional groups (-SH, -

NH_2, -COOH) (Figure 2.11). L-cysteine is a hydrophilic amino acid due to the presence of the thiol group whereas, methionine has a hydrophobic and nonpolar aliphatic side chain (Ismail, Khalili, & Orabi, 2020). The Sulfur in the -SH is divalent and gives L-Cys an additional function, acting as an antioxidant. The presence of NH_2 and -COOH functional groups in the structure of L-cysteine provides silica gel a good bio-compatibility and solubility. In addition, the functional groups -NH_2 and -COOH present in modified silica gel contribute well to the removal of heavy metals such as Pb (II) and Cd (II) by forming various complexes (Makkuni et al., 2005; Yablokov et al., 2009) in the wastewater treatment. In the arrangements typically metal-thiolate groups in metallothioneins, the metal ions are coordinated through mercaptide bonds. Thus, cysteine can interact with metals thanks to carboxylic acid, amine, and thiol groups. So cysteine is an important molecule in heavy metals complexation, but surprisingly there are few studies on this amino acid in remediation processes despite its high capacity to chelate heavy metals (Vandenbossche et al., 2015). It is immobilized on the activated silica gel support results from the attachment of the amino group of the cysteine to the hydroxyl group on the silica gel silica support. Some studies concerning remediation processes were applied using L-cysteine (Dakova1 & , P. Vasileva 2, 2011; Ma et al., 2005). Vandenbossche et al (Vandenbossche et al., 2015) reported removal of Hg^{2+}, Cd^{2+}, Pb^{2+}, Ni^{2+}, and Cu^{2+} using Poly-L-cysteine which was prepared from L-cysteine. However, homopolymers are prohibitively expensive and difficult to produce on a large scale. To overcome these problems, some scientists used monomeric amino acids and polypeptides covalently attached to a substrate. Because of their carboxylic and amine groups, amino acids are considered as bidentate chelating agents. L-cysteine is good for metals adsorption because of its mercapto, amino, and carboxyl group (Dakova1 & , P. Vasileva 2, 2011), (Vandenbossche et al., 2015).

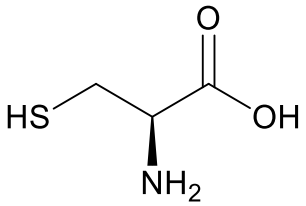


Figure 2.11. Structure of the amino acid L-cysteine

2.7.2. L-methionine (L-Meth)

The second sulfur-containing amino acid is methionine, which is one of the nine essential amino acids in humans. The chemical formula of L-methionine is [$CH_3.S.CH_2.CH_2.CH.NH_2.COOH$] and has an amine functional group (NH_2), carboxyl group (COOH), and thiolether (SCH_3) (Lenz & Martell, 1964; Ramachandran & Natarajan, 2006) (Figure 2.12). L-methionine is a principal supplier of sulfur, prevents disorders of the hair, skin, and nails. L-methionine helps to lower cholesterol levels, thus reducing liver fat and protecting the kidneys. In addition, methionine serves as a natural chelating agent for heavy metals and regulates the formation of ammonia, and creates ammonia-free urine, which reduces bladder irritation (Ramachandran & Natarajan, 2006). L-methionine is not highly nucleophilic, although it will react with some electrophilic centers. However, the thiol (or "sulfhydryl") group of cysteine is ionizable and highly nucleophilic (Poole, 2015). It is generally not a participant in the covalent chemistry that occurs in the active centers of enzymes. Methionine chelates heavy metals, such as lead and mercury aiding their excretion (Lenz & Martell, 1964).

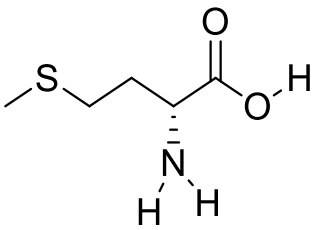


Figure 2.12. Structure of the amino acid L-methionine.

CHAPTR THREE

3. MATERIALS AND METHODS

3.1. Apparatus and equipment

The apparatus and equipment used during this research work were Fourier transform infrared spectrometer(model FT/IR6600, JAPAN), X-ray diffractometer(Shimadzu, XRD-7000S South Korea,), Scanning electron microscope (JCM-6000PLUS Bench Top SEM, JEOL, Japan), Brunauer-emmett and teller (BET) (model nova 4000e, USA). Flame atomic absorption spectrometer(FAAS-210 VGP, USA), Digital electronic balance (FA2104, made in China), Reflux apparatus, Water bath, pH/conductivity meter/TDS(model Mettler-Toledo GmbH), Oven, Crucible, Petri dish, Magnetic stirrers, and Hotplate (JHMS-6293), Magnetic stirrer bar, Filter paper (what man 125mm), Pipettes, Spatulas, Photometer(DR 3900) for phosphate, Heater (model Thermo reactor AL125), Photometer (AL450) for COD & TSS, Erlenmeyer flask, Volumetric flask, Different types of beakers, and Sample collection materials, and Centrifuge (model-LC-O4C).

3.2. Chemicals and reagents

All chemicals and reagents used in this study were analytical grades. Silica gel for column chromatography ≤ 0.063 mm, 200 - 400 meshes(Mumbai.India), amino acids L-cysteine extra pure CHR for biochemistry(Maharashtra.India), L-methionine extra pure CHR for biochemistry(Maharashtra.India), hydrochloric acid (HCl 37%), sodium hydroxide (NaOH) for pH adjustment, nitric acid (HNO_3 (68%)), salt of lead nitrate (Pb $(NO_3)_2$ for stock solution preparation), 1000 mg/L of nickel nitrate (Ni $(NO_3)_2$) standard solution for working solution preparation, and distilled water. In addition, sulfuric acid, acetone, ethanol, and detergents were used for equipment cleaning.

3.3. Sample collection and preparation

3.3.1. Description of the sample collection area

The wastewater samples were collected from the Eastern Industrial Zone (EIZ) in Dukem, Ethiopia. The EIZ of Ethiopia is located, 35 km southeast of Addis Ababa, 10 km to North West of Bishoftu Town, and 63 Km Northwest of Adama Town. EIZ is the first and largest-scale industrial park for Ethiopia. The Ethiopia Ministry of industry needs the EIZ

to focus on Chinese companies in the area of textile, apparel, building materials (including east steel, cement factory), mechanical manufacturing, and agricultural processing. The literatures (Bahiru et al., 2019; Dagne, 2020) reported that 26 Chinese companies are working and manufacturing different products for export markets having an agreement with EIZ in all targeted areas. In addition, to the present 26 manufacturing industries, more than 20 other manufacturing industries are about to join the Eastern Industrial Zone. This suggests that more wastewater from the various industry of EIZ is discharged to the surrounding through one wastewater channel; this wastewater is used as a source of irrigation water by the farmers around this industry's area.

3.3.2. Wastewater sample collection and preparation

Bottles used for collecting wastewater samples were previously washed carefully with detergent and 1M HNO_3 and rinsed with water samples at the point of collection. Care was taken not to introduce errors during sampling and storage where contamination resulted from improperly cleaned sampling devices and sample containers. Loss of metals or precipitation in sample containers was avoided by acidifying the sample properly using 1.5 mL of HNO_3 to pH < 2.

The wastewater samples were collected from discharging points of EIZ. A total sample volume of 2 L using plastic bottles was collected during the month of July 2021. The bottle was immediately acidified with 1.5 mL nitric acid after being collected, for later analysis of metal concentrations. The purpose of the acid was to keep the metals in solution and to avoid adsorption to the container walls (Dagne, 2020).

3.3.3. Physico chemical analysis of wastewater sample

3.3.3.1. pH

The intensity of acidic and basic character of a solution is indicated by pH or hydrogen ion, at a given temperature. The pH of the wastewater sample was measured using the pH meter (Mettler toledo). The pH meter was calibrated by using two standard buffer solutions of pH (4 and 7). Then the pH electrode was immersed into the wastewater sample and waited up to some minutes for a stable reading. Finally, the value was recorded.

3.3.3.2. Conductivity and total dissolved solid (TDS)

Both conductivity and total dissolved solids were measured using a Mettler toledo conductivity meter. First, the conductivity meter was calibrated using conductivity standard 4000 (µS/cm). Then electrode was immersed into a wastewater sample, and the mode of the instrument was set for each measurement. The conductivity and TDS value were reported as micro siemens per centimeter (µS/cm) and milligram per litter (mg/L), respectively.

3.3.3.3. Chemical oxygen demand (COD) determination

Chemical oxygen demand (COD) is used to measure the capacity of water to consume oxygen during the decomposition of organic matter and the oxidation of inorganic chemicals.

The COD was measured using the Photometer AL450 instrument. First, 0.2 mL wastewater sample and blank sample (disteled water) were added into COD reagent vials separately, and then added filled COD vials were to a reactor at 150 ^{o}C for two hours this would digest the sample and cause a color change. Finally, once cooled, the photometer became zero at 610 nm using a blank sample. The vial was tested in a photometer to given reading and the COD reported in mg/L (Lovibond, 2017).

3.3.3.4. Phosphate determination

The phosphate value was measured by using DR 3900 photometer in the potassium persulfate digestion method. First, 5 mL of wastewater sample was added into total phosphorous test vial, and then added one potassium persulfate powder into the vial. After that the samples were heated by a heater (model Thermoreacter AL125) at 100 ^{o}C for a half-hour, the samples were cooled at room temperature, and 2 mL of 1.54 N Sodium hydroxide was added into the vial. The photometer instrument was set and become zero at 880 nm. Finally, the sample was measured and the value was recorded (Company, 2014).

3.3.3.5. Total suspended solid (TSS) determination

The TSS was measured using the Photometer AL450 instrument in the direct reading method. Firstly, 10 mL of distilled water was added to a 24 mm cleaned vial. The instrument became zero using a blank sample. The TSS value was measured at 660 nm in mg/L and the value was recorded (Lovibond, 2017).

3.3.4. Preparation of standard stock solutions and working solutions

By dissolving 1.59845 g of Pb $(NO_3)_2$ salt, in 1000 mL of distilled water, a stock solution of 1000 mg/L Pb (II) was prepared. The progressive dilution procedure of the stock solution was employed in the preparation of working solutions. The working solutions of nickel ion were prepared from a commercially available 1000 mg/L standard solution. Standards Ni (II) samples at a required concentration were prepared using an appropriate dilution of the stock solution. The pH of the working solutions were adjusted to the required values with 0.1 M NaOH or 0.1 M HCl.

3.3.5. Preparation of silica gel (activation of silica gel)

Activation of commercially available silica gel was carried out by refluxing 50 g of silica gel with 187 mL (6 M) of concentrated hydrochloric acid (37% HCl) for 24 h (a temperature ranging 70-80 °C) with stirring on the water bath twice. Then the silica gel was filtered, washed with, disteled water several times until it was free of acid, and dried in an oven with a temperature ranging between 150-160 ^oC for 8h (Alghanmi, 2012; Kırkan & Aycik, 2016; Svraka et al., 2014).

3.4. Modification of activated silica gel

Each 4.5 g of L-cysteine, L-methionine, and mixture of L-cysteine and L-methionine were added in 300 mL disteled water separately and stirred until the solution was formed, then 25.5 g of activated silica gel was added to each solution (in 1.5 to 8.5 ratio) and mixed for 120 min, and filtered while heating at a temperature of 180 ^oC in an oven for 5 min. The filitered amples were rinsed with deionized water (300 mL x 3, disteled water for each) and centrifuged to remove unreacted L-cys and L-meth, finally dried in an oven at 100 ^oC for 30 min (Xu et al., 2017; Zhou, Cai, Xu, Zhang, & Fu, 2018) The method of taking an 8.5 : 1.5 ratio of activated silica gel and amino acids were performed by modifying the procedure proposed by Petrova et al., (Petrova et al., 2017b) (Appendix, Figure VI-1,).

3.5. Characterization

In this thesis the activated silica gel and its modified forms; activated silica gel with L-cysteine (SiO_2-Cys), activated silica gel with L-methionine (SiO_2-Meth), and activated silica gel with mixture of L-cysteine and L-methionine (SiO_2-(L-Meth + L-Cys)) were characterized by Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), Scanning electron microscope (SEM), and Brunauer -Emmett- Teller (BET) methods.

3.5.1. Fourier-transform infrared spectroscopy (FTIR) characterization

The FTIR spectra of SiO_2, SiO_2-(L-Cys + L-Meth), SiO_2-Cys, SiO_2-Meth, L-Cys, and L-Meth were recorded by FT/IR-6600typeA FTIR spectrometer in the range of 400 – 4000 cm^{-1} using the KBr disc method. For FTIR characterization, 1mg of the sample and 100 mg of potassium bromide were mixed with mortar and pestle. Then a small amount of powder from the mixture was pelletized using a mechanical presser and finally, the pellet was analyzed using a Fourier transform infrared spectrometer.

3.5.2. X-ray diffraction (XRD) characterization

The XRD was performed to investigate the crystalline or amorphous nature of the activated silica gel (SiO_2) and modified activated silica gel ((SiO_2-Cys, SiO_2-Meth, SiO_2-(L-Cys + L-Meth)) (Rius, 2015). The XRD of the adsorbents SiO_2, SiO_2-Cys, SiO_2-Meth & SiO_2-(L-Cys + L-Meth)) were tested at ASTU research laboratory of Material Science and Engineering Department using an X-ray diffractometer. The mass of approximately 1.5 g of the adsorbent samples was measured for each adsorbent from already prepared samples for XRD characterization and filled in a sample holder. Then the sample was analyzed by using an X-ray diffractometer with Cu-Kα radiation source at λ= 1.5418 Å and operating at 40 kV and 30 mA. X-ray diffractograms of ASG and its modified form powders were obtained for the 2θ angles scan range from 5˚ to 85˚ with scans step 0.02˚. All the experiments were done at room temperature, with a scans speed of 3˚/ min, and a counting time of 0.40 sec.

3.5.3. Scanning electron microscope (SEM) characterization

The SiO_2, SiO_2-Cys, SiO_2-Meth, and SiO_2-(L-Cys + L-Meth) were characterized by a scanning electron microscope using a high-energy electron, and the outcoming electrons are analyzed (by applying a 10 kV electron acceleration voltage). These coming electrons give information about morphology, composition, the orientation of grains, and crystallography information of material. It provides information about the surface features and texture, shape, size, and arrangement of the particles on the sample's surface (Grégorio Crini, Eric Lichtfouse, Lee Wilson, 2018)(S. K. Sharma et al., 2018). For SEM, 30 mg sample of ASG and its modified form were measured from the previously prepared sample and characterized by using scanning electron microscope.

3.5.4. Brunauer-Emmett -Teller (BET) characterization

Adsorption is a surface phenomenon and the degree of adsorption is proportional to the specific surface area. The adsorption capacity of adsorbents becomes higher if the solid is more finely-divided and more porous. The BET method can be used for the characterization of various types of microporous materials (Ambroz et al., 2018). The SiO_2, SiO_2-Cys, SiO_2-Meth, and SiO_2-(L-Cys + L-Meth) were characterized by the Brunauer-Emmett-teller instrument. For BET characterization the empty samples cell were weighed using an electronic balance and 0.1 g of the samples were placed in the empty samples cell for each adsorbents. Then the samples were degassed at temperature 300 ˚C for 9 h to remove impurity in the degas station of pore size and surface area analyzer according to the international union of pure and applied chemistry (IUPAC). After degassing, 0.05 g of the sample was placed in the analysis station in the range of 0.1 to 0.99 relative pressures and 10 psi of nitrogen gas using Brunauer-Emmett-teller (BET).

3.6. Optimization and modification method selection

3.6.1. Modification of activated silica gel using two alternative methods

Method 1

Each 1.5 g of L-cysteine, L-methionine, and a mixture of L-cysteine and L-methionine were added in 100 mL, disteled water separately and stirred for a 60 min until a solution was formed. Then 8.5 g of activated silica gel was added to each solution and mixed for 45 min, filtered and dried in an oven for 5 min at 180 ^{o}C and washed with disteled water to remove unreacted L-Cye and L-Meth and finally, dried in an oven at 100 ^{o}C for 30 min (Zhou, Cai, Xu, Zhang, Fu, et al., 2018) (Petrova et al., 2017b) (Figure 3.1).

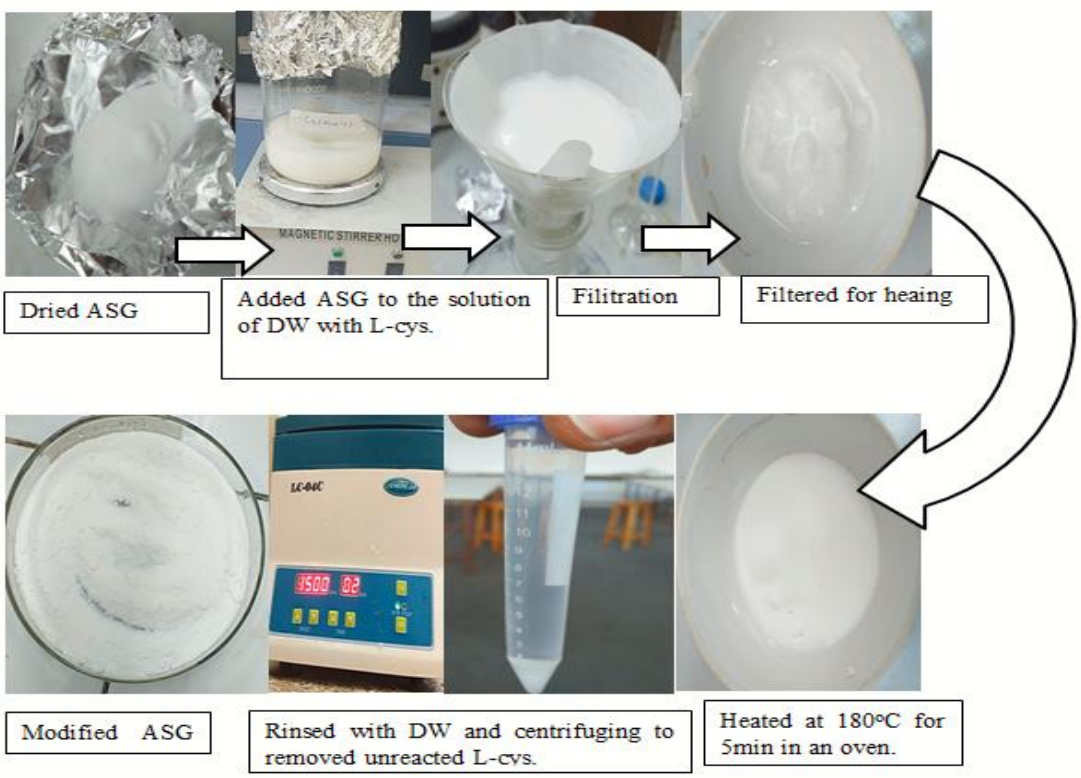


Figure 3.1. Modification of activated silica gel by L-Cys using method one.

Method 2

Each 1.5 g of L-cysteine, L-methionine, and a mixture of L-cysteine and L-methionine were added in 100 mL, disteled water separately and stirred until the solutions were formed. Then 8.5 g of activated silica gel were added to each solution and mixed for 48 h, centrifuged, washed several times with disteled water to remove unreacted L-cysteine and L-methionine, and finally dried at room temperature to a constant weight (Ismail, Khalili, & Orabi, 2020) (Figure 3.2).

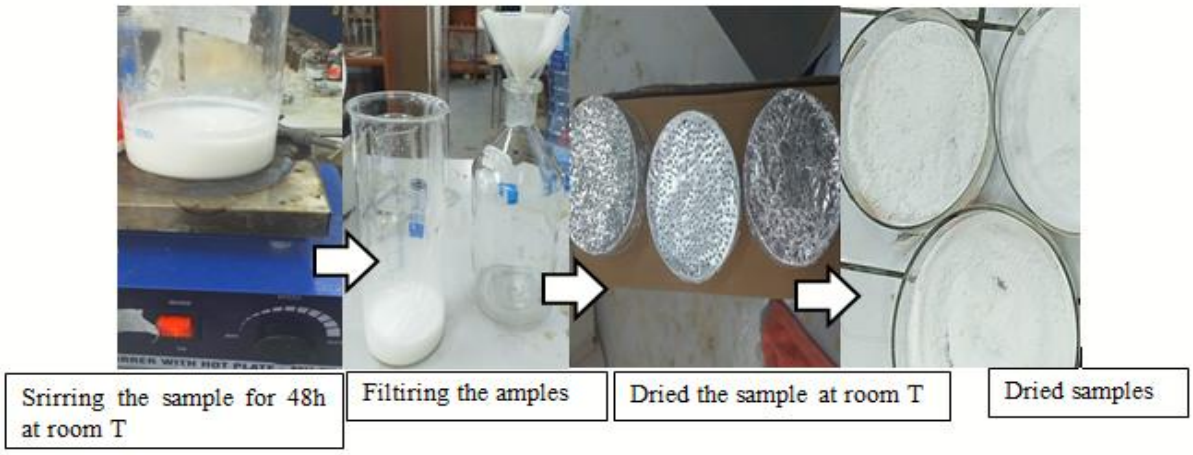


Figure 3.2. Modification of activated silica gel using method two.

The samples prepared using both methods were sent for FT-IR characterization to select one of the best methods. Both methods are expected to shows high modification resulte. Because, on the previouse literatures (Ismail, Khalili, & Orabi, 2020; Xu et al., 2017; Zhou, Cai, Xu, Zhang, & Fu, 2018) they were reported as better modification methods.

3.7. Batch adsorption experiments

All adsorption experiments were carried out in batch mode because of their simplicity and reliability for small-scale investigations (S. K. Sharma et al., 2018). Adsorption experiments were conducted for lead and nickel ions by varying at pH (5, 6, 7, 8, and 9), keeping other parameters constant (contact time 60 min, dose 0.2 g per 0.05 L of metal solution, agitation speed 160 rpm. The pH range [5-9] was selected because, most literature reported that the maximum Pb and Ni ions removal efficiency was obtained on this pH range (Dakova1 & , P. Vasileva 2, 2011). Further, the pH value depends on the pKa values of various functional groups such as carboxylic acid groups attached to the amino acid (L-cysteine and L-methionine) range from 3.5 to 5.5 and also the Si-OH group in the silica gel surface exist as deprotonated form at a pH (>2). There for, this indicates that these groups deprotonate in this specific pH working range, ranging pH [5-9] have advantages for adsorbent surface possess negatively charged adsorption sites and it is important for the adsorption process (Ismail, Khalili, & Abu Orabi, 2020) (Khalid Z. Elwakeel1, 2, Ahmed M. Elgarahy 3, Ziya A. Khan1, Muath S. Almughamisi1 & 1, 2020). In most of the literature (Bilgiç, 2019; Kushwaha et al., 2012) agitation speed for adsorption based on silica gel adsorbents were used at 200 rpm. However, for this study, it was 160 rpm. Because, using above 160 rpm agitation speed was not possible for the shaker present in

ASTU, Applied biology department laboratory. The adsorption was carried out at room temperature (Xu et al., 2017; Zhou, Cai, Xu, Zhang, & Fu, 2018) and initial concentration 10 and 3.5 for Pb(II) and Ni(II) respectively. Contact time (30, 60, 90, 120, and 150 min) (Mengistie*, 2013), initial concentration of metal ion (0.5, 2, 4, 6, 8, and 10 mg/L) and (0.5, 2, 3.5, 5, and 6.5 mg/L) for Pb (II) and Ni (II) respectively, the initial concentrations range were selected based on the literature reported that for the concentration Pb and Ni ions present in wastewater sample taken from EIZ and Modjo tannery share company respectively, were in this range. The adsorbent dose (0.2, 0.4, 0.6, 0.8, and 1g) was selected and studied based on the literatures (Ismail, Khalili, & Orabi, 2020; Mengistie*, 2013). In these optimization procedures, one parameter was varied while the others were kept constant. The pH of each solution was adjusted to the desired value by adding 0.1 M HCl and 0.1 M NaOH. The agitation of the samples was carried out in shakers using 250 mL Erlenmeyer flasks and the total volume of the reaction mixture was kept at 50 mL (Alghanmi, 2012; Dakova et al., 2011; Kushwaha et al., 2012). The mixtures were filtered through Whatman No. 125 mm filter paper. The filtrates were analyzed by flame atomic absorption spectrometry. The concentration of lead and nickel ions were measured at 283.2 nm and 341.5 nm wavelength, 0.7 and 0.2 nm slit width, 2.0 and 7.0 mA lamp current, 2.874 and 2.624 eV energy, and detection limit of 0.040 and 0.020 mg/L for lead and nickel ions respectively. The FAAS was adjusted to measure each sample. The percent adsorption efficiency and the milligram of Pb (II) and Ni (II) adsorbed per gram of adsorbent were calculated using Equations 3.1 and 3.2 respectively.

$$\%R = \left(\frac{C_o - C_f}{C_o}\right) x\ 100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (\mathbf{3.1})$$

Where %R is percent removal C_o is initial concentration and C_f concentration after adsorption.

$$q = \frac{(C_o - C_f)\mathrm{v}}{\mathrm{m}} x100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (\mathbf{3.2})$$

Where q is metal removal in mg/g (Pb (II) or Ni (II)), C_o is initial concentration, C_f concentration after adsorption, m is adsorbent mass in gram and v is volume of polluted water used during the experiment (Petrova et al., 2017b).

3.8. Determination of the concentration of Pb and Ni ions in real sample

The determination of the concentrations of Pb(II) and Ni(II) in a real sample was carried out by analyzing the wastewater sample that was obtained from the discharge point of EIZ. The sample was analyzed for the determination of the concentration of lead(II) and nickel(II) using FAAS before the adsorption experiment (Dagne, 2020). Before being analyzed by FAAS, a 100 mL sample of EIZ wastewater was first filtered into a 100 mL borosilicate glass beaker using filter paper and digested by adding 3 mL concentrated nitric acid (HNO_3). Then the mixture was boiled gently on a hot plate at a tamperture range 70 to 85 for 1–2 h until a clear solution was obtained. Later, 1.5 mL of HNO_3 was added followed by further heating until total digestion(Dagne, 2020; Uddin et al., 2016). And finally, 20 mL of digested sample was diluted to 100 mL volumetric flask using disteled water and the concentrations of Pb(II) and Ni(II) were determined using FAAS. To investigate the removal efficacy of Pb(II) by the adsorbent SiO-(L-Cys + L-Meth) from real EIZ wastewater sample. After obtaining the result of the amount of lead(II) and nickel(II) from analysis of EIZ wastewater sample. Then added 50 mL of wastewater sample in Erlenmeyer flask to study the adsorption efficiency of SiO_2-(L-Cys + L-Meth) powder was evaluated; under constant pH (6), contact time (90 min), and dose (0.8 g) of adsorbent. With the optimum condition set, SiO_2- (L-Cys + L-Meth) powder was subjected to 0.645 mg/L initial concentrations of lead (II). Adsorption efficiency in percent and milligram of Pb(II) adsorbed per gram of adsorbent was calculated using Equations 3.1 and 3.2, respectively.

3.9. Determination of adsorption models

After identifying the optimum conditions of adsorption parameters, kinetic and isotherm studies were carried out to differentiate the adsorption mechanism that occurred through the adsorption process. The adsorption kinetic studies were carried out by varying contact time (60-150 min) and keeping the other parameters constant. The experimental contact time variation data were carried out for lead and nickel ions at 10 and 3.5 mg/L initial concentration, pH 6 and 5 for lead and nickel ions respectively, and 0.2 g of SiO_2-(L-Cys + L-Meth), 160 rpm agitation speed, and at temperature room temperature for both ions. The adsorption isotherm studies were carried out by varying the adsorbate Pb(II) and Ni(II) concentration around the optimum condition obtained in the optimization procedure. The experimental adsorbate lead and nickel ions concentration variations were carried out (2-10

mg/L, with 2 interval) and (0.5-6.5, with 1.5 interval), at pH 6 and 5, contact time 90 and 60 min for Pb(II) and Ni(II) respectively, and 0.2 g of SiO_2-(L-Cys + L-Meth), agitation speed 160 rpm, and 25 ^oC temperature for both ions.

The adsorption isotherms were analyzed using the Langmuir and Freundlich isotherm models. The kinetics was also studied by pseudo-first-order and pseudo-second-order models. Satisfactory conformity between experimental data and the model-predicted values was expressed by the correlation coefficient (R^2).

3.10. Comparison of different adsorbents on the removal of Pb and Ni ions

In this study, the efficiency of adsorbents ASG(SiO_2) and its modified forms: SiO_2-(L-Cys + L-Meth), SiO_2-Cys, and SiO_2-Meth were compared. The experiment was carried out using pH 6 and 5, dose 0.8 and 0.4 g per 0.05 L metal solution, Contact time 90 and 60 min for Pb(II) and Ni(II) respectively, and initial concentration 2 mg/L, agitation speed 160 rpm, and room temperature for both Pb(II) and Ni(II).

3.11. Regeneration and desorption studies

The Pb and Ni ions removal efficiency of SiO_2-(L-Cys + L-Meth) for three consecutive adsorption−desorption cycles were investigated. The desorption and regeneration studies were carried out using optimized condtions, with 0.8 g of adsorbent SiO_2-(L-Cys + L-Meth) for Pb(II) and 0.4 g for Ni(II) was introduced into Erlenmeyer flasks containing 50 mL of 2 mg/L of each metal ion solution [Pb(II) and Ni(II)] separately, at pH 6 and 5 and contact time 90 and 60 min for Pb(II) and Ni(II) respectively. The exhausted SiO_2-(L-Cys + L-Meth) was regenerated with 0.1 M HCl. Then SiO_2-(L-Cys + L-Meth) was shaken with 2 mg/L Pb^{2+}/Ni^{+2} using optimized parameters under room temperature and 160 rpm agitation speed. Then equilibrium concentration was measured using FAAS. The adsorbent was recovered by filtration. The Residual metal ions [Pb(II) and Ni(II)] on the SiO_2-(L-Cys + L-Meth) adsorbent surface were detached (desorbed) through washing several times using distilled water and 0.1 M HCl, then dried in an oven at 50-70 °C to constant mass. The recovery of the adsorbent using disteled water and HCl was done three times and investigated the degree of adsorption (Bayuo et al., 2020; Radi et al., 2018). To investigate the degree of adsorption of the recycled adsorbent after adsorption. The filtrate was analyzed by FAAS and recorded the result. The percent adsorption efficiency and the

milligram of Pb(II) and Ni(II) adsorbed per gram of adsorbent were calculated using Equations 3.1 and 3.2, respectively.

CHAPTER FOUR

4. RESULTS AND DISCUSSION

4.1. Characterization of unmodified and modified silica gel adsorbents

In this thesis, the activated silica gel (ASG) and its modified forms:- ASG modified with L-cysteine (SiO_2-Cys), L-methionine (SiO_2-Meth), and a mixture of L-cysteine and L-methionine (SiO_2-(L-Cys + L-Meth)) were characterized by Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), Scanning electron microscopy (SEM), and Brunauer-emmett-teller (BET) method.

4.1.1. Fourier-transform infrared spectroscopy (FTIR) analysis results

The infrared spectra is a fingerprint for identification by the comparison of the spectra from an ‘‘unknown’’ with previously recorded reference spectra. The vibrational spectra of a molecule is considered to be an important physical property. It is a unique characteristic of the molecule (Aynekugnem, 2015), (Coates, 2004).

The results FTIR spectra of ASG (SiO_2), SiO_2-(L-Cys + L-Meth), SiO_2-Cys, and L-Cys are shown in Figure 4.1 while the FTIR spectra of ASG (SiO_2), SiO_2-(L-Cys + L-Meth), SiO_2-Meth and L-methionine are shown in Figure 4.2. All of the characteristic bands are listed in Table 4.1. The immobilization onto the activated silica gel surface can be confirmed through Fourier transform infrared (FTIR) spectra for the silica. The FTIR spectra of SiO_2, SiO_2-(L-Cys + L-Meth), SiO_2-Cys, and L-cysteine were compared. As shown in Figure 4.1, ASG has broadband between 3650-3000 cm^{-1} because of the presence of hydroxyl functional group of silanol (–Si-OH) part of ASG. However, FTIR spectra, SiO_2-(L-Cys + L-Meth) and SiO_2-Cys showed that a narrow peak compared with that of the spectra of activated silica gel because for modified activated silica gel with L-Cys and mixture of L-Cys and L-Meth have showed ammonium group attached to the silanol (–Si-OH).These results demonstrated that the ASG was successfully modified with a mixture of L-Cys and L-Meth, and L-cysteine.

FT-IR spectra of SiO_2 showed a band at 1099 cm^{-1} because of asymmetric stretching of Si–O–Si and symmetric stretching were observed at 804 cm^{-1} (Bilgiç, 2019) . The Si–O–Si bending mode was positioned at 551 cm^{-1} (Ismail, Khalili, & Orabi, 2020). The characteristic peaks of the Si–O–H groups of the ASG (SiO_2) were observed at 979 cm^{-1} and also abroad and a strong band at around 3477 cm^{-1} is due to the stretching vibration of the H-bonded silanol group (–Si-OH) along with H–OH vibration of the water molecules (–OH) adsorbed on the activated silica gel surface. Further, the peak observed at 1640 cm^{-1} validates the presence of physically adsorbed water molecules in the ASG (SiO_2) samples,(Kırkan & Aycik, 2016).

As shown in Figure 4.1 the broad peak at 3409 and 3435 cm^{-1} for SiO_2-(L-Cys + L-Meth) and SiO_2-Cys respectively, correspond to the ammonium ($-NH_3^+$) asymmetric stretching band (Ismail, Khalili, & Orabi, 2020). Also, the peaks were appearing at 1634 and 1628 cm^{-1} are the COO^- asymmetric stretching of SiO_2-(L-Cys + L-Meth) and SiO_2-Cys respectively, N-H bending peaks appearing were at 1582 and 1589 cm^{-1} for SiO_2-(L-Cys and L-Meth) and SiO_2-Cys, respectively and also COO^- symmetric stretching peaks appearing were at 1486 and 1490 cm^{-1} for SiO_2-(L-Cys + L-Meth) and SiO_2-Cys respectively. The existence of ammonium and carboxylate peaks show that L-cysteine molecules exist in zwitterion form for both SiO_2-(L-Cys + L-Meth) and SiO_2-Cys. In addition, a weak band of thiol (S-H) group present on the surface of SiO_2-(L-Cys + L-

Meth) at 2590 cm^{-1} and 2596 cm^{-1} for SiO_2-Cys is attributed to the S-H stretching in L-cysteine, so the presence of this band indicated that sulfur atom is not bound to silanol groups.

Generally from the spectral analysis present in Figure 4.1 modification of ASG with a mixture of L-Cys and L-Meth and L-Cys successfully achieved (Ismail, Khalili, & Orabi, 2020)(Chen et al., 2013). FTIR spectrum for the SiO_2-Meth in (Figure 4.2) showed a broad peak at 3446 cm^{-1} corresponding to the ammonium asymmetric stretching band. Additional peaks appearing at 1634 and 1643 cm^{-1} were related to COO^- asymmetric stretching, N-H bending stretching was appearing at 1582 and 1509 cm^{-1}, and S-C stretching band was appearing at 1335 and 1386 cm^{-1} for SiO_2-(L-Cys + L-Meth) and SiO_2-Meth, respectively. The differences in the spectra for activated silica gel and modified ASG (SiO_2) with a mixture of L-cysteine and L-methionine, L-cysteine or L-methionine indicated that the amino acids were successfully attached to silanol group or silica surface through the ammonium or carboxyl group. In general, the FTIR result obtained in this study is more similar to the previously reported literature for U(VI) removal from aqueous solution using modified silica nanoparticles with cysteine or methionine (Ismail, Khalili, & Abu Orabi, 2020). Further, the result is similar to the previous study for a different application that's for excellent binding effect of L-methionine for immobilizing silver nanoparticles onto cotton fabrics to improve the antibacterial durability against washing (Zhou, Cai, Xu, Zhang, Fu, et al., 2018), and antibacterial cotton fabric with enhanced durability prepared using L-cysteine and silver nanoparticles (Xu et al., 2017). For the former literature, the interaction(modification) mechanism between silica and amino acid were reported by electrostatic attraction between the amino($^+NH_3$) group of the amino acids and the hydroxyl group(-OH) of the silica nanoparticles because amino acids may exist either as uncharged molecule (H_2N-CHR-COOH) or as zwitterions (^+H_3N-CHR-COO^-) depending on the pH of the solution and the isoelectric point. The expected functional groups were reported by analyzing with FTIR. The FTIR spectrum for the modified silica nanoparticles with cysteine and methionine are obtained comparable results with this study. On the other hand, the latter two studies reported that the interaction between the cotton fabrics and the amino acids were through an esterification reaction between hydroxyl groups of cotton fabric and the carboxyl group of the amino acid.

This thesis used silica gel in place of cotton fabrics because both contain hydroxyl functional groups, the FTIR result obtained in this study also similar with the two but, they showed that the cysteine and methionine modified cotton exhibit new peaks at 1725 and 1742 cm^{-1} respectively, after the modification process. The peak is attributable to the C=O (ester group) (Xu et al., 2017) or to the asymmetric stretching of COOH groups and COOR groups (Zhou, Cai, Xu, Zhang, & Fu, 2018), implying that the esterification reactions occurred between the L-methionine/L-cysteine and the hydroxyl groups of cellulose on the cotton surface. Similarly, in this study, the presence of the C=O group was expected due to the reaction conditions (such as heating at 180 ˚C for more than 2 min) for esterification with the hydroxyl groups of cotton fabric (silica gel) have been well recognized (Zhou, Cai, Xu, Zhang, & Fu, 2018). But as shown in Figures 4.1 and 4.2 there is no spectrum ranging between 1715-1750 cm^{-1}(ester group). This may be result of the lower number of scans or there may exist peak overlapping and it may have existed around 1900-1700 cm^{-1}. Whatever the interaction between silica gel and amino acid through electrostatic interaction or esterification reaction process, it is significant to have a free S-H(thiol) group for silica gel modified with L-cysteine and thioether ($–S-CH_3$) for silica gel modified by L-methionine for the metal ion binding. From the FTIR result, these groups are existed as shown in Figures 4.1 and 4.2, and confirm the modification of silica gel with the amino acids.

In this thesis, for silica gel modification method selection based on the FT-IR results acquired activated silica gel modified with amino acids using method one was selected(Figure 4.3, 4.4 & 4.5). Because there was no significant difference between the two methods of FT-IR results obtained in the functional group present on the adsorbents. Therefore modification of activated silica gel using method one was preferable because of its simplicity and time-saving. So modified activated silica gel using method one was selected for the adsorption experiment .

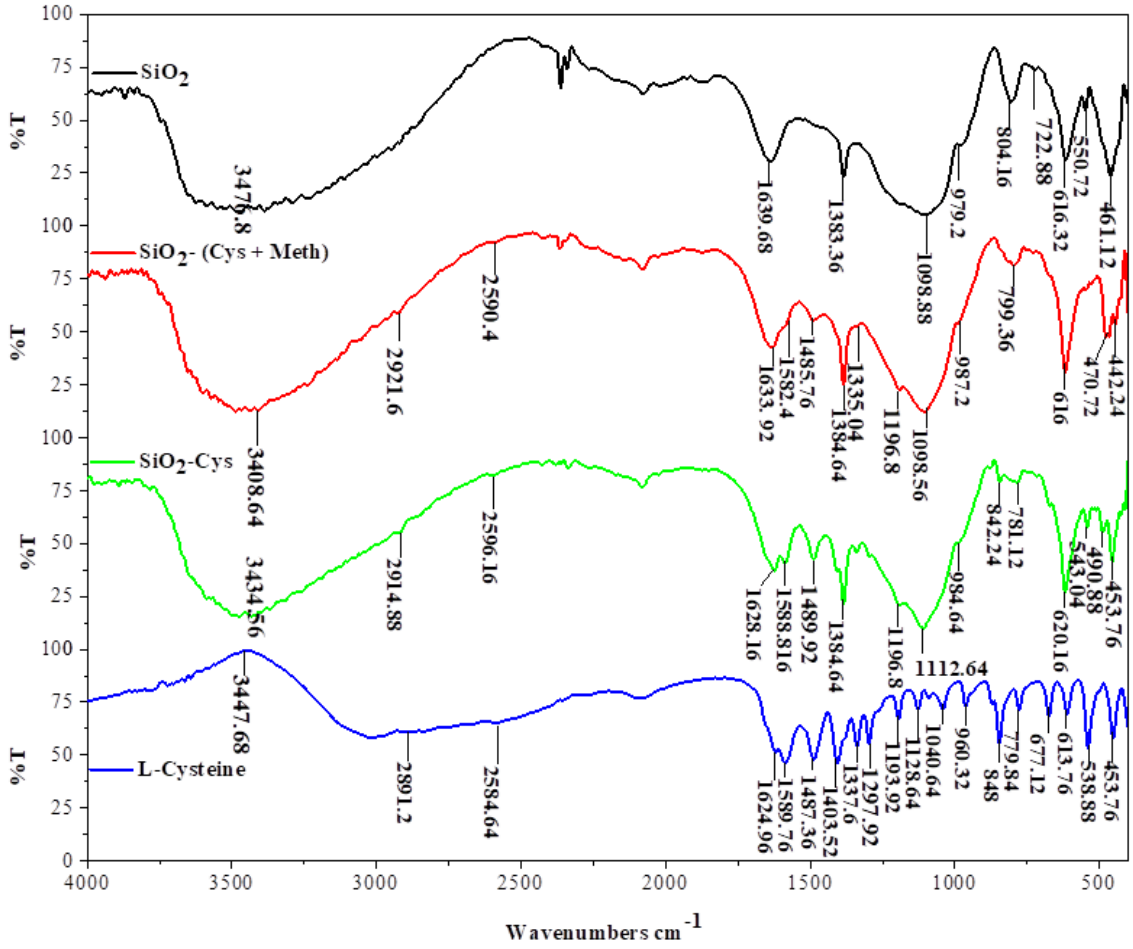


Figure 4.1 FTIR spectra for the SiO_2, SiO_2-(L-Cys + L-Meth), SiO_2-Cys and L-Cys.

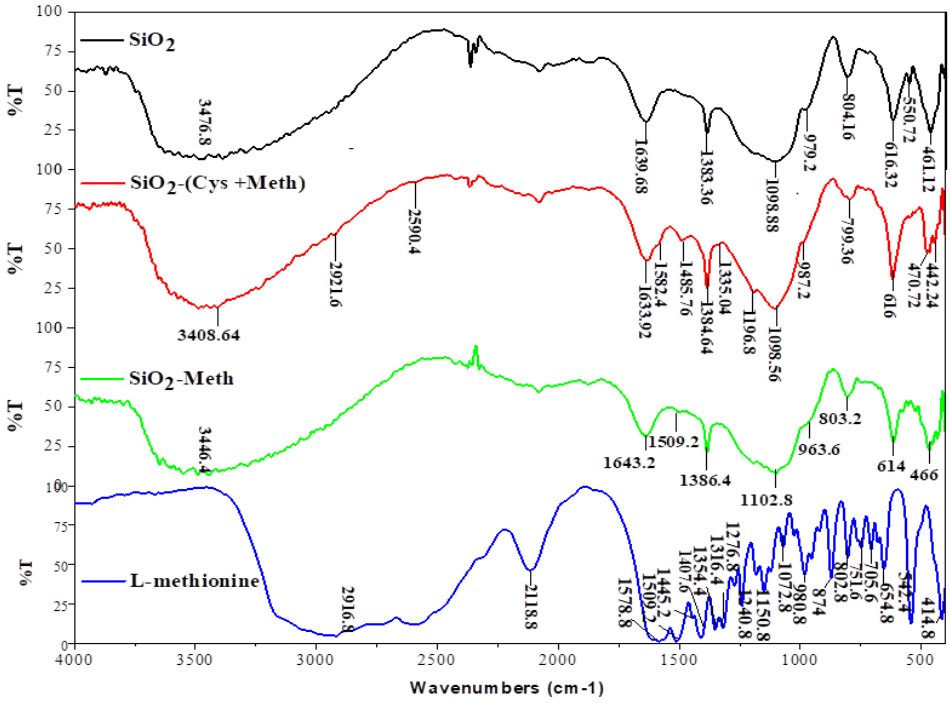


Figure 4.2 FTIR spectra for SiO_2, SiO_2-(L-Cys + L-Meth), SiO_2-Meth, and L- Meth.

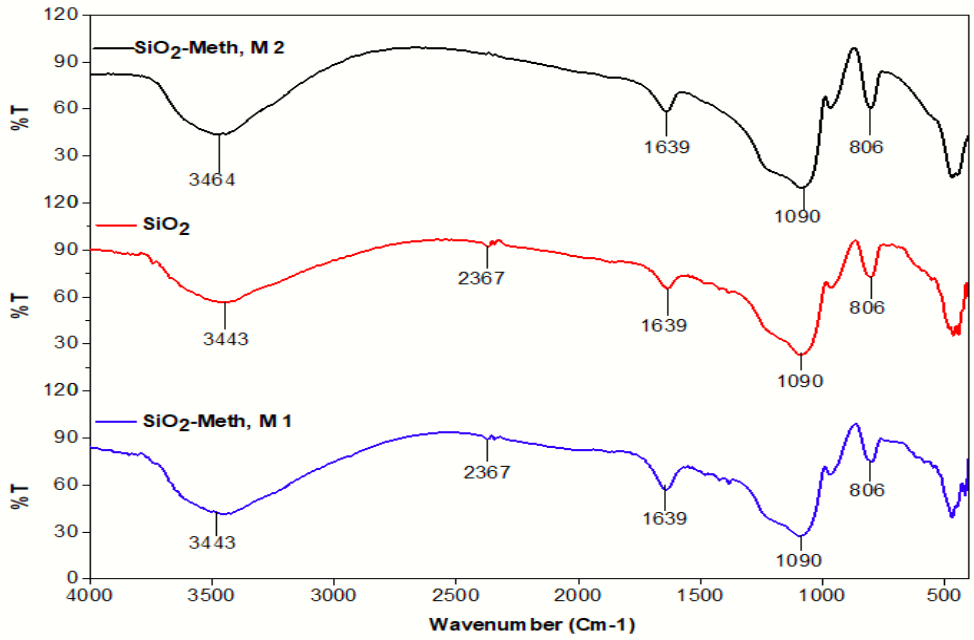


Figure 4.3 FTIR spectra for SiO_2, and SiO_2-Meth, M 1 (silica gel modified by L-Cysteine using method one), M 2 (silica gel modified by L-Cysteine using method two).

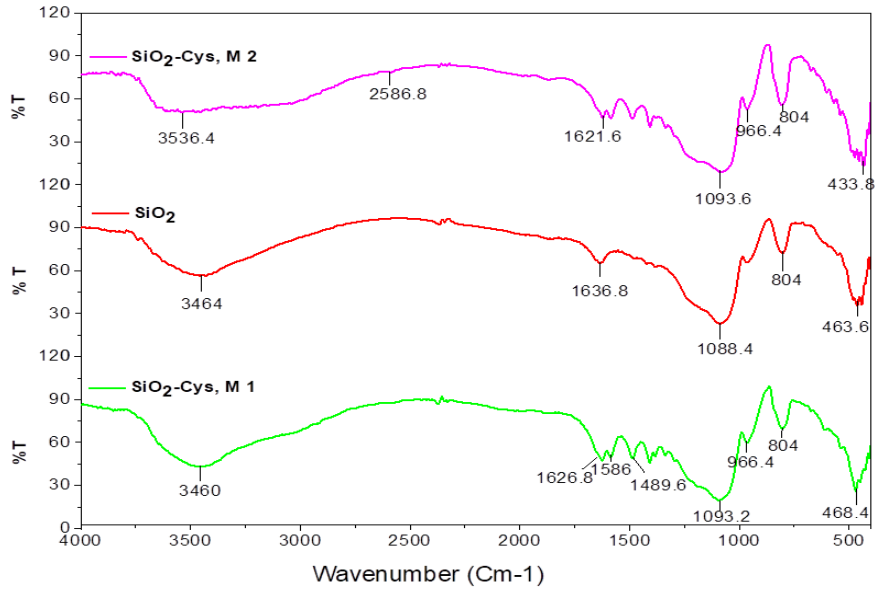


Figure 4.4 FTIR spectra for SiO_2, and SiO_2-Meth, M 1 (silica gel modified by L-methionine using method one), M 2 (silica gel modified by L-methionine using method two).

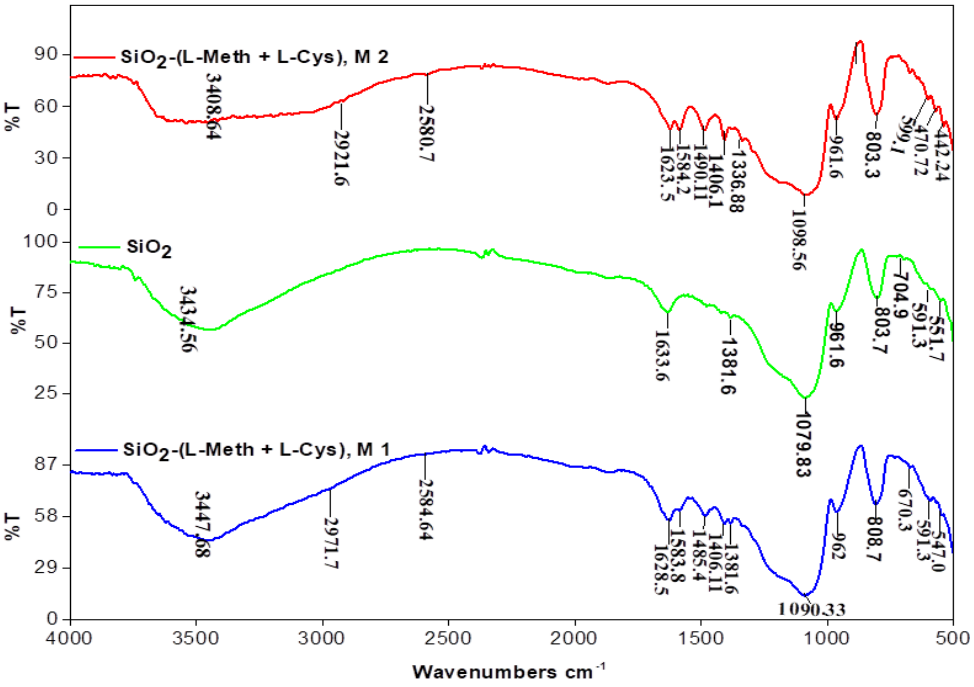


Figure 4.5 FTIR spectra for SiO_2, and SiO_2-(L-Cys + L-Meth), M 1 (silica gel modified by mixture of L-Cys and L-Meth using method one), M 2 (silica gel modified by mixture of L-Cys and L-Meth using method two).

Table 4.1. Characteristic FTIR bands for ASG and its modified forms.

Assignment	SiO_2 Band (cm^{-1})	SiO_2-(Cys + Meth) Band (cm^{-1})	SiO_2-Cys Band (cm^{-1})	L-Cys Band (cm^{-1})	SiO_2-Meth Band (cm^{-1})	L-Meth Band (cm^{-1})
Si–O–Si asymmetric	1099	1099	1113	–	1103	–
Si–O–Si symmetric	804	799	781	–	803	–
Si–O–Si bending	551	471	454	–	466	–
Si-OH stretching	979	987	985	–	964	–
$–NH_3^+$ asymmetric	. –	3409	3435	–	3446	–
$–CH_2$ asymmetric	–	2921	2915	2891	w.b*	2917
–N-H bending	–	1582	1589	1590	1509	1509
$–COO^-$ asymmetric	–	1634	1628	1625	1643	1579
$–COO^-$ symmetric	–	1486	1490	1487	w.b*	1445
–S–H stretching	–	2590	2596	2585	–	–
$–S–CH_3$ stretching	–	1335	–	–	1386	1277

***w.b** = weak band

4.1.2. X-ray diffraction (XRD) analysis results

Figure 4.6 corresponds to the x-ray diffraction pattern of the SiO_2 and its modified forms; SiO_2-(L-Cys + L-Meth), SiO_2-Cys, and SiO_2-Meth. From the XRD results, broad diffraction rise centered at 2θ angle of about 22.54° in both modified and unmodified ASG (SiO_2) is a known typical characteristic peak for amorphous silica gel in all cases (Dakova et al., 2011; Ismail, Khalili, & Orabi, 2020). As shown in Figure 4.6, the absence of any ordered crystalline structure confirms the amorphous nature of the activated silica gel. Other studies also reported similar results with the present thesis (Jafari & Allahverdi, 2014; M & Munoz, 2011). The modified ASG with L-cysteine (SiO_2-Cys) pattern showed the presence of two sharp peaks at 2θ =18.91° and 2θ =33.11° related to monoclinic crystalline L-cysteine (Ismail, Khalili, & Orabi, 2020). On the other hand, the modified ASG with L-methionine (SiO_2-Meth) pattern showed the presence of one weak peaks at 2θ = 23.69° related to monoclinic crystalline L-methionine. In addition to this peak literature (Ismail, Khalili, & Orabi, 2020) was also reported that the preasence of peak at around 2θ = 5.16°. However, for this thesis the peak was not clearly observed because of the 2θ angles scan range from 5° to 85° while, on the literature it was ranging from 0° to 85°. The modified ASG with a mixture of L-cysteine and L-methionine (SiO_2-(L-Cys + L-Meth)) pattern showed the presence of two peaks at 2θ =18.91° and 2θ =33.00° related to monoclinic crystalline L-cysteine and at 24.10° and 5.12° related to monoclinic crystalline L-methionine. The presence of sharp peaks (2θ =18.91° and 2θ =33.11° and at 24.10°) in the X-ray diffraction pattern of the modified activated silica gel ensures the existence of crystalline amino acids with activated silica gel. The previous literature (Ismail, Khalili, & Orabi, 2020) reported XRD results for silica nanoparticles modified with Cysteine or Methionine for U(VI) removal from aqueous solution is comparable with the XRD results obtained in the present study for ASG, SiO_2-Cys, SiO_2-Meth, and SiO_2-(L-Cys + L-Meth). But, the XRD result of activated silica gel modified with L-methionine particularly, for a peak appearing at 5.16° (Ismail, Khalili, & Orabi, 2020), is not clearly observed as presented in Figure 4.6 this may be because the scan range used for XRD analysis was on the rang from 5° to 85° but, they reported on the scan range starting from 0°. In addition, the ratio of the silica gel and the amino acid used in this study is not similar to the ratio they took will be another reason.

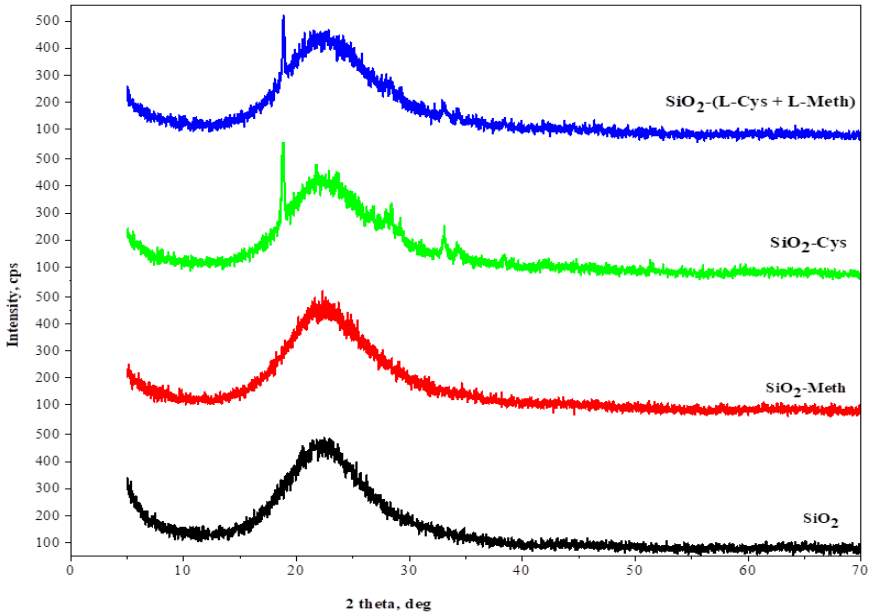


Figure 4.6 XRD pattern of SiO_2, SiO_2-(L-Cys + L-Meth), SiO_2-Cys, and SiO_2-Meth.

4.1.3. Scanning electron microscope (SEM) analysis results

The images of the adsorbent surface were examined using scanning electron microscopy (SEM) to investigate the shape, size, and porosity of the materials before and after modification. SEM image is one of the most widely used surface identification methods. Therefore SEM micrographs were acquired to observe the surface morphologies of the SiO_2 and its modified form with L-Cys, L-Meth, and a mixture of L-Cys and L-Meth. As shown in the Figure 4.7. it was observed that some little change after ASG (SiO_2) modified by L-Cys, L-Meth, and a mixture of L-Cys and L-Meth. The little change the modified form of silic gel showed that the dissimilarities in adsorption capacity happened to depend on functional groups present on its surface and not only a result of the morphology of adsorbents.The SEM images for all adsorbents before and after immobilization of the L-Cys, L-Meth, and mixture of L-Cys and L-Meth have exhibited an agglomerate, various sizes, and irregular morphology as shown in Figure 4.7. But the ASG before modification is showed relatively smooth surface particles and nonporous texture. After immobilization, it is irregular rough-surface structure, increasing pore size and pore volume has shown, indicates that the materials exist good characteristics to be employed, as an adsorbent for metal ion uptake. The SEM result of ASG and its modified form with L-Cys, L-Meth, and a mixture of L-Cys and L-Meth are agreed with the previously reported literature of the SEM results (Ismail, Khalili, & Abu Orabi, 2020) for silica nanoparticles (SiO_2-NPS) and its modified forms with L-cysteine or L-methionine, (Kushwaha et al., 2012) for activated

silica gel and its modified forms with 2-thiophenecarbonyl, 2-furoyl and L-proline, and (Bilgiç, 2019) for silica gel and its modified form with 4-acetyl-3-hydroxyaniline.

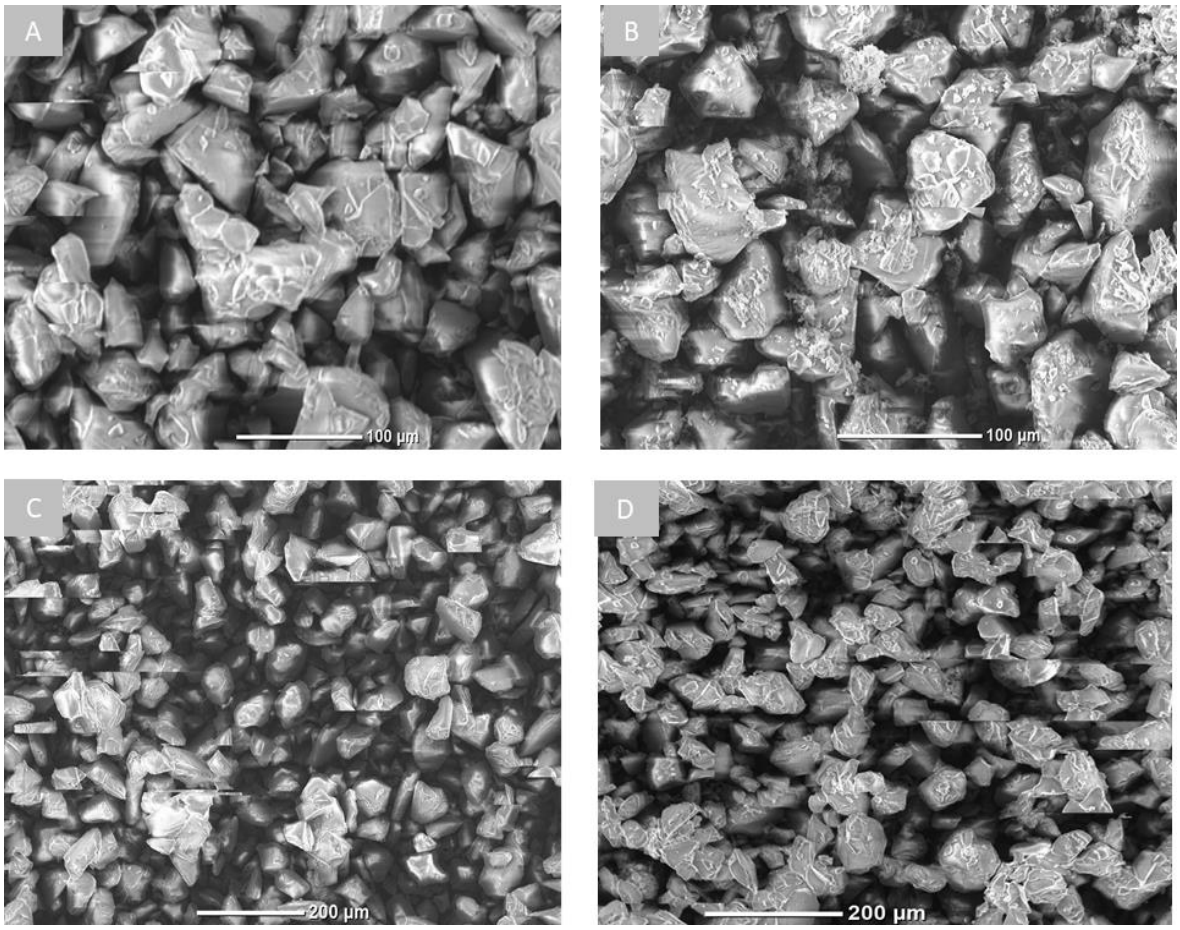


Figure 4.7 SEM micrographs for SiO_2, SiO_2-(L-Cys + L-Meth), SiO_2-Cys, & SiO_2-Meth. (a(SiO_2), b(SiO_2-Cys), c(SiO_2-Meth) & d(SiO_2-(L-Cys + L-Meth))).

4.1.4. Brunauer-emmett-teller (BET) analysis results

The degree of adsorption increases with the increase of the surface area of the adsorbent. Hence finely powdered activated silica gel and porous substances having large surface areas perform well as adsorbents. The Brunauer-emmett-teller (BET) characterization method was used to determine the specific surface area (m^2/g) and the average pore volume (cc/g), and pore size (Å) for activated silica gel (SiO_2) and its modified forms; SiO_2-(L-Cys + L-Meth), SiO_2-Cys and SiO_2-Meth. Table 4.8 summarizes the nitrogen sorption/desorption BET results. Modified ASG with L-Cys (SiO_2-Cys) has the lowest surface area (588.968 m^2/g) than SiO_2-(L-Cys + L-Meth) (772.816 m^2/g), SiO_2-L-meth (730.710 m^2/g), and SiO_2(629.425 m^2/g). The literature (Ismail, Khalili, & Abu Orabi,

2020) also observed the decrease in surface area of L-cysteine modified silica particles. The characteriztion result of SEM and BET, shown in Figure 4.7 and Table 4.2 respectively, the surface area of modified activated silica gel with a mixture of L-Cys and L-Meth and with L-methionine was obtained a better result than unmodified activated silica gel. The modification of ASG resulted in an increased average pore volume and pore size except, L-methionine modified silica gel shown lowere pore size. So, these are referred to the coverage of activated silica gel surface with amino acids (L-cysteine and L-methionine), which increase the available surface area of activated silica gel.

Table 4.1. Main BET characteristics of activated silica gel and its modified forms

	Adsorbentes			
Data types	SiO_2	SiO_2-Cys	SiO_2-Meth	SiO_2-(L-Cys + L-meth)
Surface Area (m^2/g)	629.425	588.968	730.710	772.816
Pore Volume (cc/g)	0.7944	0.7948	1.005	1.002
Pore Size (pore Radius) (Å)	22.71	22.71	16.58	22.71

4.2. Adsorption studies

4.2.1. Optimization for removal of lead and nickel ions from aqueous solution

4.2.1.1. Effect of pH

In adsorption, pH is one of the significant parameters affecting the adsorption efficacy. The pH of the solution is mainly affecting the functional group on the adsorbent, which is responsible for the binding of metal ions in the adsorbent surface. Further, it affects the ionization or dissociation capacity of the adsorbate ions. The protonation or deprotonation of N- and S- containing functional groups strongly depends on the pH of the solution

because, it is related to their pKa value (Bilgiç, 2019; Dakova et al., 2011; Petrova et al., 2018). The pH influence on the degree of adsorption of Pb(II) with 10 mg/L and Ni(II) with 3.5 mg/L initial concentrations on SiO_2-(L-Cys + L-Meth*)* was investigated in the pH range 5–9 by batch equilibrium procedure. Other parameters were kept constant at an adsorbent dose of 0.2 g per 0.05 L volume of adsorbate ion solution, contact time of 60 min, agitation speed 160 rpm, and at room temperature. The trend observed is an increased removal capacity for investigated cations with increasing pH of the solution. As shown in Figure 4.8 the adsorption capacity of SiO_2-(L-Cys + L-Meth) for Pb(II) was increased from pH 5 to 6. The increase in percent removal of Pb(II) might be on a decrease in competition between protons (H^+) and positively charged lead ions at the surface sites. And decreasing positive charge near the surface results in a lower repulsion of the adsorbing metal ion, and more negative groups for the complexation of metal cations are provided. The Ni(II) adsorption capacity of SiO_2-(L-Cys + L-Meth) decreases as the pH of the solution increase because of the presence of a higher concentration of hydroxide ion (OH^-) as it can form metal hydroxide precipitate so, the percent removal of Ni(II) also decreased. The maximum percent removal for Pb (II) and Ni(II) is 84.4 % at pH 6 and 96.77 % at pH 5, by SiO_2-(L-Cys + L- Meth) adsorbent respectively. The literature (Alghanmi, 2012) reported that the optimum pH obtained for heavy metal ions removal including Pb and Ni ions using modified silica gel was similar to the optimum pH obtained in this study.

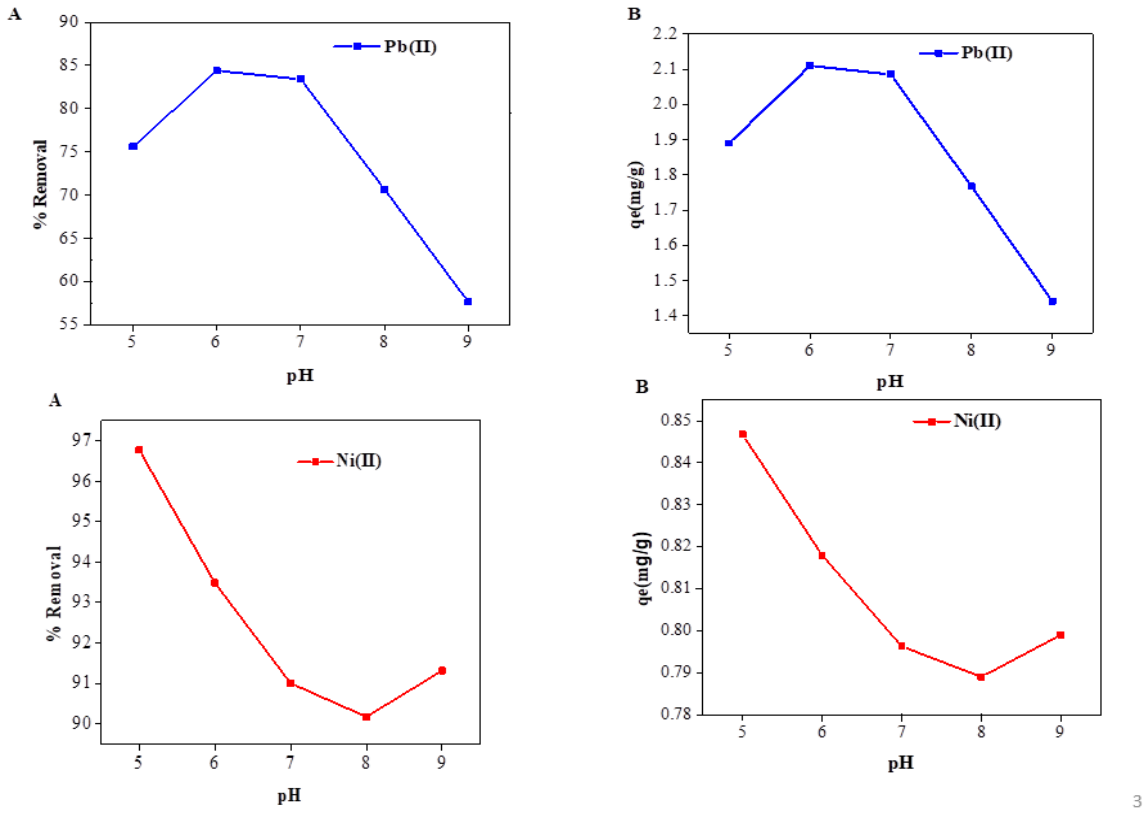


Figure 4.8 Effects of pH on Pb and Ni ions adsorption onto SiO_2-(L-Cys + L-Meth). A.Removal efficiency (%), B. Adsorbent capacity (mg/g).

4.2.1.2. Effect of contact time

The effect of contact time between the adsorbate ions and SiO_2-(L-Cys + L-Meth) on the adsorption efficiency of Pb(II) and Ni(II) on SiO_2-(L-Cys + L-Meth) were investigated by experimenting with 30, 60, 90, 120, and 150 min of contact time at 160 rpm agitation speed and room temperature. Other parameters were kept constant at pH 6 and 5 and initial concentrations 10 and 3.5 mg/L for Pb(II) and Ni(II), respectively, dose 0.2 g per 0.05 L volume of metal ion solution. From the results presented in Figure 4.9, the rate of percent removal is higher at the beginning because of the large number of vacant surface sites available for adsorption. The maximum adsorption of lead (85.2%) and nickel (94%) on SiO_2-(L-Cys + L-Meth) was obtained at contact times of 90 and 60 min, respectively. After this equilibrium contact time, a decrease in the amount of adsorbed was observed. The metal ion competes for the adsorption sites on the adsorbent in the mixture of adsorbent and metal ions. The competition of metal ions to the active sites could affect the adsorption capacity of the metal ions and the diffusion properties of the metal ions (Fay et al., 1967).

In the literature (Petrova et al., 2017a) , the effect of contact time for solid-phase extraction of Au(III) by amino acid modified silica gel sorbents was studied on the range 10-60 min with 10 min interval. The study shows that quantitative adsorption exists within 30 min and it is dissimilar from this study and this implies the time taken for this thesis is more than the time taken in the literature reported for Au(III) extraction. The reason is may be the presence of HCl in a solution containing 10 mg/L Au ions. They reported that the high degree of Au(III) adsorption on amino acid modified silica gel in the presence of HCl might be with the fact that Au(III) forms anionic chlorocomplexes $[AuCl_4]^-$. Therefore, the Au(III) adsorption is due to the strong electrostatic attraction between the positively charged adsorbent and the negatively charged chloride complex. The literature (Ismail, Khalili, & Abu Orabi, 2020) reported that the maximum removal efficiency was observed at 1400 min for study the effect of contact time on the range 200 to 1600 min with an interval of 200 min. So, the contact time needed for the adsorption is less than the literature reported for U(VI) removal. Further, another literature (Mengistie*, 2013) reported for optimal contact time for removal of Ni(II), agreed with this study.

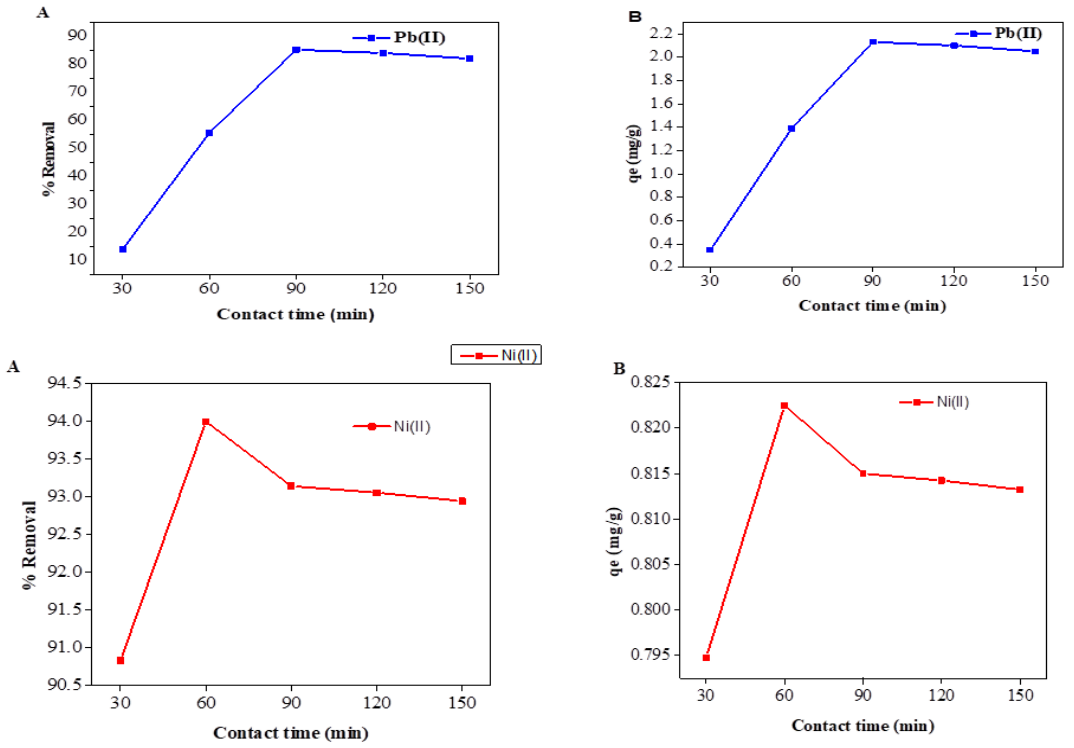


Figure 4.9 Effects of contact time on Pb and Ni ions adsorption onto SiO_2-(L-Cys + L-Meth) A. Removal efficiency (%), B. Adsorbent capacity (mg/g).

4.2.1.3. Effect of initial concentration

The effect of the initial concentration of Pb and Ni ions in the solution towards adsorption efficiency was studied. Initial concentration Pb(II) and Ni(II) were studied by varying the Pb and Ni ions concentration and keeping other variables constant. In this study the initial concentration of 0.5, 2, 4, 6, 8, and 10 mg/L for Pb(II) at pH 6 and 0.5, 2, 3.5, 5, and 6.5 mg/L at pH 5 for Ni were used. And other parameters such as adsorbent dose of 0.2 g per 0.05 L of solution, contact time 90 and 60 min for Pb(II) and Ni(II) respectively, agitation speed 160 rpm, and at room temperature. As shown in Figure 4.10, the percentage removal decreases with increasing initial concentration; this is because that the adsorbent has a fixed capacity and can adsorb only a maximum specified amount. Thus additional adsorbate concentrations do not get adsorbed. Hence, the percentage removal decreases starting from the saturation point. From Figure 4.10 A, it can be seen that adsorption efficiency initially observed high removl percent and an optimum maximum value reached at concentrations of 2 mg/L for both metal ions with percent removal of 96.7% and 99.25% for Pb(II) and Ni(II), respectively. And it becomes decreasing with an increase in initial concentration; this is due to the lack of active sites of an adsorbent SiO_2-(L-Cys + L-Meth) (Fay et al., 1967), (Ismail, Khalili, & Orabi, 2020). Removal capacity SiO_2-(L-Cys + L-Meth) in mg/g showed different trends than percent adsorption (Figure 4.10 B). The increase in the initial concentration up to a certain point shows an increasing removal of lead and nickel ions as much as available active sites. However, an additional increase in the adsorbate ions results in the reduction of removal efficiency. Because all the active sites on the adsorbent surface sites have already been occupied by the metal ions. In the literature (Ismail, Khalili, & Orabi, 2020), the effect of initial concentration for removal U(VI) by SiO_2-NPs and its modified forms were studied, with varying initial U(VI) concentrations (10, 20, 30, 40, and 50 mg/L). The increasing concentration of U(VI) in the solution led to a qe increase and % removal of U(VI) decrease. The maximum U(VI) removal efficiency they reported that less than 80% for 10 mg/L. However, the % removal for Pb and Ni ions in the present study has gained a better result than the % removal for U(II).

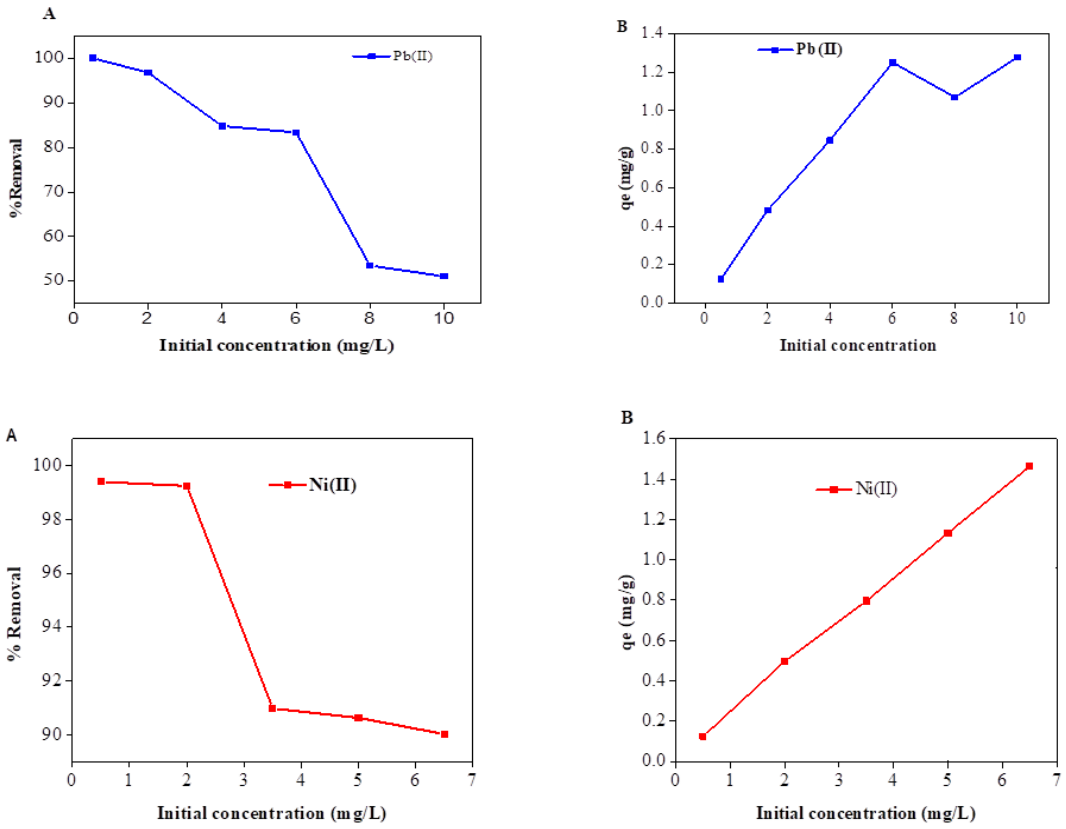


Figure 4.10 Effects of initial concentration on Pb and Ni ions adsorption onto SiO_2-(L-Cys + L-Meth) A. Removal efficiency (%), B. Adsorbent capacity (mg/g).

4.2.1.4. Effect of adsorbent dose

Optimization of the adsorbent dosage is very significant to determine the capacity of an adsorbent for a given initial concentration, separation cost, and consequently, the whole water treatment cost. The effect of dosage of adsorbent SiO_2-(L-Cys + L-Meth) on adsorption of Pb(II) and Ni(II) was studied by varying SiO_2-(L-Cys + L-Meth) dose from 0.2 - 1.0 g with 0.2 intervals per 0.05 L volume of solution and by keeping other variables constant, at pH 6 and 5 and contact time 90 and 60 min for Pb(II) and Ni(II) respectively, 2 mg/L initial concentration, agitation speed 160 rpm and at room temperature. The results in Figure 4.11 A shows an increase in the percentage uptake of Pb(II) and Ni(II) with increasing SiO_2-(L-Cys + L-Meth) dose and reaches a maximum at 0.8 and 0.4 g doses with a removal percent of 97.15% and 99.35% for lead and nickel, respectively. This increase in percent removal with an increase in adsorbent SiO_2-(L-Cys + L- Meth) dose may be due to the availability of more active sites in the adsorbent surface (Ismail, Khalili, & Orabi, 2020). As shown in Figure 4.11 B, the adsorption capacity of the adsorbent was found to decrease with the increasing adsorbent dosage because the number of adsorption

sites per unit mass decreases. And this might be due to the presence of excess adsorbent SiO_2-(L-Cys + L-Meth) in the solution than the Pb and Ni ions in the solution. Generally, from the optimization results obtained in this thesis for Pb and Ni ions removal, the % removal value is greater than the value reported by literature (Ismail, Khalili, & Abu Orabi, 2020) for U(VI) removal by modification of silica nanoparticles with cysteine or methionine from aqueous solution. In addition in the literature (Petrova et al., 2017b) reported that for solid-phase extraction of Au(III) by silica gel modified with Cystine (Sig-Cys-S-S-Cys) was exhibited a lower degree of Au(III) sorption (43 %) than the % removal achieved in this work for Pb(II) and Ni(II) removal, while, silica gel modified with N-Benzyloxycarbonyl-L -Methionine was showed comparable results (degree of Au(III) adsorption 80-98%) with this work.

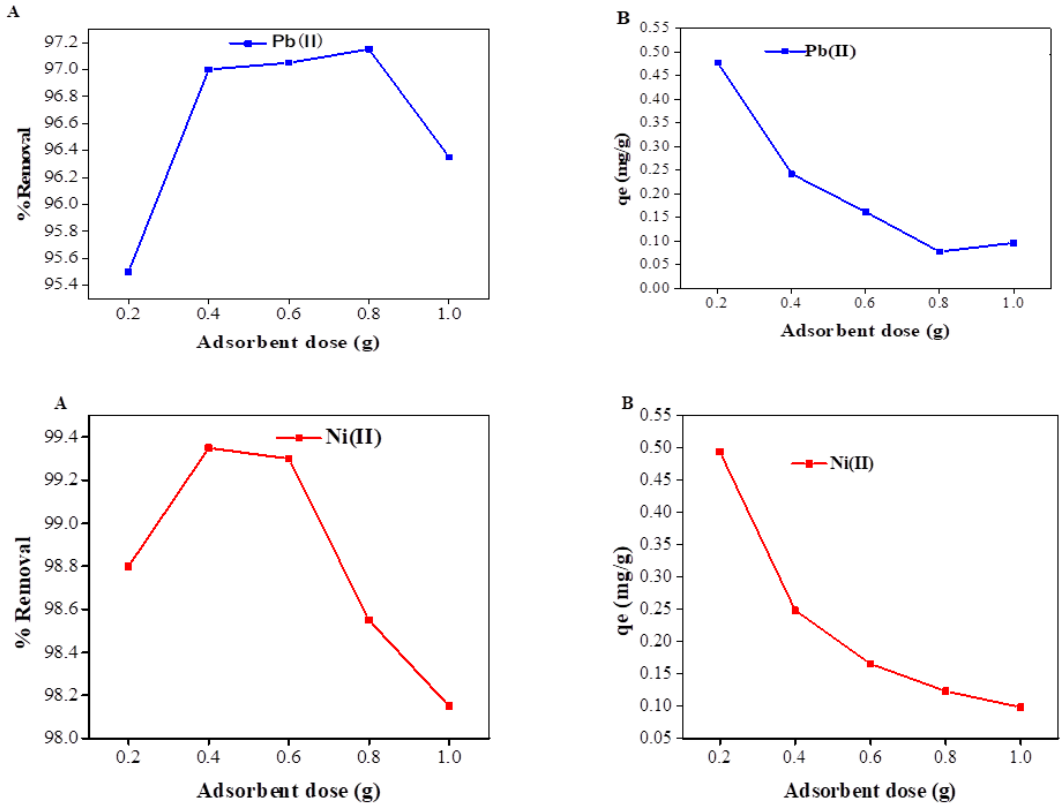


Figure 4.11 Effects of adsorbent dose on Pb and Ni ions adsorption onto SiO_2-(L-Cys + L-Meth) A. Removal efficiency (%) B. Adsorbent capacity (mg/g).

4.2.2. Kinetics study

Kinetics studies help to select optimum operating conditions for the full-scale batch process, which have been applicable to investigate the mechanism of adsorption and potential rate-controlling steps. The kinetic parameters, which are significant for the

prediction of adsorption rate, and give useful information for designing and modeling the adsorption processes (Batool et al., 2018). Therefore, the kinetics of lead and nickel ions adsorption onto SiO_2-(L-Cys + L-Meth) was analyzed using pseudo-first-order and pseudo-second-order kinetic models. The kinetics study were done using pH 6 and 5 for Pb(II) and Ni(II), respectively, initial concentration of 10 mg/L for Pb(II) and 3.5 mg/L for Ni(II), the adsorbent dosage of 0.2 g per 0.05 mL of solution, agitation speed 160 rpm, and at room temperature for both ions. By using the correlation coefficient significance, the conformity between experimental data and the model-predicted values was expressed. The relative greater is the more applicable model to the kinetic study.

4.2.2.1. Pseudo-first order kinetics

To determine whether the adsorption process fits with the pseudo-first-order model or not. The experimental data using contact time ranging from 60 - 150 min and pH 6 and 5 for Pb(II) and Ni(II) respectively, initial concentration of 10 mg/L for Pb(II) and 3.5 mg/L for Ni(II), the adsorbent dosage of 0.2 g per 0.05 mL of solution and at room temperature, and 160 rpm agitation speed for both were introduced to Equation 2.6 (Figure 4.12).

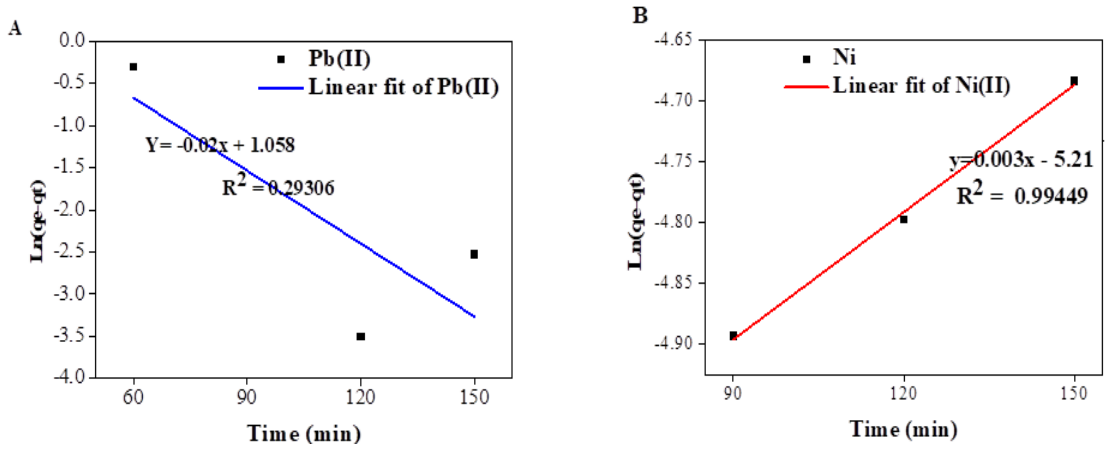


Figure 4.12 Pseudo-first order kinetic plots for the adsorption of lead and nickel ions onto SiO_2-(L-Cys + L-Meth) A. For lead ion B. For nickel ion.

The linearized form of the pseudo-first-order equation is already expressed in Equation 2.6. The straight-line plot of Ln (qe–qt) against time (Figure 4.12) gives a linear relationship from which the pseudo-first-order rate constant (K_1) and equilibrium adsorption capacity (qe) were calculated from the slope and intercept, respectively, as shown in Table 4.3. The adsorption kinetics of Pb and Ni ions removal using SiO_2-(L-Cys + L-Meth) (Figure 4.12) was not predicted by the pseudo-first-order kinetics model since the correlation factor was

very low for Pb(II). In addition the correlation factor for Ni(II) showed relatively lesser value for pseudo-first-order kinetics model than the result pseudo-second-order model.

As presented in the Figure 4.12 the R^2 value of first order kinetic model was relatively lower than the R^2 value of second-order kinetics. The calculated and experimental values of Pb and Ni ions removal were not close to each other, as can be seen in Table 4.3. The rate constant and qe (cal) were calculated from the slope and intercepts of the graph Ln (qe-qt) against time (Adane et al., 2015).

Table 4.3. Results of line fit model of pseudo-first order kinetics.

Contaminant	C_i (mg/L)	Intercept	qe(exp) (mg/g)	qe(cal) (mg/g)	Slope	K_1	R^2
Lead(II)	10	1.05895	2.13	2.88334189	-0.02882	0.000192133	0.29306
Nickel(II)	3.5	-5.21062	0.8225	0.00545828	0.0035	2.33333E-05	0.99449

4.2.2.2. Pseudo-second order kinetic model

In addition to the first-order kinetics model the linearized form of the kinetic rate expression for a pseudo-second-order model was applied to the experimental data. Calculated equilibrium adsorption capacity qe(cal), pseudo-second-order rate constant (K_2), and the initial adsorption rate (h) were obtained from the model using Equation 2.9. The linear plots of t/qt against time are shown in Figure 4.10 for Pb and Ni ions adsorbed on SiO_2-(L-Cys + L-Meth). Figure 4.10 and Table 4.4 showed the values of R^2 on pseudo-second-order for Pb and Ni ions are relatively higher than on first-order kinetics. The calculated adsorption capacity qe(cal) was closer to the experimental adsorption capacity qe (exp), indicating that the pseudo-second-order kinetic model describes the adsorption process of Pb(II) and Ni(II) by SiO_2-(L-Cys + L-Meth) perfectly. Also, the chemisorption process is the rate-controlling step for adsorption of Pb (II) and Ni (II) by SiO_2-(L-Cys + L-Meth). A similar fit to this model has also been reported for U(IV) adsorption on silica nanoparticles modified by L-cysteine and L-methionine (Ismail, Khalili, & Orabi, 2020).

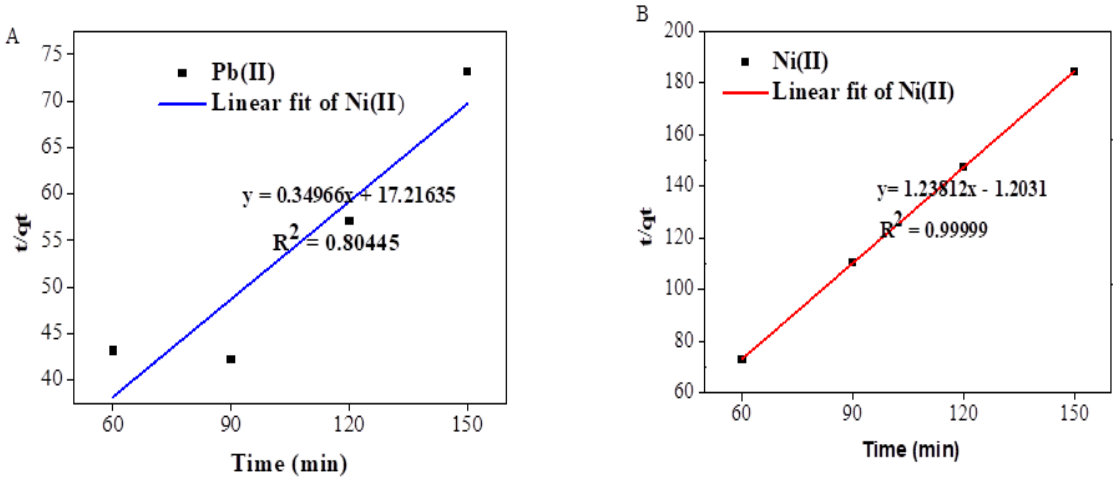


Figure 4.13 Pseudo-second order kinetic plots for the adsorption of lead and nickel ions onto SiO_2-(L-Cys + L-Meth). A. For lead ion B. For nickel ion.

Table 4.4. Results of line fit model of pseudo – second order kinetics.

Metals	C_i (mg/L)	Intercept	Slope	qe(exp) (mg/g)	qe(cal) (mg/g)	q_e^2	k_2	R^2
Lead (II)	10	17.21635	0.34968	2.13	2.859757	8.178212	0.007102	0.80445
Nickel (II)	3.5	-1.2031	1.23812	0.8225	0.807676	0.652340	-1.27416	0.99999

4.2.3. Adsorption isotherm results

The adsorption equilibrium provides important physicochemical data for evaluating the applicability of the adsorption process as a unit operation. In this study, the equilibrium data were analyzed using Langmuir and Freundlich isotherm models. These are generally related to the type of coverage, the possibility of interaction between the adsorbent and adsorbate species, the heterogeneity and homogeneity of the adsorbent. Isotherms models relate adsorbate per unit weight of adsorbent (qe) to the equilibrium adsorbate concentration in the bulk fluid phase Ce. This helps to optimize the design of an adsorption system for removal of contaminants and the selection of the appropriate adsorbent. Additionally, the isotherm plays a significant role in the predictive modeling procedures for analysis (Adane et al., 2015) (P. Senthil Kumar*, C. Vincent, K. Kirthika, 2010).

4.2.3.1. Langmuir adsorption isotherm model result

From all isotherms commonly used for describing adsorption, the Langmuir adsorption isotherm model is the best known, and it has been successfully applied to various adsorption processes. The Langmuir isotherm is effective for adsorption of a solute from a liquid solution as monolayer adsorption on a surface containing a fixed number of identical sites (Adane et al., 2015). The experimental data were analyzed according to the linear form of the Langmuir isotherm as described in Equation 2.1. The linear plots of 1/qe versus 1/Ce suggest that Langmuir isotherms for the removal of Pb (II) by SiO_2-(L-Cys + L-Meth) is applicable, while for Ni(II), it is not applicable. Figure 4.11 showed that the experimental results obtained from the Langmuir isotherm experiment. And the experimental conditions of pH 6 and 5, contact time 90 and 60 min for Pb(II) and Ni(II) respectively, dose 0.2 g per 0.05 L volume, agitation speed 160 rpm, and at room temperature for both being kept constant with various initial concentration ranging from 2 to 10 mg/L with 2 mg/L intervals for Pb(II) and initial concentration ranging from 0.5 to 6.5 mg/L with 1.5 mg/L intervals for Ni(II). The values of q_{mix} and K_L of linear expression of Langmuir adsorption isotherm were calculated from the slopes and intercept of the linear plot of 1/qe versus 1/Ce shown in Figure 4.11.

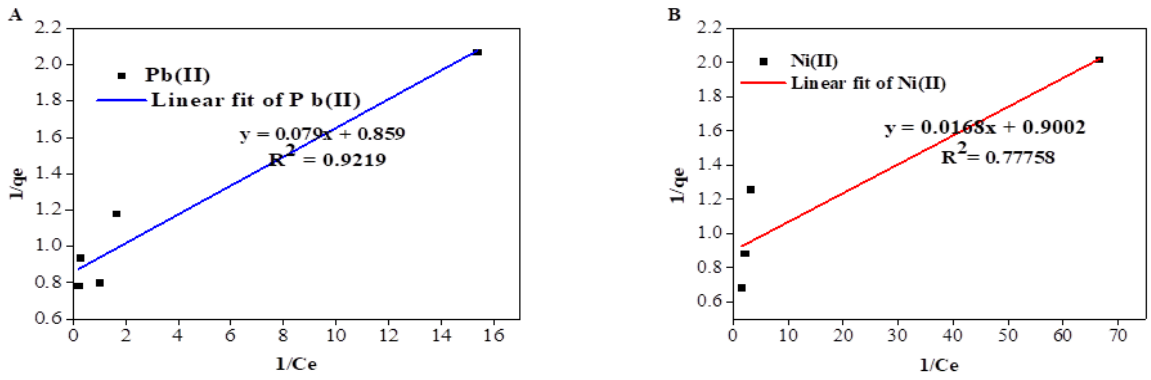


Figure 4.14 Langmuir adsorption isotherm model.

A . For lead ion and B. For nickel ion.

As presented in Table 4.5, the calculated values of isotherm parameters and the adsorption of Pb(II) and Ni(II) on SiO_2-(L-Cys + L-Meth) shows high correlation coefficients for both the Langmuir and Freundlich isotherm model. The possible reason is that both the

monolayer and multilayer adsorption existed in the adsorption process of Pb (II) and Ni(II) and the presence of homogenous and heterogeneous sites on SiO_2-(L-Cys + L-Meth) surface. However, Langmuir's adsorption isotherm model shows a greater R^2 value than Freundlich adsorption isotherm for lead(II) and Freundlich adsorption isotherm for nickel(II). The value of the separation factor (R_L) called equilibrium parameter can be estimated by Langmuir isotherm. The obtained R_L values were greater than 0 but less than 1 as shown in Table 4.5, indicating that the adsorption processes of Pb(II) and Ni(II) on SiO_2-(L-Cys + L-Meth) was favorable. Furthermore, the value of R_L of Pb(II) and Ni(II) on SiO_2-(L-Cys + L-Meth) lean towards zero (the completely ideal irreversible case) rather than unity (which represents a completely reversible case). For Pb(II), the adsorption isotherm was better fitted by the Langmuir model (Ismail, Khalili, & Orabi, 2020).

Table 4.5. Summary table for the line fit graph of langmuir isotherm model.

Contaminant	Ci (mg/L)	qe (mg/g)	Intercept	Slope	q_{max} (mg/g)	K_L	R_L	R^2
Lead (II)	2	0.48375	0.8597	0.0791	1.1631694	10.8564	0.04402	0.9219
Nickel (II)	2	0.4962	0.9002	0.0168	1.1108642	53.5833	0.00924	0.77758

4.2.3.2. Freundlich adsorption isotherm model

The Freundlich isotherm model is the second model used to describe the adsorption data of Pb(II) and Ni(II), the Freundlich constant K_F ($mg.g^{-1}$), and n is characteristic constants related to the relative adsorption capacity of the adsorbent and the intensity of adsorption, respectively. The values of n were larger than one (Table 4.6), which indicates that the adsorption of Ni(II) onto SiO_2-(L-Cys + L-Meth) was favorable (Ismail, Khalili, & Orabi, 2020), (Adane et al., 2015). The Freundlich equation is purely experimental based on adsorption on the heterogeneous surface and is commonly given by a non-linear equation on Equation 2.2. The K_f and 1/n can be obtained from the intercept and slope of the linear plot of log qe versus log Ce.

The applicability of the Freundlich adsorption isotherm was also analyzed, using the same set of experimental data as for the Langmuir model. The Freundlich plots between log qe versus log Ce for the adsorption of Pb(II) and Ni(II) are shown in Figure 4.12. The K_f and 1/n were 1.058766 and -0.21109 for lead(II), and 1.352882 and 0.24961 for nickel(II), respectively. The slope ranges between 0 and 1 and it is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero. Whereas a value below 1 implies the chemisorptions process whereas, 1/n above 1 is indicative of cooperative adsorption. It was found that, Freundlich isotherm provides a good model of the Ni(II) adsorption system with correlation coefficient values R^2 is higher than the correlation coefficient values obtained from the Langmuir isotherm model. Therefore, Freundlich's adsorption isotherm is applicable for the adsorption of Ni(II) with an R^2 value of 0.78181. This suggests that the Langmuir isotherm provides, comparatively, a good model for Pb (II), and the Freundlich isotherm model is a good model for Ni (II) adsorption system.

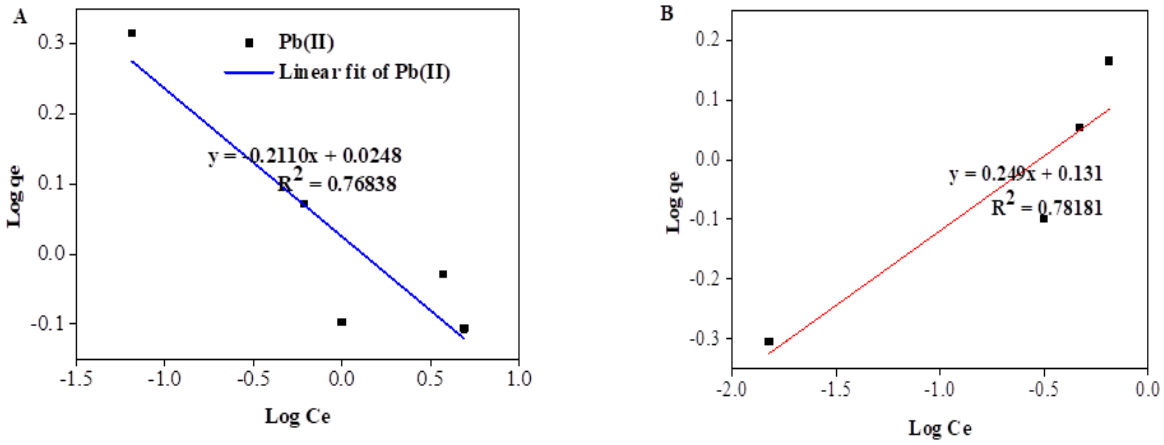


Figure 4.15 Freundlich adsorption isotherm model.

A. For lead ion, B. For nickel.

Table 4.6. Result of the line fit graph of freundlich isotherm model.

Contaminant	Ci (mg/L)	qe (mg/g)	Intercept	Slope	1/n	K_f	R^2
Lead(II)	2	0.48375	0.0248	-0.21109	-0.21109	1.058766	0.76838
Nickel(II)	2	0.4962	0.13126	0.24961	0.24961	1.352882	0.78181

4.3. Comparison results of differents adsorbents for Pb and Ni ions removal

In this study, as shown in Figure 4.13, the efficiency of adsorbents SiO_2 and its modified forms, SiO_2-(L-Cys + L-Meth), SiO_2-Cys, and SiO_2-Meth were compared for Pb(II) and Ni(II) removals. The experiments were carried out using optimized parameters at pH 6 and 5, contact time 90 and 60, and adsorbent dose of 0.8 and 0.4 g for Pb(II) and Ni(II), respectively, and initial concentration of adsorbate 2 mg/L, volume 0.05 L, agitation speed 160 rpm, and at room temperature for Pb and Ni ions removals were used.

The Pb(II) removal efficiency of the adsorbent were in the order of SiO_2-(L-Cys + L-Meth) (97.15%) > SiO_2-Meth (93.65%) > SiO_2 (92.6%) > SiO_2-Cys (55%) for Pb(II) removal. The highest removal efficiency of Pb(II) (97.15%) was obtained using SiO_2-(L-Cys + L-Meth) as showen (Figure 4.13 A).

Nickel removal experiment results showed that the removal efficiency of adsorbents was 99.35%, 62.75%, 65%, and 65.95% for SiO_2-(L-Cys + L-Meth), SiO_2-Meth, SiO_2-Cys, and SiO_2, respectively. The highest removal efficiency of nickel ion (99.35%) was obtained using SiO_2-(L-Cys + L-Meth) (Figure 4.13 B). For both contaminants, the adsorption process by SiO_2-(L-Cys + L-Meth) was high removal capacity than others. This indicates that the mixture of L-cysteine and L-methionine can improve the removal efficiency ASG. The literature (Petrova et al., 2017a) for solid-phase extraction of Au (III) using silica gel modified with cystine(Sig-Cys-S-S-Cys) and N-benzyloxycarbonyl-L-methionine (Sig-Z-Met-OH), the % extraction of Au(III) by Sig-Z-Met-OH is greater than silica gel modified by cystine. Due to the presence of two amino groups and two S atoms in the cystine molecule ($[HOOC(NH_2)CHCH_2S-]_2$) in comparison with Sig-Z-Met-OH (Z-NH-

$CH(CH_2CH_2SCH_3)$-COOH), with one amino group and one S atom per mol amino acid, a more considerable adsorption capacity is expected. However, it is reported that Sig-Cys-S-S-Cys does not ensure satisfactory extraction (less than 44 % studied) of Au (III), while the adsorption on Sig-Z-Met-OH is higher. This is due to the low adsorption activity or slow kinetics of the adsorption process on the surface of Sig-Cys-S-S-Cys. On the other hand in literature (Ismail, Khalili, & Abu Orabi, 2020) reported that modified silica nanoparticles with cysteine (% removal 33) and methionine (% removal 30). The higher in % removal for silica nanoparticles with cysteine (SiO_2-Cys) is may be related to the percentage loading of cysteine on silica nanoparticles surface, which is more than the percentage loading of methionine (Ismail, Khalili, & Orabi, 2020).

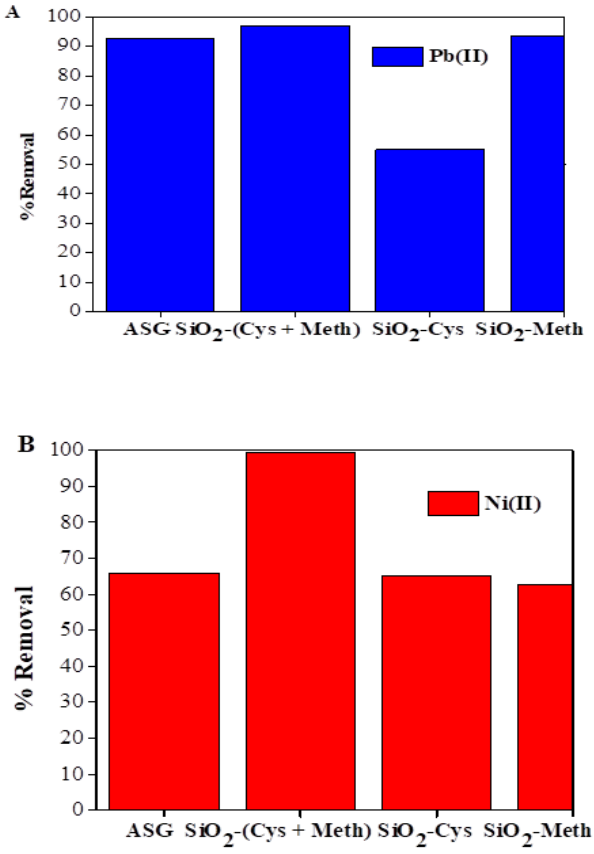


Figure 4.16 Removal efficiency of ASG and its modified forms

A. For Pb (II) B. For Ni (II).

4.4. Regeneration and reusability result of the SiO_2-(L-Cys + L-Meth)

The desorption processes are significant for the regeneration of adsorbents for reuse in other adsorption processes. Figure 4.14 and Table 4.7 showed that the removal efficiency

of cycles for SiO_2-(L-Cys + L-Meth) using 0.1 M HCl by cation exchange mechanism. Several adsorption-desorption cycles were conducted for Pb(II) and Ni(II) to determine the adsorption-desorption potential of SiO_2-(L-Cys + L-Meth). The reusability of the used adsorbent SiO_2-(L-Cys + L-Meth) was investigated by performing three successive adsorption-desorption cycles of Pb and Ni ions on the adsorbent SiO_2-(L-Cys + L-Meth) using 0.1 M HCl as desorption eluent. There was a gradual decrease in Pb(II) and Ni(II) removal efficiencies with an increasing number of cycles as shown in Figures 4.14 A & B, respectively. It was observed that cycles 1 and 2 showed good removal efficiency for both metal ions accumulated on the adsorbent surface. For Pb(II), the removal efficiencies of cycles 1, 2, and 3 were found to be 97.15%, 65.5%, and 55.5%, respectively, as presented in Figure 4.14 A. While in Figure 4.14 B, the removal efficiencies of Ni(II) for cycles 1, 2, and 3 were found to be 99.35%, 65.4%, and 45%, respectively. Hence, after the sequence of two cycles, the Pb(II) and Ni(II) uptake capacity on the adsorbent SiO_2-(L-Cys + L-Meth) was reduced from 97.17% to 65.5%, 65.5% to 55.5%, and 99.35% to 65.4%, 65.4% to 45%, respectively. The regeneration experiments presented in Figures 4.14 A & B showed that the SiO_2-(L-Cys + L-Meth) recyclability for adsorption and removal of Pb and Ni ions the % removal reduce as the number of cycle increased.

Table 4.7. Recyclability for SiO_2-(L-Cys + L-Meth) for lead and nickel ions removal.

Cycle	%Removal (Pb(II))	%Removal (Ni(II))	Desorption eluent used
1	97.15	99.35	Distilled water and 0.1 M HCl
2	65.5	65.4	Distilled water and 0.1 M HCl
3	55.5	45	Distilled water and 0.1 M HCl

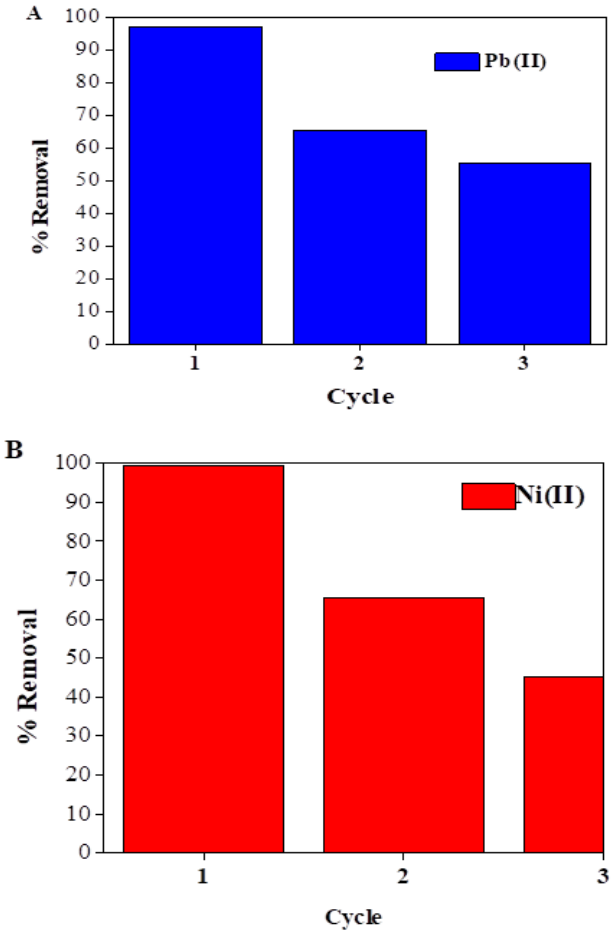


Figure 4.17 Recyclability of SiO_2-(L-Cys + L-Meth).

A. For lead ion removal. B. For nickel ion removal.

4.5. Application of the adsorption method in real wastewater sample

Assessment of the wastewater sample is significant to apply the method on industrial wastewater samples. Therefore, the levels of some physicochemical properties of industrial wastewater samples were studied. The wastewater samples were collected from the discharge point of EIZ in Dukem, Ethiopia. The samples were first assessed for their Physico-chemical properties that are used to identify and quantify toxicants and to provide data that for regulatory purposes, could be compared to allowable limits for specific water recipients (Dagne, 2020), (Mengistie*, 2013). The results of the Physico-chemical parameters of the wastewater samples studied in this thesis are presented in Table 4.8. The contaminated water samples were first determined for their initial concentration by digesting with concentrated nitric acid. The concentration of Pb(II) and Ni(II) in wastewater samples from EIZ has been determined using FAAS. As shown in Table 4.8,

the results obtained revealed that the concentration of heavy metal lead ions was found above permissible level, which could pose an enormous threat to human health and the natural environment. However, nickel ion was below the detection limit. Previous studies (Dagne, 2020) also found that the level of lead ion in a sample taken from EIZ was above the permissible limit set by WHO and US EPA, for irrigation. The samples were treated under optimized experimental parameters at pH 6, contact time 90 min, adsorbent dose 0.8 g per 50 mL of volume, and at room temperature with an initial concentration of lead ion 0.645 mg/L. The filtrate obtained after treatment was analyzed by FAAS. The adsorbent SiO_2-(L-Cys + L-Meth) effectively removed the Pb ion contaminants from real wastewater samples with 100% adsorption efficiency, as can be seen in Table 4.9 the 100% removal effeciencey was achieved because of the presence of lower lead ions concentration in real sample than synthetic.

Table 4.8. Some physicochemical characteristics of EIZ industrial wastewater sample.

Parameters	Values	Tolerance limit value
color	Light gray and bricks red	-
Turbidity	high turbidity	-
pH	8.4	6.0-8.5 (BOI, 2011)
Total dissolved solids (TDS)	244.2 mg/L	1200 µg/L (Angiro et al., 2020)
Conductivity	469.3 µS/cm	400 µS/cm (Angiro et al., 2020)
Total suspended solids (TSS)	35 mg/L	50 mg/L (BOI, 2011)
Chemical oxygen demand (COD)	80 mg/L	250 mg/L (BOI, 2011)
PO_4^{3-}	4.4 mg/L	5 mg/L (BOI, 2011)
Pb(II)	0.645 mg/L	0.05 mg/L WHO and 0.015 mg/L USEPA (Dagne, 2020)
Ni(II)	Below Detection Limit	3.0 mg/L (BOI, 2011)

Table 4.9. Adsorption studies on removal of Pb (II) from real wastewater.

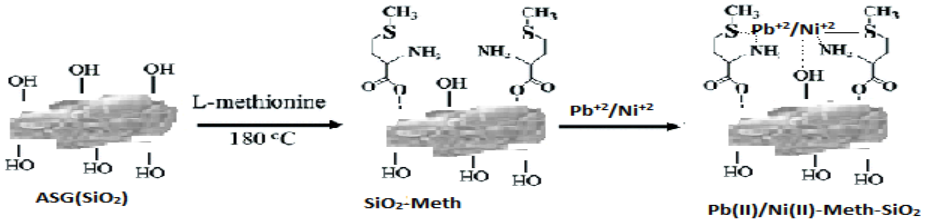
Wastewater sample contaminants	Conc. before adsorption (mg/L)	Dose of adsorbent SiO_2-(L-Cys + L Meth) (g/L)	pH	Contact time (min)	Conc. after adsorption (mg/L)	% Removal
Lead(II)	0.645	0.8	6	90	BDL	100
Nickel(II)	BDL	-	-	-	-	-

BDL = Below Detection Limit

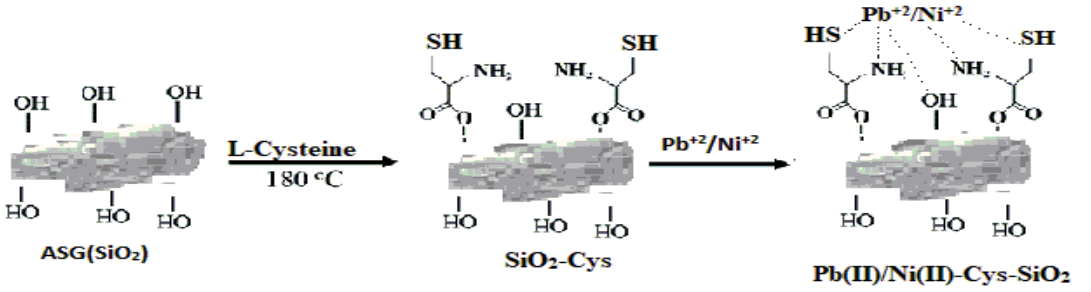
Conc. = Concentration

4.6. Possible reaction mechanism

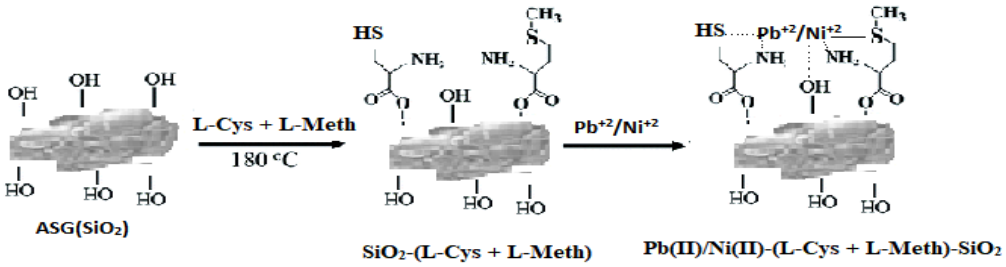
The amino acid L-Cys and L-Meth were chosen to introduce thiol and S-methyl thioether groups on the silica gel surface; since they contain both carboxylic acid and amino groups play a role to react with the silanol(Si-OH) group through esterification reaction and electrostatic interaction respectively, allowing the covalent immobilization of the thiol and S-methyl thioether groups onto silica gel surface (Ismail, Khalili, & Orabi, 2020; Petrova et al., 2018; Xu et al., 2017; Zhou, Cai, Xu, Zhang, Fu, et al., 2018). Scheme 4.1, 4.2, and 4.3 show the modification process on a silica gel. First, the carboxylic groups of the L-Cys, L-Meth, and mixture of L-Cys and L-Meth react with the hydroxyl groups of the silica gel at 180 ^{o}C. The linked L-Cys and L-Meth then act as a binder to adsorb the Pb^{+2}/Ni^{+2} by the coordination bonds between the thiol and S-methyl thioether groups, respectively.



Scheme 4.1. Scheme of surface modification on activated silica gel by L-methionine and attaching Pb(II)/Ni(II)(Zhou, Cai, Xu, Zhang, Fu, et al., 2018).



Scheme 4.2. Scheme of surface modification on activated silica gel by L-cysteine and attaching Pb(II)/Ni(II) (Xu et al., 2017; Zhou, Cai, Xu, Zhang, Fu, et al., 2018).



Scheme 4.3. Scheme of surface modification on activated silica gel by mixture of L-cysteine and L-methionine and attaching Pb(II)/Ni(II) (Xu et al., 2017; Zhou, Cai, Xu, Zhang, Fu, et al., 2018).

5. CONCLUSION AND RECOMMENDATION

5.1. Conclusion

Heavy metals like lead are very toxic and carcinogenic chemicals even in small amounts, and they are hazardous for humans and animals. Similarly, exposure to a higher level of nickel(II) can cause several adverse health effects on animals, plants, and humans. Therefore toxic heavy metals need more attention than other pollutants due to cumulative exposure and non-biodegradable.

This study examined the removal of lead and nickel ions from aqueous solution using low cost(great abundance on earth), environmentally friendly and available adsorbent, silica gel. To improve the adsorption capacity and increase the –OH group of silanol (-Si-OH) on raw silica gel, it was activated using concentrated hydrochloric acid, followed by modification by amino acids(L-cysteine and L-methionine). Activated Silica gel and its modified forms with L-cysteine or L-methionine and a mixture of L-cysteine and L-methionine amino acids can be used as efficient adsorbents for removal-separation of Pb and Ni ions from aqueous solution. In this study, to confirm the modification of activated silica gel and adsorbent selection for optimization using a batch technique, FTIR, XRD, SEM & BET characterization were used, and from the characterization results, the activated silica gel modified with a mixture of amino acids is obtained as a better adsorbent than others for optimization methods. Batch adsorption studies were used to evaluate the effects of pH, contact time, initial concentration of adsorbate, and adsorbent dose. The adsorption removal efficiency of adsorbent SiO_2-(L-Cys + L-Meth) was found to be highly affected by these factors. It was found that percent removal increases with an increase pH from 5 to 6 for Pb(II), contact time (30 – 150 min), and dose ((0.2 g–1 g)/50 mL) for both, the degree of increase was 84.4, 85.2 and 94, 97.15 and 99.35 for Pb (II) and Ni (II) respectively. There is also decreasing trend with an increased pH (5-9) for Ni (II) and initial concentration of Pb(II) and Ni(II) in the solution at fixed adsorbent dosage. In this work, 97.15 and 99.35 % for Pb(II) and Ni(II) removal were obtained at pH 6 and 5, 90 and 60 min, and 0.8 and 0.4 g per 50 mL of adsorbent dose for Pb(II) and Ni(II) respectively, and initial concentration 2 mg/L for both. The data from kinetic experiments was found to fit well with the pseudo-second-order kinetic model with a high R^2 value of 0.80445 and 0.99999 for Pb(II) and Ni(II), respectively, then pseudo-first-order kinetic

model. So the pseudo-second-order kinetic model is observed more applicable for both ions and this indicates the presence of chemisorption. The adsorption process of this thesis is well described by the Langmuir model for Pb(II) and Freundlich model for Ni(II). It is found that the uptake of Pb(II) and Ni(II) ions improved by using modified ASG with a mixture of L-cysteine and L-methionine (SiO_2-(L-Cys + L-Meth)) and L-Meth than unmodified activated silica gel. In addition to the results obtained for SiO_2-(L-Cys + L-Meth) powder can be used for the removal of Pb(II) from EIZ wastewater. Further SiO_2-(L-Cys + L-Meth) could be reused repeatedly in adsorption and removal of Pb and Ni ions without significantly losing their adsorption properties.

5.2. Recommendations

The ASG and its modified forms can also be used as a possible alternative for the removal of heavy metals due to its multi-functionality. From different kinds of literature reports, silica gel modified by L-Cys (SiO_2-Cys) or L-meth(SiO_2 –Meth) has shown a high affinity for meals. Therefore, other researches should be conducted to assess the applicability of modified ASG with mixture of L-Cys and L-Meth (SiO_2-(L-Cys + L-Meth)) for different cations adsorption from industrial wastewater. In addition, the silica gel modification method is preferable for lead and nickel ions and also for other metals removal. Because of its time saving, simplicity, low cost, and green, so it is better for researcher further studies on this adsorbent. It is also possible to study the thermodynamics of the system as well as desorption using different eluent to get a full picture of the removal capacity of the SiO_2-(L-Cys + L-Meth) for heavy metal removal from different types of wastewater.

Further, we recommended that for a researcher it is better to assess by expanding this study using agricultural waste like rice husk as the cheapest source for silica gel preparation and modifying with a mixture of L-cysteine and L-methionine. Finally, it is recommended for EIZ to use these adsorbents for the removal of Pb(II) and also for other heavy metals because they have been discharging Pb(II) contaminated wastewater to the environment. This wastewater is directly released to the land used for farming as irrigation water. Therefore, it is risky for people living around this factory because, heavy metals have bioaccumulative nature so, they have the responsibility to treat more and more before discharging to the environment. Similarly, it is also recommended for Modjo tannery share company to use these adsorbents for Ni(II) removal.

Research Fund Acknowledgment

This work is financially supported by Adama Science and Technology University and the Ministry of Innovation and Technology of Ethiopia under the grant number **ASTU/SM-R/370/21**, Adama, Ethiopia.

6. REFERENCE

(FAO), F. and A. O. of the U. N. (2 C.E.). *On-farm practices for the safe use of wastewater in urban and peri-urban horticulture* (Vol. 148).

Abbasi, S., & Noorizadeh, H. (2017). *Adsorption of Nile Blue A from aqueous solution by different nanostructured carbon adsorbents*. *23*, 30–37. https://doi.org/10.5714/CL.2017.23.030

Abdulrazak, S., Hussaini, K., & Sani, H. M. (2017). Evaluation of removal efficiency of heavy metals by low-cost activated carbon prepared from African palm fruit. *Applied Water Science*, *7*(6), 3151–3155. https://doi.org/10.1007/s13201-016-0460-x

Acker, E. G., Ave, R., Hurley, F. R., & Drive, F. H. (1967). *United States Patent Office*. 3–5.

Adane, B., Siraj, K., & Meka, N. (2015). Kinetic, equilibrium and thermodynamic study of 2-chlorophenol adsorption onto Ricinus communis pericarp activated carbon from aqueous solutions. *Green Chemistry Letters and Reviews*, *8*(3–4), 1–12. https://doi.org/10.1080/17518253.2015.1065348

Aghalari, Z., Dahms, H. U., Sillanpää, M., Sosa-Hernandez, J. E., & Parra-Saldívar, R. (2020). Effectiveness of wastewater treatment systems in removing microbial agents: A systematic review. *Globalization and Health*, *16*(1), 1–11. https://doi.org/10.1186/s12992-020-0546-y

Aguado, J., Arsuaga, J. M., Arencibia, A., Lindo, M., & Gascón, V. (2009). Aqueous heavy metals removal by adsorption on amine-functionalized mesoporous silica. *Journal of Hazardous Materials*, *163*(1), 213–221. https://doi.org/10.1016/j.jhazmat.2008.06.080

Ahmad, A., & Azam, T. (2019). Water Purification Technologies. In *Bottled and Packaged Water*. Elsevier Inc. https://doi.org/10.1016/b978-0-12-815272-0.00004-0

Ahmad, M. S. A., & Ashraf, M. (2011). Essential roles and hazardous effects of nickel in plants. In *Reviews of Environmental Contamination and Toxicology* (Vol. 214). https://doi.org/10.1007/978-1-4614-0668-6_6

Al-Lami, A. M. A., Khudhaier, S. R., & Aswad, O. A. (2020). Effects of heavy metals pollution on human health. *Annals of Tropical Medicine and Public Health*, *23*(11). https://doi.org/10.36295/asro.2020.231125

Alaba, P. A., Oladoja, N. A., Sani, Y. M., Ayodele, O. B., Mohammed, I. Y., Olupinla, S. F., Mohd, W., & Daud, W. (2018). Insight into Wastewater Decontamination Using Polymeric Adsorbents. *Biochemical Pharmacology*. https://doi.org/10.1016/j.jece.2018.02.019

Alcock, L. J., Perkins, M. V., & Chalker, J. M. (2018). Chemical methods for mapping cysteine oxidation. *Chemical Society Reviews*, *47*(1), 231–268. https://doi.org/10.1039/c7cs00607a

Alghanmi, R. M. (2012). ICP-OES determination of trace metal ions after preconcentration using silica gel modified with 1,2-dihydroxyanthraquinone. *E-Journal of Chemistry*, *9*(2), 1007–1016. https://doi.org/10.1155/2012/279628

Ali, H., Khan, E., & Ilahi, I. (2019). Environmental Chemistry and Ecotoxicology of Hazardous Heavy Metals : Environmental Persistence , Toxicity , and Bioaccumulation. *Journal of Chemistry*, *2019*(Cd).

Ali, M., & Nas, F. S. (2018). The effect of lead on plants in terms of growing and biochemical parameters: a review. *MOJ Ecology & Environmental Sciences*, *3*(4), 265–268. https://doi.org/10.15406/mojes.2018.03.00098

Amare, A. (2019). Corporate environmental responsibility in Ethiopia: a case study of the Akaki River Basin. *Ecosystem Health and Sustainability*, *5*(1), 57–66. https://doi.org/10.1080/20964129.2019.1573107

Ambroz, F., Macdonald, T. J., Martis, V., & Parkin, I. P. (2018). Evaluation of the BET theory for the characterization of meso and microporous MOFs. *Small Methods*, *2*(11), 1–17. https://doi.org/10.1002/smtd.201800173

Ametepey, S. T., Cobbina, S. J., Akpabey, F. J., Duwiejuah, A. B., & Abuntori, Z. N. (2018). Health risk assessment and heavy metal contamination levels in vegetables from tamale metropolis, Ghana. *International Journal of Food Contamination*, *5*(1). https://doi.org/10.1186/s40550-018-0067-0

Angevine, C. L., Heller, P. L., & Paola, C. (2006). World Health Organization (WHO). WHO Guidelines for the Safe use of wastewater, excreta and greywater. *Quantitative Sedimentary Basin Modeling*, *2*. https://doi.org/10.1306/ce32509c2

Angiro, C., Abila, P. P. O., & Omara, T. (2020). Effects of industrial effluents on the quality of water in Namanve stream, Kampala Industrial and Business Park, Uganda. *BMC Research Notes*, *13*(1), 4–9. https://doi.org/10.1186/s13104-020-05061-x

Arega. (2020). Assesssment of downriver pollution profile of gondar city wastewater and its influence on keha river. *Applied Journal of Environmental Engineering Science*, *6*(3), 291–309.

Ariffin, N., Abdullah, M. M. A. B., Zainol, M. R. R. M. A., Murshed, M. F., Hariz-Zain, Faris, M. A., & Bayuaji, R. (2017). Review on Adsorption of Heavy Metal in Wastewater by Using Geopolymer. *MATEC Web of Conferences*, *97*. https://doi.org/10.1051/matecconf/20179701023

Assi, M. A., Hezmee, M. N. M., Haron, A. W., Sabri, M. Y. M., & Rajion, M. A. (2016). The detrimental effects of lead on human and animal health. *Veterinary World*, *9*(6), 660–671. https://doi.org/10.14202/vetworld.2016.660-671

Aurich, A., Hofmann, J., Oltrogge, R., Wecks, M., Gläser, R., Blömer, L., Mauersberger, S., Müller, R. A., Sicker, D., & Giannis, A. (2017). Improved Isolation of Microbiologically Produced (2R,3S)-Isocitric Acid by Adsorption on Activated Carbon and Recovery with Methanol. *Organic Process Research and Development*, *21*(6), 866–870. https://doi.org/10.1021/acs.oprd.7b00090

Aynekugnem, A. (2015). *Chromium Removal from Chromium Rich Tannery Wastewater using Eucalyptus camaldulensis Dehnh. Bark Powder as an Adsorbent, the Case of Modjo Tannery, Ethiopia. BY:*

Baccile, N., Babonneau, F., Thomas, B., Coradin, T., Baccile, N., Babonneau, F., Thomas, B., & Coradin, T. (2017). *Introducing ecodesign in silica sol-gel materials . To cite this version : HAL Id : hal-00437449 Introducing ecodesign in silica sol-gel materials*. 8537–8559.

Bahiru, D. B., Teju, E., Kebede, T., & Demissie, N. (2019). *Levels of some toxic heavy*

metals (Cr , Cd and Pb) in selected vegetables and soil around eastern industry zone , central Ethiopia. *14*(2), 92–101. https://doi.org/10.5897/AJAR2018.13324

Bamdad, H., Hawboldt, K., & MacQuarrie, S. (2018). A review on common adsorbents for acid gases removal: Focus on biochar. *Renewable and Sustainable Energy Reviews*, *81*(October 2016), 1705–1720. https://doi.org/10.1016/j.rser.2017.05.261

Batool, F., Akbar, J., Iqbal, S., Noreen, S., & Bukhari, S. N. A. (2018). Study of Isothermal, Kinetic, and Thermodynamic Parameters for Adsorption of Cadmium: An Overview of Linear and Nonlinear Approach and Error Analysis. *Bioinorganic Chemistry and Applications*, *2018*. https://doi.org/10.1155/2018/3463724

Bayu, A., Nandiyanto, D., Oktiani, R., & Ragadhita, R. (2019). *Indonesian Journal of Science & Technology How to Read and Interpret FTIR Spectroscope of Organic Material*. *1*, 97–118.

Bayuo, J., Abukari, M. A., & Pelig-Ba, K. B. (2020). Desorption of chromium (VI) and lead (II) ions and regeneration of the exhausted adsorbent. *Applied Water Science*, *10*(7), 1–6. https://doi.org/10.1007/s13201-020-01250-y

Bazrafshan, E., Mohammadi, L., Ansari-Moghaddam, A., & Mahvi, A. H. (2015). Heavy metals removal from aqueous environments by electrocoagulation process - A systematic review. *Journal of Environmental Health Science and Engineering*, *13*(1). https://doi.org/10.1186/s40201-015-0233-8

Bekele Bahiru, D., & Yegrem, L. (2021). Levels of Heavy Metal in Vegetable, Fruits and Cereals Crops in Ethiopia: A Review. *International Journal of Environmental Monitoring and Analysis*, *9*(4), 96. https://doi.org/10.11648/j.ijema.20210904.11

Bilgiç, A. (2019). Removal of chromium (VI) from polluted wastewater by chemical modi fi cation of silica gel with 4-acetyl-. *RSC Advances*, *9(64)*, 37403–37414. https://doi.org/10.1039/c9ra05810a

Bin, P., Huang, R., & Zhou, X. (2017). Oxidation resistance of the sulfur amino acids: Methionine and cysteine. *BioMed Research International*, *2017*. https://doi.org/10.1155/2017/9584932

BOI. (2011). *Board of Investment of Sri Lanka*. 1–21.

Boles, G. C., Stevenson, B. C., Hightower, R. L., Berden, G., Oomens, J., & Armentrout, P. B. (2021). Zinc and cadmium complexation of L-methionine: An infrared multiple photon dissociation spectroscopy and theoretical study. *Journal of Mass Spectrometry*, *56*(4). https://doi.org/10.1002/jms.4580

Bolisetty, S., Peydayesh, M., & Mezzenga, R. (2019). Sustainable technologies for water purification from heavy metals: review and analysis. *Chemical Society Reviews*, *48*(2), 463–487. https://doi.org/10.1039/c8cs00493e

Borchate, S. S., Kulkarni, G. S., Kore, V. S., & Kore, S. V. (2014). A Review on Applications of Coagulation- Flocculation and Ballast Flocculation for Water and Wastewater. *International Journal of Innovations in Engineering and Technology*, *4*(4), 216–223.

Briffa, J., Sinagra, E., & Blundell, R. (2020). Heavy metal pollution in the environment and their toxicological effects on humans. *Heliyon*, *6*(9), e04691. https://doi.org/10.1016/j.heliyon.2020.e04691

Bullen, J. C., Saleesongsom, S., Gallagher, K., & Weiss, D. J. (2021). A Revised Pseudo-Second-Order Kinetic Model for Adsorption, Sensitive to Changes in Adsorbate and Adsorbent Concentrations. *Langmuir*, *37*(10), 3189–3201. https://doi.org/10.1021/acs.langmuir.1c00142

Canosa, E., Norrehed, S., Karlsson, A., Fischer, A., & Rigbrandt, C. (2019). Adsorbents for Pollution Reduction in Cultural Heritage Collections. *Researchgate Review*, *November*.

Chakraborty, R., Asthana, A., Singh, A. K., Jain, B., & Susan, A. B. H. (2020). Adsorption of heavy metal ions by various low-cost adsorbents: a review. *International Journal of Environmental Analytical Chemistry*, *00*(00), 1–38. https://doi.org/10.1080/03067319.2020.1722811

Chen, H., Bian, H., Li, J., Guo, X., Wen, X., & Zheng, J. (2013). Molecular conformations of crystalline l -cysteine determined with vibrational cross angle measurements. *Journal of Physical Chemistry B*, *117*(49), 15614–15624. https://doi.org/10.1021/jp406232k

Coates, J. (2004). Encyclopedia of Analytical Chemistry -Interpretation of Infrared Spectra, A Practical Approach. *Encyclopedia of Analytical Chemistry*, 1–23.

Company, H. (2014). *Phosphorus , Total*. 1–8. –%0Awww.hach.com%0A; E-mail – techhelp@hach.com

Crini, G., & Lichtfouse, E. (2019). Advantages and disadvantages of techniques used for wastewater treatment. *Environmental Chemistry Letters*, *17*(1), 145–155. https://doi.org/10.1007/s10311-018-0785-9

Crini, G., Lichtfouse, E., Wilson, L. D., & Morin-Crini, N. (2018). Conventional and non-conventional adsorbents for wastewater treatment. *Environmental Chemistry Letters*, *17*(1), 195–213. https://doi.org/10.1007/s10311-018-0786-8

Cui, Y., Chang, X., Zhu, X., Luo, H., Hu, Z., Zou, X., & He, Q. (2007). Chemically modified silica gel with p-dimethylaminobenzaldehyde for selective solid-phase extraction and preconcentration of Cr(III), Cu(II), Ni(II), Pb(II) and Zn(II) by ICP-OES. *Microchemical Journal*, *87*(1), 20–26. https://doi.org/10.1016/j.microc.2007.04.004

Dagne, B. B. (2020). Determination of Heavy Metals in Wastewater and Their Toxicological Implications around Eastern Industrial Zone, Central Ethiopia. *Journal of Environmental Chemistry and Ecotoxicology*, *12*(2), 72–79. https://doi.org/10.5897/jece2019.0453

Dakova, I., Vasileva, P., & Karadjova, I. (2011). Cysteine modified silica submicrospheres as a new sorbent for preconcentration of Cd (II) and Pb (II). *Bulgarian Chemical Communications*, *43*(2), 210–216.

Dakova1, I., & , P. Vasileva 2, I. K. 1. (2011). *Cysteine modified silica submicrospheres as a new sorbent for Cysteine modified silica submicrospheres as a new sorbent for preconcentration of Cd (II) and Pb (II). January*.

Das, K. K., Reddy, R. C., Bagoji, I. B., Das, S., Bagali, S., Mullur, L., Khodnapur, J. P., & Biradar, M. S. (2018). *Primary concept of nickel toxicity – an overview https://doi.org/10.1515/jbcpp-2017-0171*. 1–12.

De Magalhães Padilha, P., De Melo Gomes, L. A., Federici Padilha, C. C., Moreira, J. C.,

& Dias Filho, N. L. (1999). Determination of metal ions in natural waters by flame-AAS after preconcentration on a 5-amino-1,3,4-thiadiazole-2-thiol modified silica gel. *Analytical Letters*, *32*(9), 1807–1820. https://doi.org/10.1080/00032719908542935

Debebe, D., Behulu, F., & Getaneh, Z. (2020). *Predicting children ' s blood lead levels from exposure to school drinking water in Addis Ababa, Ethiopia Dawit Debebe , Fiseha Behulu and Zerihun Getaneh*. 595–601. https://doi.org/10.2166/wh.2020.248

Diana Iruretagoyena Ferrer. (2016). Supported Layered Double Hydroxides as CO2 Adsorbents for Sorption-enhanced H2 production. In *Springer Theses*.

Dickin, S. K., Schuster-Wallace, C. J., Qadir, M., & Pizzacalla, K. (2016). Health risks and pathways of wastewater exposure. *Environ Health Perspect*, *124*(7), 900–909. https://ehp.niehs.nih.gov/wp-content/uploads/124/7/ehp.1509995.alt.pdf

Duffus, J. H. (2002). Metales pesados: ¿Un plazo significativo? *Pure and Applied Chemistry*, *74*(5), 793–807. http://www.degruyter.com/view/j/pac.2002.74.issue-5/pac200274050793/pac200274050793.xml

Duressa, T. F. (n.d.). Assessment of Lead Toxicity Awareness among Battery Charging Garage and Workshop Workers and Levels of Lead in Piped Drinking Water of Addis Ababa, Ethiopia. *Signature*, *18*(February 2008).

Edokpayi, J. N., Odiyo, J. O., & Durowoju, O. S. (2017). Household Hazardous Waste Management in - Impact of Wastewater on Surface Water Quality in sub-Saharan Africa Developing Countries : A Case Study of South Africa. *Water Quality*, *18*, 1–16.

Englande, A. J., Krenkel, P., & Shamas, J. (2015). Wastewater Treatment &Water Reclamation☆. In *Reference Module in Earth Systems and Environmental Sciences*. Elsevier Inc. https://doi.org/10.1016/b978-0-12-409548-9.09508-7

Engwa, G. A., Ferdinand, P. U., Nwalo, F. N., & Unachukwu, M. N. (2019). *Mechanism and Health Effects of Heavy Metal Toxicity in Humans*.

Farrukh, A., Akram, A., Ghaffar, A., Oluz, Z., Duran, H., & Yameen, B. (2014). *Conference paper Surface-functionalized silica gel adsorbents for efficient*

remediation of cationic dyes. *86*(7), 1177–1188. https://doi.org/10.1515/pac-2014-0105

Farrukh, A., Akram, A., Ghaffar, A., Tuncel, E., Oluz, Z., Duran, H., Ur Rehman, H., & Yameen, B. (2014). Surface-functionalized silica gel adsorbents for efficient remediation of cationic dyes. *Pure and Applied Chemistry*, *86*(7), 177–1188. https://doi.org/10.1515/pac-2014-0105

Fay, D. L., Akhavan, S., & Goldberg, V. M. (1967). 済無No Title No Title No Title. *Angewandte Chemie International Edition, 6(11), 951–952.*, *27*(465), 106–111.

Feinle, A., Leichtfried, F., & Hu, N. (2017). *Carboxylic acid-functionalized porous silica particles by a co-condensation approach*. 138–146. https://doi.org/10.1007/s10971-016-4090-4

Flora, G., Gupta, D., & Tiwari, A. (2012). *Toxicity of lead : A review with recent updates*. *5*(2), 47–58. https://doi.org/10.2478/v10102-012-0009-2

Gabelman, A. (2017). *Adsorption Basics: Part 2 | AIChE*. *August*, 38–45. https://www.aiche.org/sites/default/files/docs/pages/adsorption_basics_part_2.pdf

Ganokar, A. V, Bhoyar, S. U., Raut, N. S., & Gupta, K. R. (2018). *The magic particle silica : Past to present*. *5*(3), 123–129. https://doi.org/10.18231/2394-2797.2018.0019

Gashaye, D. (2020). Wastewater-irrigated urban vegetable farming in Ethiopia: A reviewon their potential contamination and health effects. *Cogent Food & Agriculture*, *00*(00). https://doi.org/10.1080/23311932.2020.1772629

Genchi, G., Carocci, A., Lauria, G., Sinicropi, M. S., & Catalano, A. (2020). Nickel: Human health and environmental toxicology. *International Journal of Environmental Research and Public Health*, *17*(3). https://doi.org/10.3390/ijerph17030679

Ghaedi, M., & Mosallanejad, N. (2013). *Removal of Heavy Metal Ions from Polluted Waters by Using of Low Cost Adsorbents : Review*. *3*(1), 7–22.

Ghaedi, M., Rezakhani, M., Khodadoust, S., Niknam, K., & Soylak, M. (2012). The solid phase extraction of some metal ions using palladium nanoparticles attached to silica gel chemically bonded by silica-bonded N-propylmorpholine as new sorbent prior to

their determination by flame atomic absorption spectroscopy. *The Scientific World Journal*, *2012*. https://doi.org/10.1100/2012/764195

Ghasemi, Z., Sourinejad, I., Kazemian, H., & Rohani, S. (2018). Application of zeolites in aquaculture industry: a review. *Reviews in Aquaculture*, *10*(1), 75–95. https://doi.org/10.1111/raq.12148

Girmaye, B. (2014). *Assessment of heavy metals in vegetables irrigated with Awash River in selected farms around Adama*. *8*(7), 428–434. https://doi.org/10.5897/AJEST2014.1732

Grégorio Crini, Eric Lichtfouse, Lee Wilson, N. M.-C. (2018). Adsorption-oriented processes using conventional and non-conventional adsorbents for wastewater treatment. In *Environmental Chemistry Letters* (Vol. 17, Issue 1). https://doi.org/10.1007/s10311-018-0786-8

Guevara-Flores, A., De Jesús Martínez-González, J., Rendón, J. L., Del Arenal, I. P., Nagahara, N., & Wrobel, M. (2017). The architecture of thiol antioxidant systems among invertebrate parasites. *Molecules*, *22*(2), 1–35. https://doi.org/10.3390/molecules22020259

Harasim, P., & Filipek, T. (2015). Nickel in the environment. *Journal of Elementology*, *20*(2), 525–534. https://doi.org/10.5601/jelem.2014.19.3.651

Herdyastuti, N., Rusmini, & Cahyaningrum, S. E. (2019). Characteristic and Adsorption Capacity of Activated Carbon and Bentonite to Heavy Metal. *Eurasian Journal of Analytical Chemistry*, *14*(3), 48–54.

Ho, Y. S. (2006). Review of second-order models for adsorption systems. *Journal of Hazardous Materials*, *136*(3), 681–689. https://doi.org/10.1016/j.jhazmat.2005.12.043

Ibrahim, T. N. B. T., Othman, F., & Mahmood, N. Z. (2020). Baseline Study of Heavy Metal Pollution in a Tropical River in a Developing Country. *Sains Malaysiana*, *49*(4), 729–742. https://doi.org/10.17576/jsm-2020-4904-02

Iftekhar, S., Ramasamy, D. L., Srivastava, V., Asif, M. B., & Sillanpää, M. (2018). Understanding the factors affecting the adsorption of Lanthanum using different adsorbents: A critical review. *Chemosphere*, *204*, 413–430.

https://doi.org/10.1016/j.chemosphere.2018.04.053

Iman, T. D. (n.d.). *Effect of dimethylformamide on the gels structure of SiO 2 -gels materials from TMOS and TEOS*.

Ince, M., & Kaplan Ince, O. (2020). Heavy Metal Removal Techniques Using Response Surface Methodology: Water/Wastewater Treatment. *Biochemical Toxicology - Heavy Metals and Nanomaterials*, 1–19. https://doi.org/10.5772/intechopen.88915

Intizar Hussain, Liqa Raschid, Munir A. Hanjra, F. M. and W. van der H. (2020). Wastewater Re-use in Agriculture. In *WASTEWATER USE IN AGRICULTURE: REVIEW OF IMPACTS AND METHODOLOGICAL ISSUES IN VALUING IMPACTS*. https://doi.org/10.4324/9781849771023-27

Inyinbor Adejumoke A., Adebesin Babatunde O., Oluyori Abimbola P., Adelani-Akande Tabitha A., D. A. O. and O. T. A. (2018). Water Pollution: Effects, Prevention, and Climatic Impact. *Water Challenges of an Urbanizing World*. https://doi.org/10.5772/intechopen.72018

Ismail, L., Khalili, F., & Abu Orabi, F. M. (2020). Modification of Silica Nanoparticles with Cysteine or Methionine Amino Acids for the Removal of Uranium (VI) from Aqueous Solution. *Silicon*, *12*(11), 2647–2661. https://doi.org/10.1007/s12633-019-00361-9

Ismail, L., Khalili, F., & Orabi, F. M. A. (2020). *Modification of Silica Nanoparticles with Cysteine or Methionine Amino Acids for the Removal of Uranium (VI) from Aqueous Solution*. *Vi*.

Issakhov, A., Alimbek, A., & Zhandaulet, Y. (2021). The assessment of water pollution by chemical reaction products from the activities of industrial facilities : Numerical study. *Journal of Cleaner Production*, *282*, 125239. https://doi.org/10.1016/j.jclepro.2020.125239

Jafari, V., & Allahverdi, A. (2014). Synthesis and Characterization of Colloidal Nanosilica via an Ultrasound Assisted Route Based on Alkali Leaching of Silica Fume. *International Journal of Nanoscience and Nanotechnology*, *10*(3), 145–152.

Jaishankar, M., Tseten, T., Anbalagan, N., Mathew, B. B., & Beeregowda, K. N. (2014).

Toxicity , mechanism and health effects of some heavy metals. *7*(2), 60–72. https://doi.org/10.2478/intox-2014-0009

Jasim, N. A. (2020). The design for wastewater treatment plant (WWTP) with GPS X modelling. *Cogent Engineering*, *7*(1). https://doi.org/10.1080/23311916.2020.1723782

Jeong, S., Naidu, G., Leiknes, T., & Vigneswaran, S. (2017). Membrane biofouling: Biofouling assessment and reduction strategies in seawater reverse osmosis desalination. In *Comprehensive Membrane Science and Engineering: Second Edition* (Vol. 4). Elsevier Ltd. https://doi.org/10.1016/b978-0-12-409547-2.12261-9

Jiang, J., Ma, X. S., Xu, L. Y., Wang, L. H., Liu, G. Y., Xu, Q. F., Lu, J. M., & Zhang, Y. (2015). Applications of chelating resin for heavy metal removal from wastewater. *E-Polymers*, *15*(3), 161–167. https://doi.org/10.1515/epoly-2014-0192

Johnson, P. D., Girinathannair, P., Ohlinger, K. N., Ritchie, S., Teuber, L., & Kirby, J. (2008). Enhanced Removal of Heavy Metals in Primary Treatment Using Coagulation and Flocculation. *Water Environment Research*, *80*(5), 472–479. https://doi.org/10.2175/106143007x221490

Jung, I., Sihn, Y., & Yun, J. (2019). *Study on the Functional Group Affinity Toward Aqueous Cesium*. *C*, 9–10.

Kanamarlapudi, S. L. R. K., Chintalpudi, V. K., & Muddada, S. (2018). Application of Biosorption for Removal of Heavy Metals from Wastewater. *Biosorption*. https://doi.org/10.5772/intechopen.77315

Kane, S. N., Mishra, A., & Dutta, A. K. (2016). Removal of nickel ion from electroplating wastewater using double chamber electrodeposition cell (DCEC) reactor partitioned with water hyacinth (Eichhornia crassipes) leaves. *Journal of Physics: Conference Series*, *755*(1). https://doi.org/10.1088/1742-6596/755/1/011001

Karnib, M., Kabbani, A., Holail, H., & Olama, Z. (2014). Heavy metals removal using activated carbon, silica and silica activated carbon composite. *Energy Procedia*, *50*, 113–120. https://doi.org/10.1016/j.egypro.2014.06.014

Kaur, R., Sharma, S., & Kaur, N. (2019). *2 International Conference " Food Security ,*

Nutrition and Sustainable Agriculture - Emerging Technologies " Heavy metals toxicity and the environment. 247–249.

Keraita, B., Jimenez, B., & Drechsel, P. (2008). Extent and implications of agricultural reuse of untreated, partly treated and diluted wastewater in developing countries. *CAB Reviews: Perspectives in Agriculture, Veterinary Science, Nutrition and Natural Resources*, *3*(January 2010). https://doi.org/10.1079/PAVSNNR20083058

Kesari, K. K., Soni, R., Jamal, Q. M. S., Tripathi, P., Lal, J. A., Jha, N. K., Siddiqui, M. H., Kumar, P., Tripathi, V., & Ruokolainen, J. (2021). Wastewater Treatment and Reuse: a Review of its Applications and Health Implications. *Water, Air, and Soil Pollution*, *232*(5). https://doi.org/10.1007/s11270-021-05154-8

Khalid Z. Elwakeel, Ahmed M. Elgarahy, Ziya A. Khan, Muath S. Almughamisi, A. S. A.-B. (2020). *Perspectives regarding metals/minerals-incorporated materials for water purification: with special focus on cr(vi) removal*. https://doi.org/10.1039/D0MA00153H

Khalil, L. B., Attia, A. A., & El-Nabarawy, T. (2001). Modified silica for the Extraction of Cadmium(II), Copper (II) and Zinc(II) ions from their aqueous solutions. *Adsorption Science and Technology*, *19*(7), 511–523. https://doi.org/10.1260/0263617011494367

Khanvilkar, P. B. B. * 1 and V. V. (2019). *SILICA GEL: A KEYSTONE IN CHROMATOGRAPHIC TECHNIQUES*. *10*(1), 12–22. https://doi.org/10.13040/IJPSR.0975-8232.10(1).12-22

Khulbe, K. C., & Matsuura, T. (2018). Removal of heavy metals and pollutants by membrane adsorption techniques. *Applied Water Science*, *8*(1). https://doi.org/10.1007/s13201-018-0661-6

Kierys, A., Goworek, J., Rawski, M., & Halasz, I. (2015). *On the molecular basis of silica gel morphology*. *February*. https://doi.org/10.5185/amlett.2015.amwc1194

Kırkan, B., & Aycik, G. A. (2016). Solid phase extraction using silica gel modified with azo-dyes derivative for preconcentration and separation of Th(IV) ions from aqueous solutions. *Journal of Radioanalytical and Nuclear Chemistry*, *308*(1), 81–91. https://doi.org/10.1007/s10967-015-4382-0

Knippenberg, M. T., Stuart, S. J., Cooper, A. C., & Pez, G. P. (2006). *Physical Adsorption Strength in Open Systems*. 22957–22960.

Koller, M., & Saleh, H. M. (2018). Introductory Chapter: Introducing Heavy Metals. *Heavy Metals*, 3–12. https://doi.org/10.5772/intechopen.74783

Kushwaha, A. K., Gupta, N., & Chattopadhyaya, M. C. (2012). Adsorption behavior of lead onto a new class of functionalized silica gel. *ARABIAN JOURNAL OF CHEMISTRY*. https://doi.org/10.1016/j.arabjc.2012.06.010

Kweinor Tetteh, E., & Rathilal, S. (2020). Application of Organic Coagulants in Water and Wastewater Treatment. *Organic Polymers*, 1–18. https://doi.org/10.5772/intechopen.84556

Lakherwal, D. (2014). Adsorption of Heavy Metals : A Review. *International Journal of Environmental Research and Development*, *4*(1), 41–48.

Lalmi, A., Bouhidel, K. E., Sahraoui, B., & Anfif, C. el H. (2018). Removal of lead from polluted waters using ion exchange resin with Ca(NO3)2 for elution. *Hydrometallurgy*, *178*(2017), 287–293. https://doi.org/10.1016/j.hydromet.2018.05.009

Lenz, G. R., & Martell, A. E. (1964). Metal Chelates of Some Sulfur-Containing Amino Acids. *Biochemistry*, *3*(6), 745–750. https://doi.org/10.1021/bi00894a001

Li, Y., Yang, X., Chen, Z., & Zhang, B. (2015). *Comparative toxicity of lead (Pb2+), copper (Cu2+), and mixtures of lead and copper to zebrafish embryos on a microfluidic chip*. *024105*, 1–11.

Lichtfouse, E. (2021). *reen Adsorbents to Remove Metals, Dyes and Boron from Polluted Water* (Inamuddin Abdullah M. Asiri Editors Eric Lichtfouse Mohd Imran Ahamed (ed.)). Environmental Chemistry for a Sustainable World. https://doi.org/doi:10.1007/978-3-030-47400-3

Liu, C., He, S., Shen, K., & Feng, X. (2014). *L -Cysteine Functionalized Silica Gel as an Efficient Adsorbent for the Determination of Heavy Metals in Foods by ICP-MS*. https://doi.org/10.1007/s12161-014-0061-y

Lovibond, M. 600. (2017). Photometer System. *Tintometer GmbH*.

M, E., & Munoz, R. (2011). Hydroxyapatite-Based Materials : Synthesis and Characterization, Biomedical Engineering - Frontiers and Challenges. *Biomedical Engineering - Frontiers and Challenges*, 78–88.

Ma, J., Jia, K., Cheng, G., & Zhang, S. (2005). *Solid-Phase Extraction of Pb (II) Ions Based on L-Cysteine Functionalized Fe 3 O 4 = SiO 2 Core-Shell Nanoparticles*. *2*(Ii), 1–7. https://doi.org/10.1061/(ASCE)EE

Maharana, M., Manna, M., Sardar, M., & Sen, S. (2021). *Heavy Metal Removal by Low-Cost Adsorbents*. *September 2020*, 245–272. https://doi.org/10.1007/978-3-030-47400-3_10

Mahboob, S., Alkkahem Al-Balwai, H. F., Al-Misned, F., Al-Ghanim, K. A., & Ahmad, Z. (2014). A study on the accumulation of nine heavy metals in some important fish species from a natural reservoir in Riyadh, Saudi Arabia. *Toxicological and Environmental Chemistry*, *96*(5), 783–798. https://doi.org/10.1080/02772248.2014.957485

Makkuni, A., Bachas, L. G., Varma, R. S., Sikdar, S. K., & Bhattacharyya, D. (2005). Aqueous and vapor phase mercury sorption by inorganic oxide materials functionalized with thiols and poly-thiols. *Clean Technologies and Environmental Policy*, *7*(2), 87–96. https://doi.org/10.1007/s10098-004-0260-0

Masindi, V., & Muedi, K. L. (2018). Environmental Contamination by Heavy Metals. *IntechOpen*, *Heavy Met*. https://doi.org/10.5772

Mayssara A. Abo Hassanin Supervised, A. (2014). 済無No Title No Title No Title. *Paper Knowledge . Toward a Media History of Documents*.

Mengistie*, B. H. A. and A. A. (2013). *Removal of Ni(II) from aqueous solution using leaf, bark and seed of moringa stenopetala adsorbents*. *27*(1), 35–47. https://doi.org/http://dx.doi.org/10.4314/bcse.v27i1.4

Mladenova, E., Dakova, I., Karadjova, I., & Karadjov, M. (2012). Column solid phase extraction and determination of ultra-trace Au, Pd and Pt in environmental and

geological samples. *Microchemical Journal*, *101*, 59–64. https://doi.org/10.1016/j.microc.2011.10.007

Mokarram, M., Saber, A., & Sheykhi, V. (2020). Effects of heavy metal contamination on river water quality due to release of industrial effluents. *Journal of Cleaner Production*, *277*, 123380. https://doi.org/10.1016/j.jclepro.2020.123380

Morante-Carballo, F., Montalván-Burbano, N., Carrión-Mero, P., & Jácome-Francis, K. (2021). Worldwide research analysis on natural zeolites as environmental remediation materials. *Sustainability (Switzerland)*, *13*(11), 1–21. https://doi.org/10.3390/su13116378

Moyo, M., Chikazaza, L., Nyamunda, B. C., & Guyo, U. (2013). *Adsorption Batch Studies on the Removal of Pb (II) Using Maize Tassel Based Activated Carbon*. *2013*.

Naidoo, S., & Olaniran, A. O. (2013). Treated wastewater effluent as a source of microbial pollution of surface water resources. *International Journal of Environmental Research and Public Health*, *11*(1), 249–270. https://doi.org/10.3390/ijerph110100249

Najafi, M., Yousefi, Y., & Rafati, A. A. (2012). Synthesis, characterization and adsorption studies of several heavy metal ions on amino-functionalized silica nano hollow sphere and silica gel. *Separation and Purification Technology*, *85*, 193–205. https://doi.org/10.1016/j.seppur.2011.10.011

Narain-Ford, D. M., Bartholomeus, R. P., Dekker, S. C., & van Wezel, A. P. (2020). Natural Purification Through Soils: Risks and Opportunities of Sewage Effluent Reuse in Sub-surface Irrigation. *Reviews of Environmental Contamination and Toxicology*, *250*, 85–117. https://doi.org/10.1007/398_2020_49

Natu, D. rerum, (U., Nat.), D. rer., & Angeno. (1984). *Int teractio n of am mino ac ids with different iono enic groups g Von*.

Ngeontae, W., Aeungmaitrepirom, W., & Tuntulani, T. (2007). Chemically modified silica gel with aminothioamidoanthraquinone for solid phase extraction and preconcentration of Pb(II), Cu(II), Ni(II), Co(II) and Cd(II). *Talanta*, *71*(3), 1075–1082. https://doi.org/10.1016/j.talanta.2006.05.094

Obasi, P. N., & Akudinobi, B. B. (2020). Potential health risk and levels of heavy metals in water resources of lead–zinc mining communities of Abakaliki, southeast Nigeria. *Applied Water Science*, *10*(7). https://doi.org/10.1007/s13201-020-01233-z

Oljira, L. (2016). Adsorption of heavy metal from constituent waste water by tea waste adsorbent. ..*(Masters of Science Dissertation, Addis Ababa University)*.

Ouazene, N., & Sahmoune, M. N. (2010). Equilibrium and kinetic modelling of astrazon yellow adsorption by sawdust: Effect of important parameters. *International Journal of Chemical Reactor Engineering*, *8*. https://doi.org/10.2202/1542-6580.2413

Ozaki, H., Ichise, H., Kitaura, E., Yaginuma, Y., Yoda, M., Kuno, K., & Watanabe, I. (2019). Immutable heavy metal pollution before and after change in industrial waste treatment procedure. *Scientific Reports*, *9*(1), 1–12. https://doi.org/10.1038/s41598-019-40634-2

P. Senthil Kumar*, C. Vincent, K. Kirthika, and K. S. K. (2010). *Kinetics and equilibrium studies of pb 2 + ion removal from aqueous solutions by use of nano-silversol-coated activated carbon*. *27*(02), 339–346.

Pang, F. M., Teng, S. P., Teng, T. T., & Mohd Omar, A. K. (2009). Heavy metals removal by hydroxide precipitation and coagulation-flocculation methods from aqueous solutions. *Water Quality Research Journal of Canada*, *44*(2), 174–182. https://doi.org/10.2166/wqrj.2009.019

Patel, H. (2019). Fixed-bed column adsorption study: a comprehensive review. *Applied Water Science*, *9*(3), 1–17. https://doi.org/10.1007/s13201-019-0927-7

Petrova, P., Chochkova, M., Karadjova, I., Dakova, I., & Karadjov, M. (2018). *Amino acid functionalized silica gel as a selective sorbent for enrichment of Pt (II)*. *50*(Ii), 20–24.

Petrova, P., Karadjova, I., Chochkova, M., Dakova, I., & Karadjov, M. (2017a). New amino acid modified silica gel sorbents for solid phase extraction of Au (III). *Petrova, P., Karadjova, I., Chochkova, M., Dakova, I., & Karadjov, M. (2017). New Amino Acid Modified Silica Gel Sorbents for Solid Phase Extraction of Au (III). Iii, 95–100.*, *Iii*, 95–100.

Petrova, P., Karadjova, I., Chochkova, M., Dakova, I., & Karadjov, M. (2017b). *New amino acid modified silica gel sorbents for solid phase extraction of Au (III)*. *Iii*, 95–100.

Petrova, P., Karadjova, I., Chochkova, M., Dakova, I., & Karadjov, M. (2017c). New amino acid modified silica gel sorbents for solid phase extraction of Au (III). *Bulgarian Chemical Communications*, *49*(Iii), 95–100.

Pica, M. (2021). Treatment of wastewaters with zirconium phosphate based materials: A review on efficient systems for the removal of heavy metal and dye water pollutants. *Molecules*, *26*(8). https://doi.org/10.3390/molecules26082392

Poole, L. B. (2015). The basics of thiols and cysteines in redox biology and chemistry. *Free Radical Biology and Medicine*, *80*, 148–157. https://doi.org/10.1016/j.freeradbiomed.2014.11.013

Pranudta, A., El-Moselhy, M. M., Kamal, S. M., Chanlek, N., Nguyen, T. T., & Padungthon, S. (2021). Silica gel modified with a novel sulfur-containing organic ligand (2-(benzo[d]thiazol-2-yl)-3,3-dimercapto acrylonitrile) for enhance Hg and Pb removal. *Chemical Engineering Journal Advances*, *6*(February), 100110. https://doi.org/10.1016/j.ceja.2021.100110

Purwanto, A., & Putri, A. (2017). *Adsorption of Pb (II) Using Silica Gel Composite from Rice Husk Ash Modified 3-aminopropyltriethoxysilane (APTES) - Activated Carbon from Coconut Shell*. *020034*(Ii). https://doi.org/10.1063/1.4978107

Qasem, N. A. A., Mohammed, R. H., & Lawal, D. U. (2021). Removal of heavy metal ions from wastewater: a comprehensive and critical review. *Npj Clean Water*, *4*(1). https://doi.org/10.1038/s41545-021-00127-0

Qiu, H., Lv, L., Pan, B. C., Zhang, Q. J., Zhang, W. M., & Zhang, Q. X. (2009). Critical review in adsorption kinetic models. *Journal of Zhejiang University: Science A*, *10*(5), 716–724. https://doi.org/10.1631/jzus.A0820524

Quintero-Jaramillo, J. A., Carrero-Mantilla, J. I., & Sanabria-Gonzalez, N. R. (2021). A review of caffeine adsorption studies onto various types of adsorbents. *Scientific World Journal*, *2021*. https://doi.org/10.1155/2021/9998924

Rabia, A. R., Ibrahim, A. H., & Zulkepli, N. N. (2018). Activated alumina preparation and characterization: The review on recent advancement. *E3S Web of Conferences*, *34*, 1–8. https://doi.org/10.1051/e3sconf/20183402049

Radi, S., El Abiad, C., Carvalho, A. P., Santos, S. M., Faustino, M. A. F., Neves, M. G. P. M. S., & Moura, N. M. M. (2018). An efficient hybrid adsorbent based on silica-supported amino penta-carboxylic acid for water purification. *Journal of Materials Chemistry A*, *6*(27), 13096–13109. https://doi.org/10.1039/c8ta02560f

Rahman, O., Rahman, N., Ahmed, G. M. F., Hasan, S., & Chandra, N. (2020). Synthesis and implication of grafted polymeric adsorbent for heavy metal removal. *SN Applied Sciences*. https://doi.org/10.1007/s42452-020-2908-8

Ramachandran, E., & Natarajan, S. (2006). Gel growth and characterization of β-DL-methionine. *Crystal Research and Technology*, *41*(4), 411–415. https://doi.org/10.1002/crat.200510595

Rasheed, A., Carvalho, A. A. C., de Carvalho, G. G. A., Ghous, T., Nomura, C. S., & Esposito, B. P. (2020). Chromium removal from aqueous solutions using new silica gel conjugates of desferrioxamine or diethylenetriaminepentaacetic acid. *Environmental Science and Pollution Research*, *27*(13), 15635–15644. https://doi.org/10.1007/s11356-020-08097-5

Renu, Agarwal, M., & Singh, K. (2017). Heavy metal removal from wastewater using various adsorbents: A review. *Journal of Water Reuse and Desalination*, *7*(4), 387–419. https://doi.org/10.2166/wrd.2016.104

Repo, E., Warchoł, J. K., Bhatnagar, A., Mudhoo, A., & Sillanpää, M. (2013). Aminopolycarboxylic acid functionalized adsorbents for heavy metals removal from water. *Water Research*, *47*(14), 4812–4832. https://doi.org/10.1016/j.watres.2013.06.020

Repo, E., Warchoł, J. K., & Sillanpää, M. (2017). Metal recovery and preconcentration by aminopolycarboxylic acid modified silica surfaces. *Journal of Sustainable Development of Energy, Water and Environment Systems*, *5*(1), 89–100. https://doi.org/10.13044/j.sdewes.d5.0135

Rius, J. (2015). Structure from diffraction methods. In *Crystallography Reviews* (Vol. 21, Issue 3). https://doi.org/10.1080/0889311x.2014.991393

Rudi, N. N., Muhamad, M. S., Te Chuan, L., Alipal, J., Omar, S., Hamidon, N., Abdul Hamid, N. H., Mohamed Sunar, N., Ali, R., & Harun, H. (2020). Evolution of adsorption process for manganese removal in water via agricultural waste adsorbents. *Heliyon*, *6*(9). https://doi.org/10.1016/j.heliyon.2020.e05049

Samer, M. (2015). Biological and Chemical Wastewater Treatment Processes. *Wastewater Treatment Engineering*, 1–50. https://doi.org/10.5772/61250

Samiey, B., Cheng, C. H., & Wu, J. (2014). Organic-inorganic hybrid polymers as adsorbents for removal of heavy metal ions from solutions: A review. *Materials*, *7*(2), 673–726. https://doi.org/10.3390/ma7020673

Sankhla, M. S. (2019). Contaminant of Heavy Metals in Groundwater & its Toxic Effects on Human Health & Environment. *International Journal of Environmental Sciences & Natural Resources*, *18*(5). https://doi.org/10.19080/ijesnr.2019.18.555996

Sarkar, A., & Paul, B. (2016). Chemosphere The global menace of arsenic and its conventional remediation - A critical review. *Chemosphere*, *158*, 37–49. https://doi.org/10.1016/j.chemosphere.2016.05.043

Separation, G. (2017). *Polymer-based adsorbent for heavy metals removal from aqueous solution Polymer-based adsorbent for heavy metals removal from aqueous solution*. https://doi.org/10.1088/1757-899X/206/1/012100

Series, I. O. P. C., & Science, M. (2019). *Synthesis of silica gel from glass waste for adsorption of Mg 2 + , Cu 2 + , and Ag + metal ions Synthesis of silica gel from glass waste for adsorption of Mg 2 + , Cu 2 + , and Ag + metal ions*. 1–6. https://doi.org/10.1088/1757-899X/509/1/012028

Shabkhizan, S., & Mousazadeh, H. (2011). Sol – gel processed pyridinium ionic liquid-modified silica as a new sorbent for separation and quantification of iron in water samples. *ARABIAN JOURNAL OF CHEMISTRY*. https://doi.org/10.1016/j.arabjc.2011.07.006

Sharma, P., Tripathi, S., & Chandra, R. (2021). Highly efficient phytoremediation potential

of metal and metalloids from the pulp paper industry waste employing Eclipta alba (L) and Alternanthera philoxeroide (L): Biosorption and pollution reduction. *Bioresource Technology*, *319*(August 2020), 124147. https://doi.org/10.1016/j.biortech.2020.124147

Sharma, S. K., Verma, D. S., Khan, L. U., Kumar, S., & Khan, S. B. (2018). Handbook of Materials Characterization. In *Handbook of Materials Characterization* (Issue February). https://doi.org/10.1007/978-3-319-92955-2

Sheet, I., Kabbani, A., & Holail, H. (2014). Removal of heavy metals using nanostructured graphite oxide, silica nanoparticles and silica/graphite oxide composite. *Energy Procedia*, *50*, 130–138. https://doi.org/10.1016/j.egypro.2014.06.016

Shi, J., Yang, Z., Dai, H., Lu, X., Peng, L., Tan, X., Shi, L., & Fahim, R. (2017). Preparation and application of modified zeolites as adsorbents in wastewater treatment. *Water Science and Technology*, *2017*(3), 621–635. https://doi.org/10.2166/wst.2018.249

Shimazaki, Y., Takani, M., & Yamauchi, O. (2009). Metal complexes of amino acids and amino acid side chain groups. Structures and properties. *Dalton Transactions*, *38*, 7854–7869. https://doi.org/10.1039/b905871k

Sing, K. (2001). The use of nitrogen adsorption for the characterisation of porous materials. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *187–188*, 3–9. https://doi.org/10.1016/S0927-7757(01)00612-4

Sing, K. S. W. (1982). Reporting physisorption data for gas / solid systems with Special Reference to the Determination of S. *Pure & Appl. Chem.*, *54*(11), 2201–2218.

Singh, Reena, Gautam, N., Mishra, A., & Gupta, R. (2011). Heavy metals and living systems: An overview. *Indian Journal of Pharmacology*, *43*(3), 246–253. https://doi.org/10.4103/0253-7613.81505

Singh, Rimmy, & Bhateria, R. (2020). *Experimental and Modeling Process Optimization of Lead Adsorption on Magnetite Nanoparticles via Isothermal , Kinetics , and Thermodynamic Studies*. https://doi.org/10.1021/acsomega.0c00450

Singh, S., Wasewar, K. L., & Kansal, S. K. (2020). Low-cost adsorbents for removal of

inorganic impurities from wastewater. In *Inorganic Pollutants in Water*. INC. https://doi.org/10.1016/b978-0-12-818965-8.00010-x

Srivastava, V., Sarkar, A., Singh, S., Singh, P., de Araujo, A. S. F., & Singh, R. P. (2017). Agroecological responses of heavy metal pollution with special emphasis on soil health and plant performances. *Frontiers in Environmental Science*, *5*(OCT), 1–19. https://doi.org/10.3389/fenvs.2017.00064

Svraka I., Memić M., Sulejmanović J., M.-Š. T. (2014). *Preconcentration of Metal Ions Using Silica Gel 60 F 254*. *July*.

Svraka, I., Memić, M., Sulejmanović, J., & Muhić, T. (2014). *Preconcentration of Metal Ions Using Silica Gel 60 F 254*. *June 2015*.

Sytar, O., Kumar, A., Latowski, D., Kuczynska, P., Strzałka, K., & Prasad, M. N. V. (2013). Heavy metal-induced oxidative damage, defense reactions, and detoxification mechanisms in plants. *Acta Physiologiae Plantarum*, *35*(4), 985–999. https://doi.org/10.1007/s11738-012-1169-6

Szatyłowicz, E., & Skoczko, I. (2017). Studies on the efficiency of grundwater treatment process with adsorption on activated alumina. *Journal of Ecological Engineering*, *18*(4), 211–218. https://doi.org/10.12911/22998993/74272

Tang, X., Zheng, H., Teng, H., Sun, Y., Guo, J., Xie, W., Yang, Q., & Chen, W. (2016). Chemical coagulation process for the removal of heavy metals from water: a review. *Desalination and Water Treatment*, *57*(4), 1733–1748. https://doi.org/10.1080/19443994.2014.977959

Tangjuank, S., Insuk, N., Udeye, V., & Tontrakoon, J. (2009). *Chromium (III) sorption from aqueous solutions using activated carbon prepared from cashew nut shells*. *4*(8), 412–417.

Tchounwou, P. B., Yedjou, C. G., Patlolla, A. K., & Sutton, D. J. (2012). Molecular, clinical and environmental toxicicology Volume 3: Environmental Toxicology. In *Molecular, Clinical and Environmental Toxicology* (Vol. 101). https://doi.org/10.1007/978-3-7643-8340-4

Teh, C. Y., Budiman, P. M., Shak, K. P. Y., & Wu, T. Y. (2016). Recent Advancement of

Coagulation-Flocculation and Its Application in Wastewater Treatment. *Industrial and Engineering Chemistry Research*, *55*(16), 4363–4389. https://doi.org/10.1021/acs.iecr.5b04703

Tigabu, T. (2017). Production and characterization of silica gel for textile wastewater treatment (methylene blue dye). *(Masters of Science Dissertation, Addis Ababa University).*

Tomasz Kalak 1,*, K. M. 1 and J. P.-S. (2021). *Highly Effective Adsorption Process of Ni(II) Ions with the Use of Sewage Sludge Fly Ash Generated by Circulating Fluidized Bed Combustion (CFBC) Technology*. https://doi.org/https://doi.org/10.3390/ma14113106

Tripathi, A., & Rawat Ranjan, M. (2015). Heavy Metal Removal from Wastewater Using Low Cost Adsorbents. *Journal of Bioremediation & Biodegradation*, *06*(06). https://doi.org/10.4172/2155-6199.1000315

U.S Geological Survey. (1997). Nickel Hazards to Fish , Wildlife , and Invertebrates : A Synoptic Review. *Contaminant Hazard Reviews*, *34*, 1–109.

Uddin, A. H., Khalid, R. S., Alaama, M., Abdualkader, A. M., Kasmuri, A., & Abbas, S. A. (2016). Comparative study of three digestion methods for elemental analysis in traditional medicine products using atomic absorption spectrometry. *Journal of Analytical Science and Technology*, *7*(1). https://doi.org/10.1186/s40543-016-0085-6

Ullah, M., Nazir, R., Khan, M., Khan, W., Shah, M., Afridi, S. G., & Zada, A. (2020). The effective removal of heavy metals from water by activated carbon adsorbents of Albizia lebbeck and Melia azedarach seed shells. *Soil and Water Research*, *15*(1), 30–37. https://doi.org/10.17221/212/2018-SWR

Ulrich, K., & Jakob, U. (2019). The role of thiols in antioxidant systems. *Free Radical Biology and Medicine*, *140*(April), 14–27. https://doi.org/10.1016/j.freeradbiomed.2019.05.035

Ungureanu, N., Vlăduț, V., & Voicu, G. (2020). Water scarcity and wastewater reuse in crop irrigation. *Sustainability (Switzerland)*, *12*(21), 1–19. https://doi.org/10.3390/su12219055

Vandenbossche, M., Jimenez, M., Casetta, M., & Traisnel, M. (2015). Remediation of heavy metals by biomolecules: A review. *Critical Reviews in Environmental Science and Technology*, *45*(15), 1644–1704. https://doi.org/10.1080/10643389.2014.966425

Veronica B. Cashina, Daniel S. Eldridgea, D. Z. and A. Y. (2017). Surface functionalization and manipulation of mesoporous silica adsorbents for improved removal of pollutants: A Review. *Environmental Science Water Research and Technology DOI: 10.1039/C7EW00322F*. https://doi.org/10.1039/C7EW00322F

Wani, A. L., Ara, A., & Usmani, J. A. (2015). Lead toxicity: A review. *Interdisciplinary Toxicology*, *8*(2), 55–64. https://doi.org/10.1515/intox-2015-0009

Xu, Q., Gu, J., Zhao, Y., Ke, X., & Liu, X. (2017). *Antibacterial Cotton Fabric with Enhanced Durability Prepared Using L-cysteine and Silver Nanoparticles*. *18*(11), 2204–2211. https://doi.org/10.1007/s12221-017-7567-z

Yablokov, V. A., Vasina, Y. A., Zelyaev, I. A., & Mitrofanova, S. V. (2009). Kinetics of thermal decomposition of sulfur-containing amino acids. *Russian Journal of General Chemistry*, *79*(6), 1141–1145. https://doi.org/10.1134/S1070363209060188

Yadessa Chibssa, S. S. (2015). Heavy Metal Concentrations and Physicochemical Characteristics of Effluent along the Discharge Route from Hawassa Textile Factory, Ethiopia. *Journal of Environmental & Analytical Toxicology*, *05*(04). https://doi.org/10.4172/2161-0525.1000285

Yamauchi, O., Odani, A., & Takani, M. (2002). Metal-amino acid chemistry. Weak interactions and related functions of side chain groups. *Journal of the Chemical Society, Dalton Transactions*, *18*, 3411–3421. https://doi.org/10.1039/b202385g

Yasinzai, M., Mustafa, G., Asghar, N., Ullah, I., Zahid, M., Lieberzeit, P. A., Han, D., & Latif, U. (2018). Ion-imprinted polymer-based receptors for sensitive and selective detection of mercury ions in aqueous environment. *Journal of Sensors*, *2018*. https://doi.org/10.1155/2018/8972549

Yeshiwas, Y., & Tadele, E. (2017). Review on Heavy Metal Contamination in Vegetables Grown in Ethiopia and Its Economic Welfare Implications. *Journal of Biology, Agriculture and Healthcare*, *7*(17), 31–44.

Yu, J., Yue, B., Wu, X., Liu, Q., & Jiao, F. (2016). *Removal of mercury by adsorption : a review*. 5056–5076. https://doi.org/10.1007/s11356-015-5880-x

Zaharudin, N. S., Mohamed Isa, E. D., Ahmad, H., Abdul Rahman, M. B., & Jumbri, K. (2020). Functionalized mesoporous silica nanoparticles templated by pyridinium ionic liquid for hydrophilic and hydrophobic drug release application. *Journal of Saudi Chemical Society*, *24*(3), 289–302. https://doi.org/10.1016/j.jscs.2020.01.003

Zelalem KA1 and Chandravanshi BS. (2015). Levels of essential and non-essential elements in raw and processed. *African Social Science Journals*, *14*(5), 2015–2035.

Zhan, M., Jia, H., Fan, J., Yu, H., Amador, E., & Chen, W. (2019). Two D-π-A Schiff-Base-Functionalized Silica Gel Adsorbents for Preconcentration of Copper Ions in Foods and Water for Detection [Research-article]. *Analytical Chemistry*, *91*(9), 6103–6110. https://doi.org/10.1021/acs.analchem.9b00647

Zhou, J., Cai, D., Xu, Q., Zhang, Y., & Fu, F. (2018). *Excellent binding e ff ect of L - methionine for immobilizing silver nanoparticles onto cotton fabrics to improve the antibacterial durability*. 24458–24463. https://doi.org/10.1039/C8RA04401E

Zhou, J., Cai, D., Xu, Q., Zhang, Y., Fu, F., Diao, H., & Liu, X. (2018). Excellent binding effect of l-methionine for immobilizing silver nanoparticles onto cotton fabrics to improve the antibacterial durability against washing. *RSC Advances*, *8*(43), 24458–24463. https://doi.org/10.1039/c8ra04401e

Appendix

Appendix I. Results for BET analysis

a. BET results for adsorbents characterization.

	Adsorbents			
Parameters	SiO_2	SiO_2-Cys	SiO_2-Meth	SiO_2-(L-Cys + L-Meth)
Surface area data (MultiPoint BET method)	6.294e+02 m^2/g	5.890e+02 m^2/g	7.307e+02 m^2/g	7.728e+02 m^2/g
NLDFT method cumulative pore volume	7.944e-01 cc/g	7.948e-01 cc/g	1.005e+00 cc/g	1.002e+00 cc/g
NLDFT pore radius (size) (Mode)	2.271e+01 Å	2.271e+01 Å	1.658e+01 Å	2.271e+01 Å

b. BET relativepressure & volume @ STP data for SiO_2.

Relativepressure (P/Po)	Volume @ STP (cc/g)	1 / [W((Po/P) - 1)]
9.68280e-02	86.5494	9.9110e-01

3.24603e-01	205.9027	1.8676e+00
5.44294e-01	347.6638	2.7488e+00
7.65348e-01	567.3843	4.5995e+00

c. BET relativepressure & volume @ STP data for SiO_2-Cys.

Relativepressure (P/Po)	Volume @ STP (cc/g)	1 / [W((Po/P) - 1)]
1.11105e-01	111.9695	8.9317e-01
3.19966e-01	212.0016	1.7758e+00
5.41098e-01	346.8215	2.7202e+00
7.76507e-01	563.7307	4.9313e+00

d. BET relativepressure & volume @ STP data for SiO_2-Meth.

Relativepressure (P/Po)	Volume @ STP (cc/g)	1 / [W((Po/P) - 1)]
1.17441e-01	151.0836	7.0471e-01
3.30997e-01	270.6542	1.4626e+00
5.41409e-01	443.2268	2.1312e+00
7.80929e-01	713.0833	3.9998e+00

e. BET relativepressure & volume @ STP data for SiO_2-(L-Cys + L-Meth).

Relativepressure (P/Po)	Volume @ STP (cc/g)	1 / [W((Po/P) - 1)]
9.91820e-02	116.4784	7.5631e-01

3.17038e-01	251.5715	1.4764e+00
5.41027e-01	427.8917	2.2042e+00
7.67665e-01	708.8706	3.7294e+00

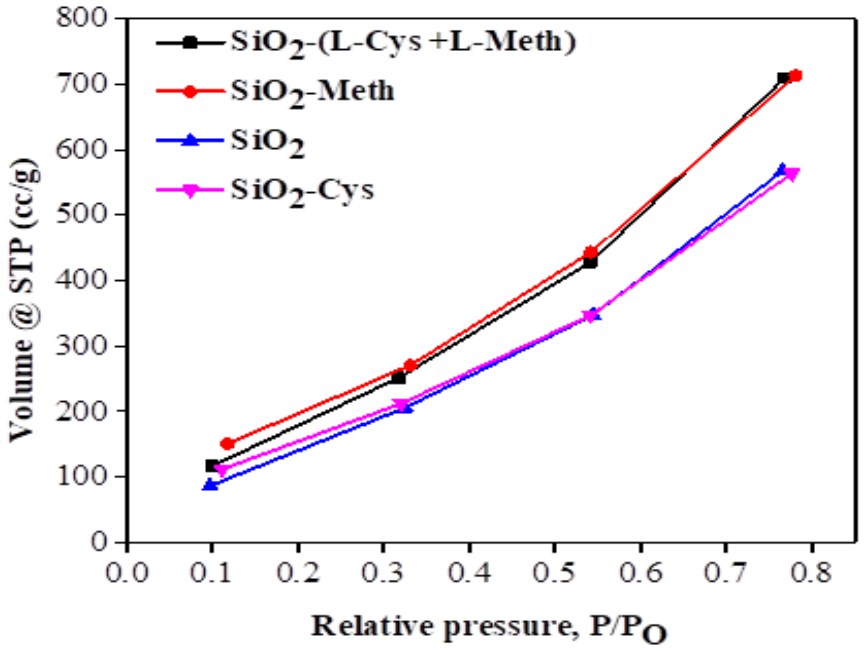


Figure I-1 Nitrogen sorption/desorption isotherm for SiO_2, SiO_2-(L-Cys + L-Meth), SiO_2-Cys, and SiO_2-Meth.

Appendix II. Results of analysis for the optimum condition

a. The result of the effect pH for Pb(II) adsorption.

Effect of pH on Pb(II) removal

pH	Ci(mg/L)	Cf(mg/L)	Ci-Cf(mg/L)	qe(mg/g)	% Removal of Pb(II)
5	10	2.44	7.56	1.89	75.6
6	10	1.56	8.44	2.11	84.4
7	10	1.66	8.34	2.085	83.4

8	10	2.932	7.068	1.767	70.68
9	10	4.235	5.765	1.44125	57.65

b. The result of the effect of pH for Ni(II) adsorption.

Effect of pH on Ni(II) removal					
pH	Ci(mg/L)	Cf(mg/L)	Ci-Cf(mg/L)	qe(mg/g)	% Removal of Ni(II)
5	3.5	0.113	3.387	0.84675	96.77143
6	3.5	0.228	3.272	0.818	93.48571
7	3.5.	0.315	3.185	0.79625	91
8	3.5	0.344	3.156	0.789	90.17143
9	3.5	0.304	3.196	0.799	91.31429

c. The result of the effect of contact time for Pb(II) adsorption.

Effect of contact time on Pb(II) removal					
Time (min)	Ci(mg/L)	Cf(mg/L)	Ci-Cf(mg/L)	qe(mg/g)	% Removal of Pb(II)
30	10	8.6	1.4	0.35	14
60	10	4.44	5.56	1.39	55.6
90	10	1.48	8.52	2.13	85.2
120	10	1.6	8.4	2.1	84
150	10	1.8	8.2	2.05	82

d. The result of the effect of contact time for Ni(II) adsorption.

Effect of contact time on Ni(II) removal					
Time(min)	Ci(mg/L)	Cf(mg/L)	Ci-Cf(mg/L)	qe(mg/g)	% Removal of Ni(II)
30	3.5	0.321	3.179	0.79475	90.82857
60	3.5	0.21	3.29	0.8225	94
90	3.5.	0.24	3.26	0.815	93.14286
120	3.5	0.243	3.257	0.81425	93.05714
150	3.5	0.247	3.253	0.81325	92.94286

e. The result of the effect of initial concentration for Pb(II) adsorption.

Effect of initial concentration on Pb(II) removal				
Ci(mg/L)	Cf(mg/L)	Ci-Cf(mg/L)	qe(mg/g)	% Removal of Pb(II)
0.5	0.00	0.5	0.125	100
2	0.065	1.935	0.48375	96.75
4	0.609	3.391	0.8477	84.775
6	0.998	5.002	1.2505	83.3667
8	3.72	4.28	1.07	53.5
10	4.89	5.11	1.2775	51.1

f. The result of the effect of initial concentration for Ni(II) adsorption

Effect of initial concentration on Ni(II) removal				
Ci(mg/L)	Cf(mg/L)	Ci-Cf(mg/L)	qe(mg/g)	% Removal of Ni(II)
0.5	0.003	0.497	0.12425	99.4
2	0.015	1.985	0.49625	99.25
3.5	0.316	3.184	0.796	90.97142857
5	0.469	4.531	1.13275	90.62
6.5	0.649	5.851	1.46275	90.01538462

g. The result of the effect of dose for Pb(II) adsorption

Effect of dose of adsorbent on Pb(II) removal					
Dose(g/0.05L)	Ci(mg/L)	Cf(mg/L)	Ci-Cf(mg/L)	qe(mg/g)	% Removal of Pb(II)
0.2	2	0.09	1.91	0.4775	95.5
0.4	2	0.06	1.94	0.2425	97
0.6	2	0.059	1.941	0.16175	97.05
0.8	2	0.057	1.943	0.07772	97.15
1	2	0.073	1.927	0.09635	96.35

h. The result of the effect of dose for Ni(II) adsorption

Effect of dose of adsorbent on Ni(II) removal					
Dose(g/0.05L)	Ci(mg/L)	Cf(mg/L)	Ci-Cf(mg/L)	qe(mg/g)	% Removal of Ni(II)
0.2	2	0.024	1.976	0.494	98.8
0.4	2	0.013	1.987	0.248375	99.35
0.6	2	0.014	1.986	0.1655	99.3
0.8	2	0.029	1.971	0.123188	98.55
1	2	0.037	1.963	0.09815	98.15

Appendix III. Operating condition of FAAS

For analysis of lead and nickel using flame atomic absorption spectrophotometry the following conditions were used.Calibration of FAAS (**Figure III-1**).

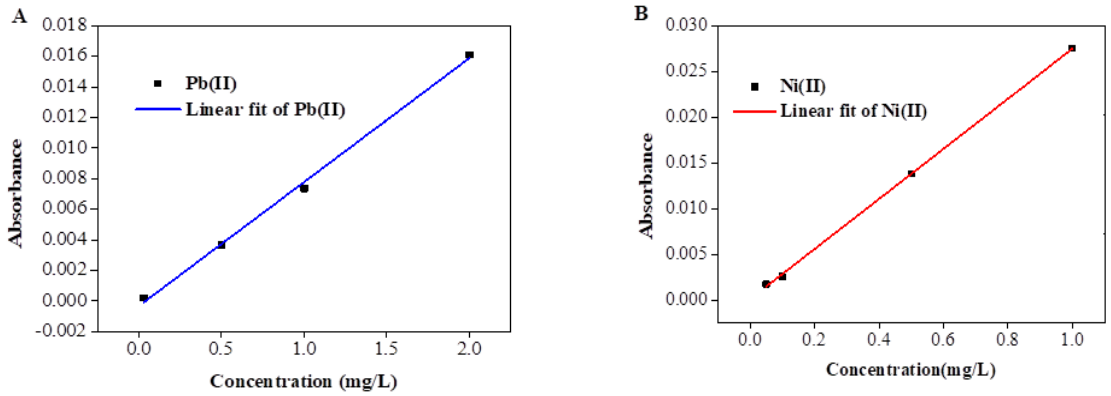


Figure III-1 Calibration curve of FAAS

A. For lead and B. For nickel.

Table III-1 Summery of table of Figure III-1

Metal		Equation	y = a + b*x	Standard Error
Pb(II)	Intercept	-3.3301E-4		3.0901E-4
	Slope	0.00811		2.69703E-4
	Adj.R-Square	0.99669		
Ni(II)	Intercept	1.14668E-4		2.03648E-4
	Slope	0.02737		3.62488E-4
	Adj.R-Square	0.99947		

Appendix VI. Experimental pictures

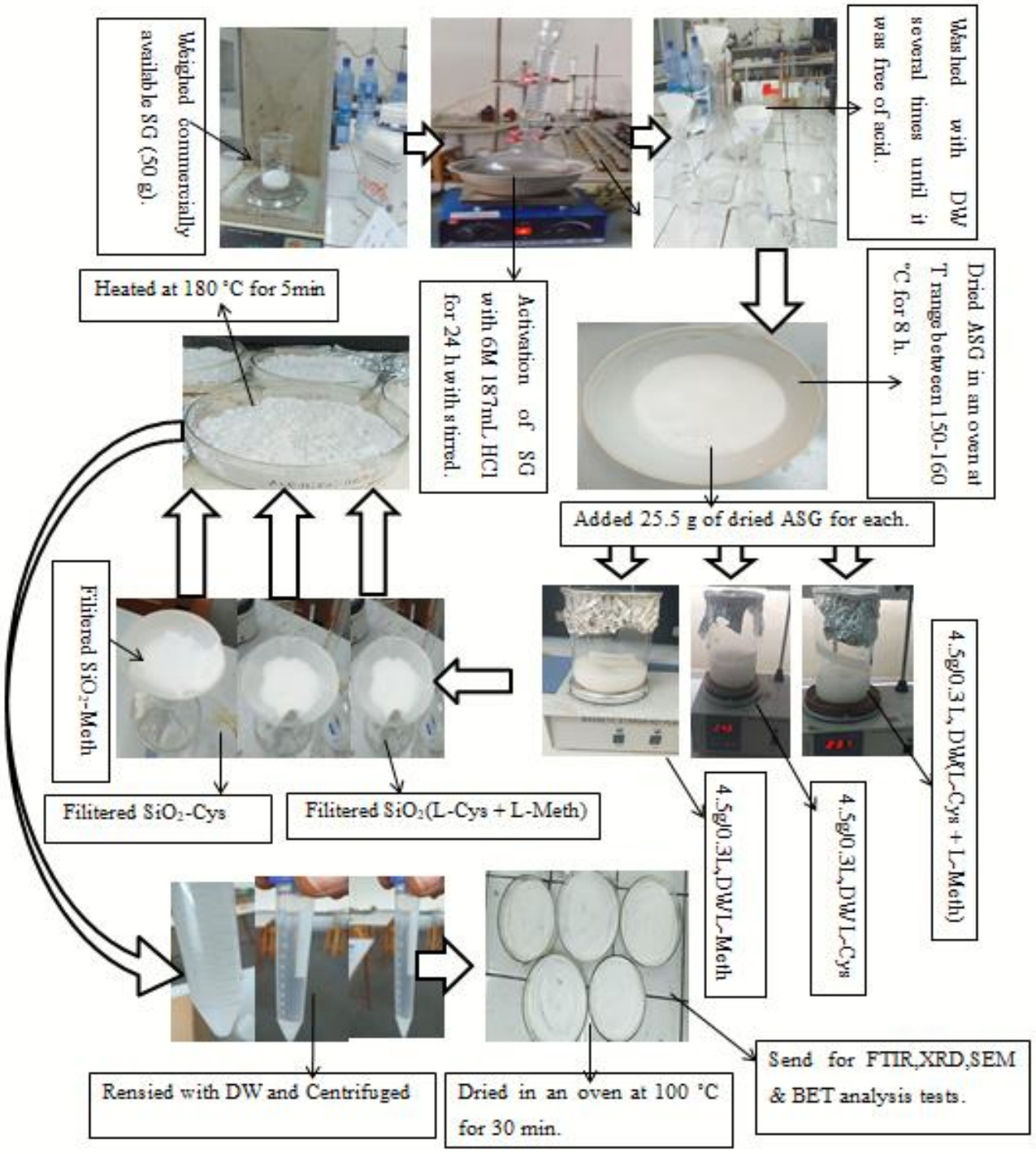


Figure VI-1. Silica gel modification method

AppendixV. Some instruments used and wastewater sample

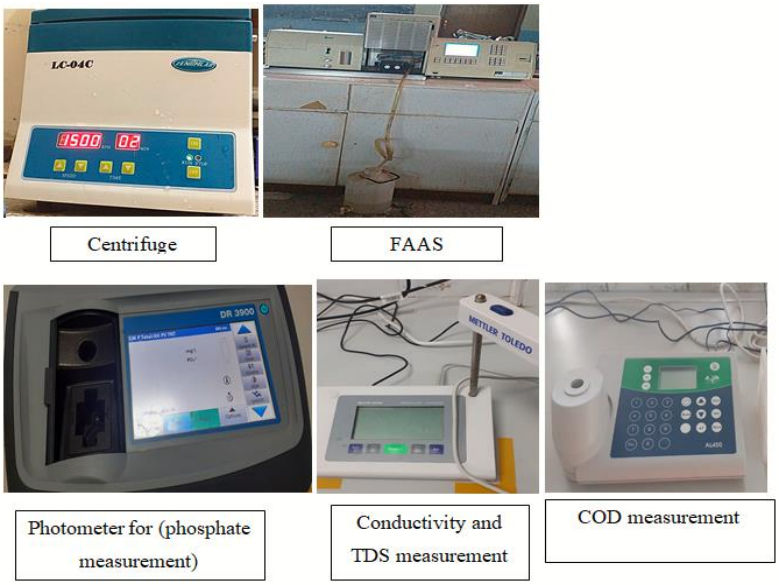


Figure V-1. Some instruments used during laboratory work.

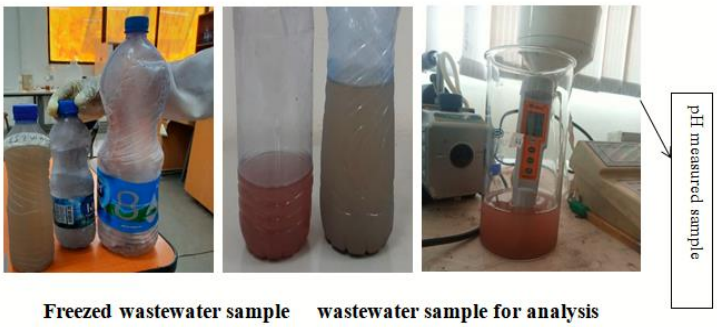


Figure V-2. Wastewater samples

Figure V-3. Picture during lead ions standared solution preparation.