INVESTIGATION OF THE TRANSPORT OF Pb (II) ON A POROUS BED

BY

EMMANUEL AKPOVWENE IGHOVWEMEREHOR
ENG1603794

DEPARTMENT OF CHEMICAL ENGINEERING
FACULTY OF ENGINEERING
UNIVERSITY OF BENIN
BENIN CITY

DECEMBER 2022.

INVESTIGATION OF THE TRANSPORT OF PB (II) ON A POROUS BED

BY

EMMANUEL AKPOVWENE IGHOVWEMEREHOR
ENG1603794

A PROJECT SUBMITTED TO THE DEPARTMENT OF CHEMICAL ENGINEERING, FACULTY OF ENGINEERING, UNIVERSITY OF BENIN, BENIN CITY

IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE AWARD OF BACHELOR OF ENGINEERING (B.ENG) DEGREE IN CHEMICAL ENGINEERING

DECEMBER 2022.

CERTIFICATION

This is to certify that this research work was carried out by the Department of Chemical Engineering at the University of Benin, Benin City, Edo State, Nigeria.

…….. ……..……...……

Engr. Dr. S.E. Uwadiae Date

Project Supervisor

…….. ……..……..……

Engr. Dr. (Mrs.) E.A. Oyedoh Date

Head of Department

…….. ……..……

Dr. O.U. Osazuwa Date

Project Coordinator

…….. ……..……

External Examiner Date

DEDICATION

This research work is dedicated to God almighty, my source of strength in completing this work.

ACKNOWLEDGEMENTS

My profound gratitude goes to my project supervisor, Engr. Dr. S. E. Uwadiae, for his support in making this work what it is now. His guidance, mentorship, creativity and correction aided this research work.

Special thanks also to my immediate family; mom and dad, Mr. and Mrs. Ighovwemerehor, my sisters; Faith, Rachael and Gift for their moral, prayers, and financial support throughout my stay in the university. Extended gratitude goes to my all my friends who contributed in their own effort.

I would not fail to appreciate the staff adviser, Engr. Dr. N. A. Amenaghawon for his advice towards the completion of this research work.

Lastly, a special appreciation to the lab technologist of the department, Mr. Collins, who took time and effort into making sure my experimental work in the laboratory went smoothly.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

ABSTRACT

Heavy metals are classified as hazardous chemical substances. They are major environmental pollutants and these pollutants affects the welfare of the environment, reduces the quality of life and eventually causes death. They are a collection of metals and metalloids that have an atomic density larger than 4 g/cm3. A major source of Pb (II) pollutant is the automobile battery waste in automobile worship. This study was done to investigate the transport of Pb (II) in soil using response surface methodology.

This investigation was carried out using a packed bed, which is a cylindrical vessel filled with uncontaminated sand. The bulk density, porosity, moisture content and pH of the soil were determined using standard procedures. The soil was then contaminated with stock solutions of Pb (II). A two - level, two - factor central composite design (CCD) was used for the design of the study. The factors considered for this study were depth and time while the concentration of Pb (II) was the response. The concentration level of Pb (II) at each point was determined using the atomic adsorption spectrophotometer (AAS).

The results showed that the transport of heavy metals in soil is greatly influenced by the physico – chemical properties of the soil. The time factor had only a marginal effect on the concentration level of Pb (II) while an increase in depth showed a significant decrease in Pb (II) concentration. The optimum concentration level was found to be at 30cm deep, after 36hrs of contamination. The findings from this investigation shows that time and depth of the soil is the predominant factor in the transport of Pb (II) on packed bed.

CHAPTER ONE

INTRODUCTION

1.1 BACKGROUND TO THE STUDY

Various forms of activities, including agriculture, manufacturing, transportation and anthropogenic activities produce a vast amount of waste and new types of pollutants in today's global globe. Soil has been the store of society's wastes since antiquity (Evans, 1989). Agricultural, industrial, municipal, and nuclear waste are the four most frequent types of waste (Alloway and Davies, 1971). It has been established that solid waste management is posing an increasing threat to many of Africa's rapidly developing areas (Ferronato and Torretta, 2019). Urban solid waste growth is now expected to be faster than urbanization. As at 2002, it was estimated that 2.9 billion urban people generated 0.64 kg of garbage per person per day. This figure increased to 1.2kg per person per day in 2012, with a total urban population of 3 billion. By 2025, it is expected that there will be approximately 4.3 billion urban dwellers producing 1.42kg of waste each day on average (Ziraba et al., 2016). Heavy metals are gotten from industrial operations such as manufacturing, smelting, mining as well as dumpsites. Heavy metal pollution in soil has become a worldwide environmental issue that has attracted considerable public attention largely from the increasing concern for the security of agricultural products (Hu et al., 2017). Across the globe, there are about 5 million sites of soil pollution which is covering 500 million hectares of land. These soils are contaminated by different heavy metals or metalloids, with the present soil concentrations higher than the geo – baseline or regulatory levels (Liu et al., 2018). Heavy metal pollution in soil has a combined worldwide economic impact estimated to be in excess of $10 billion per year (He et al., 2015).

These heavy metals were defined chemically as metals and metalloids with an atomic mass larger than 20 and a specific gravity greater than 5, such as cadmium (Cd), mercury (Hg), copper (Cu), arsenic (As), lead (Pb), chromium (Cr), nickel (Ni), and zinc (Zn). From a biological standpoint, "heavy" refers to a group of metals, including metalloids, that can be hazardous to plants and animals even at low concentrations (Li et al., 2019). Because of rapid development in agriculture and industry, as well as disruption of the natural ecosystem due to the tremendous growth in world population, heavy metal poisoning has become a severe threat to the environment and food security (Sarwar et al., 2016). In contrast to organic pollutants, heavy metal pollution is undetectable, persistent, and irreversible, and it not only degrades the quality of water bodies, the atmosphere, and food crops, but it also poses a serious threat to the health and well-being of organisms and humans through accumulation in the food chain. (Kankia and Abdulhamid, 2014). Cadmium for example has been known to have effect such as; poisoning on cellular molecules which is caused primarily by the oxidant – antioxidant imbalance. Also, cadmium has been implicated in the pathogenesis of many cancers, itai–itai disease, myocardial infarction, peripheral artery disease, hypertension, and diabetic nephropathy (Ghosh and Indra, 2018). Chronic exposure arsenic causes various types of symptoms including high blood pressure, neurological effects, obstetric problems, diabetes mellitus, diseases of blood vessels and of the respiratory system, as well as skin lesions such as melanosis, leucomelanosis, and keratosis (Rahman et al., 2009). Moreover, lead is not an essential element to the human body and when its intake is in excess, can have adverse impacts on the immune, nervous, enzymatic, endocrine, skeletal and circulatory systems (Kankia and Abdulhamid, 2014).

The improper disposal of these materials could endanger human life and the environment. (Fakunle et al., 2021). As a result, it is critical to efficiently manage these wastes. To manage these garbage, methods such as landfills and open dumps have been devised without minding what the effect would be on soil and groundwater (Vaccari et al., 2018). The disposal of vehicle battery waste on land and/or in open landfills is a major source of heavy metal contamination because these metals become corroded and penetrate the soil and groundwater to contaminate them when rain and dew fall on them (Orjiakor and Atuanya, 2015). Automobile battery manufacturing enterprises in Nigeria and other developing countries dispose of their waste in open dumps. (Fakunle et al., 2021). In many places of Nigeria, hand-dug wells and motorized boreholes, which are now the primary sources of water for home and industrial use, are now impacted. Nwachukwu et al (2010) discovered that these heavy metals, once into the human system or plants are destructive, non – degradable and accumulative. They can enter the human body by eaten food, drink, or air; they are absorbed and remain in the body instead of being expelled. One of the reasons chronic heavy metal exposure is dangerous is because of its potential to bio – accumulate. Heavy metal contamination of the groundwater is thus a severe threat to life and health in Nigeria. Degradation of precious land resources and the production of long-term environmental and human health problems have occurred from open land dumping (Afolayan and Hassan, 2017).

1.2 STATEMENT OF PROBLEM

Heavy metal contaminated soil possesses great threat to human health, water, plants as well as causing air pollution. Food crops rely on an uncontaminated soil for proper growth, as is good drinking water for man. Over time, there have been inadequate

information on these contaminated soils and how deep and fast heavy metals travel down the soil. This has made it difficult for researchers to be able to carry out efficient remediation processes on these soils.

1.3 AIM AND OBJECTIVES TO THE STUDY

The aim of this study is to evaluate the vertical transport pattern of heavy metals on soil contaminated by prepared solution of Lead (II) nitrate.

The objectives of this study are;

1. Preparation of soil samples which includes; air drying, crushing, sieving and finally storing for physico – chemical analysis.
2. Collection of contaminated soil samples at different depths and time.
3. Determination of soil bulk density, moisture content, pH and Pb (II) concentration level using the Atomic Absorption Spectrophotometer (AAS).
4. Modelling Pb (II) transport in soil using central composite design model (CCD).

1.4 SCOPE OF STUDY

The scope of this study is to model the transport of Pb (II) in soil from a packed bed using central composite design (CCD) model of the response surface methodology. The uncontaminated soil samples were collected from a field site at the University of Benin, Ugbowo, Benin city, Edo State.

1.5 RELEVANCE OF STUDY

The adverse effect of heavy metals cannot be over emphasized especially Pb – ion to the environment and human health. These heavy metal contaminate the soil as they travel down the soil. Crops planted on these soil take-in these heavy metals and humans eat some of these food crops. This study aims to provide researchers with sufficient data which are gotten from mathematical models that describe the transport pattern of these heavy metals and they can be used in remediation process. These mathematical models are useful tools in learning the science which can be used to improve explanations, generate discussion, make predictions, provide visual representations of abstract concepts and generate mental models as regards our research.

CHAPTER TWO

LITERATURE REVIEW

2.1 POLLUTION

Pollutants are substances which are released to the environment and in the process causes objectionable effects, which adversely affects the welfare of the environment, reducing the quality of life and may eventually cause death. These pollutants are present in the environment beyond a tolerance limit.

Hence, the presence of these pollutants in the environment air, water and soil is known as environmental pollution. It has been established that they may be poisonous or toxic and can cause harm to living things in the polluted environment (Nagajyoti et al., 2010).

2.2 TYPES OF POLLUTION

2.2.1 SOIL POLLUTION

Soil pollution can be simulated which is a deliberate or non – deliberate process. The simulated pollution includes animal manure, wastewater irrigation, pesticides, leaded paint, sewage sludge, coal combustion residue, mine ore waste, fertilizers, and waste dumping and so on. Untreated sewage and wastewater have caused a lot of heavy metals in farming lands and these metals are being absorbed by crops that are then eaten by humans (Masindi and Muedi, 2018).

The non-deliberate pollution are caused as a result of flood from rivers and seas which brings these sewage and contaminated water to land (Aronsson and Perttu, 2001). These heavy metals remain in the soil for a very long time due to their inability to undergo microbial or chemical degradation and thus are non-degradable. The environment is being damaged due to heavy metals entering the food chain (Jackson

and Alloway, 1991). Organic contaminants become less biodegradable due to the presence of heavy metals, which damages the environment twice. (Muchuweti et al., 2006). These metals in the soil pose a threat to the entire biosphere because they are absorbed by plants through direct ingestion, posing a risk to both the plant and the food chain that consumes it, altering soil properties such as colour, natural chemistry, pH and porosity, lowering soil quality, and contaminating groundwater (Gupta et al., 2012).

2.2.2 WATER POLLUTION

One of the exceptional essentials for the presence of life on earth is water. It is a source of life and necessity, but a large number of people around the world are suffering from a lack of clean drinking water (Vardhan et al., 2019).

Water pollution occurs as a result of urbanisation and industrialisation. Runoff from small villages, cities, towns and even factories transfer the metals, which then accumulate in the sediments of water bodies (Masindi and Muedi, 2018). Even if traces are transferred to bodies of water, they may still be extremely harmful to humans and other ecosystems. The toxicity of heavy metals is determined by a variety of factors. They include the type, nature and biological role of metal present, The organism exposed and the time period of exposure are also factors that affects toxicity of heavy metals (Stoveland et al., 1979). When every any organism is harmed, the entire food chain feels the impact. This is because humans have been known to be at the receiving end of the food chain and this will have an even greater impact on us because by then, we would have absorbed more heavy metal as concentration rises up the food chain. Mostly, home and industrial wastes are discharged into the sewer system. Heavy metals are present in high amounts in raw sewage and are not reduced during treatment (Briffa et al., 2020). They are either eliminated in the final effluent

or in the resulting sludge with the sewage treatment being influenced by the properties of the pollutants in the sewage. The existence of these pollutants can be in a variety of states, which including surface solutions, water and suspensions. They can be transported by water over a long distance, with particle materials sinking to the bottom. Droplets of liquid might either fall into the sediment or rise to the surface (Di Bonito, 2008).

2.2.3 AIR POLLUTION

Just like the water pollution, air pollution occurs as a result of industrialisation and urbanisation. Particles, droplets, or gaseous forms are ways in which these pollutants enters the atmosphere. Droplets and particle do not travel great distances and typically fall to the ground after a short distance, though they can travel further if they are small. Whereas, particle in the gaseous state travel farther due to air masses (Masindi and Muedi, 2018).

Chimneys are one of the most common causes of pollution in the atmosphere, as they discharge a variety of gases. The distance travelled by the pollutant depends on the weather and the chimney's height. The further the pollutant travels, the taller the chimney. Other sources of atmospheric pollution are the jet engines and the internal combustion engines. Apart from engine improvements, catalytic converters and unleaded gasoline have contributed to minimize car emissions. Despite this, diesel engines, obsolete cars, and an excess of vehicles continue to be an issue. Pesticide application, along with refrigerators, aerosols, and radioactive pollution, is another source of contaminants.

2.3 BATTERY

A battery is a device that uses an electrochemical oxidation-reduction (redox) cycle to convert the chemical energy contained in its active components directly into electrical

energy (Palizban and Kauhaniemi, 2016). Batteries feature a unique mechanism that allows them to transfer electric current via circuits irrespective of the lack of moving parts. The batteries are classified into two main categories;

1. primary non-rechargeable batteries;

   These batteries includes the zinc – carbon, alkaline – manganese, magnesium – manganese dioxide, zinc – air batteries, lithium – iodine, lithium – sulphur dioxide, lithium – silver vanadium oxide, lithium – manganese dioxide, *etc.*

2. Secondary rechargeable batteries;

   These batteries includes the lead – acid, iron – silver oxide, nickel – iron, zinc – alkaline – manganese dioxide, nickel – cadmium, nickel – zinc, nickel – hydrogen, *etc*.

2.3.1 THE LITHIUM – ION BATTERY

The Lithium – ion batteries (LIBS) were introduced commercially in the 1990s. They are widely utilized in cell phones, laptops, cameras and other electronic devices. They are also excellent choice for portable application where constant energy is required due to its rechargeable nature and high energy density (Winslow et al., 2018). Lately, the lithium –ion batteries have found an opening as a source of power for electric vehicles; thereby replacing the nickel – metal hybrid batteries (Wang et al., 2016).

The Lithium – ion battery is usually made up of four main components. They are the anode, cathode, outer casing and the electrolyte separator. Their masses and chemical composition vary between different manufacturers (Zhang et al., 2013). While the cathode consists of 20 – 30% of the battery's total weight, the anode on the other hand consist of 15 – 30% of the battery weight (Gaines, 2014). An inert binder, such as

polyvinylidene fluoride, is employed to fuse the anode and cathode components (PVF). This facilitates their adhesion to their individual metal collector sheets. (Zeng et al., 2014).

An electrolyte dissolved in an organic solvent is contained in a separator between the anode and the cathode. During the cycling process, the electrolyte allows for the controlled movement of lithium ions between the electrodes. The electrolyte separator, cathode, and anode are all housed within the battery. The interior components are protected from the outside environment by an exterior casing made of steel, aluminium, or plastic (Kushnir, 2015).

2.3.2 THE LEAD – ACID BATTERY

The Lead – acid batteries are produced commercially ranging from 1 – 3000Ah in size. They are applied in various automotive and industrial applications, as well as portable applications. The designs of the lead – acid battery includes the pasted and the tubular electrodes that are flooded with sulphuric acid. Alternatively, there are newer designs that are valve – regulated (Bullock, 1994).

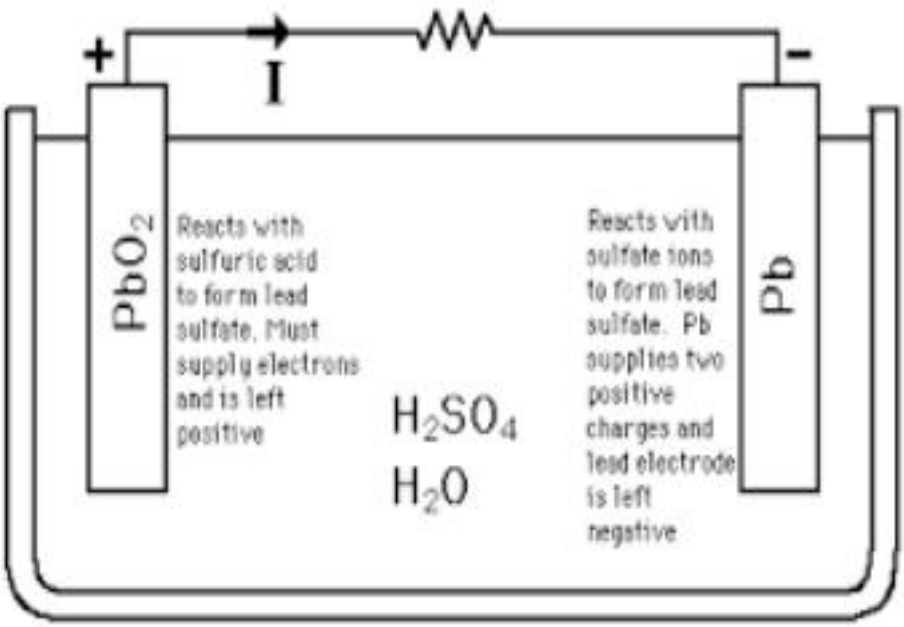


Figure 2. 1 Lead acid battery

The overall discharge reaction in a lead – acid battery is:

$$Pb_2 + Pb + 2H_2SO_4 \longrightarrow 2PbSO_4 + 2H_2O \quad (2.1)$$

2.4 HAZARDS OF WASTE BATTERY

Hazard is a chemical or physical condition which can cause damage to properties and people in the environment (May et al., 2018), (Maslin and Maier, 2000). A waste battery is a battery that is no longer wanted or unusable for its purpose which it is intended for and is later stored, recycled or disposed. Batteries contains toxic heavy metals such as lead, nickel, cadmium, copper, mercury or zinc, which are all harmful to the environment and human health. The Basel Convention, on the other hand, only deems lead, mercury and cadmium batteries to be harmful. Non-hazardous batteries are those that do not include cadmium, lead, or mercury, such as alkaline manganese and zinc carbon (Zhang et al., 2017).

Due to the expansion of the industrial sector, the demand for lead has continued to rise year after year. Over two-third of lead is used in automotive batteries, hence the batteries industry is responsible for 80% of global lead consumption. (Omar et al., 2019)

Most waste batteries end up in landfills when they are disposed in the trash. The heavy metals then pollute the environment by seeping into soil and water, contaminating water bodies and rendering them unsafe for human and wildlife usage. Certain harmful metals may be released into the air through stack gases or accumulate in the ash produced by the combustion process when burned.

The waste gotten from automobile battery producing companies are known for their high level of released lead on soil. These wastes have been known to be responsible for some of the world's most polluted sites (Adie and Osibanjo, 2009).

2.5 WASTE MANAGEMENT

The United States' Environmental Protection Agency (EPA) list of common household hazardous waste includes; paint thinners, laundry bleaches, rat poisons, herbicides, photographic chemicals, products from drains and toilet cleaners, diesel, kerosene, antifreeze, electronic wastes, gas/oil mix, batteries, automobile batteries, insecticides and refrigerants (Lannelongue et al., 2017). Of all the listed items, spent batteries make up for the most general article of common hazardous wastes (Kuchhal and Sharma, 2019). Recycling a dead battery results in lots of wastewater and other pollution as a result of these batteries being energy dependent. If they are disposed in landfills, the toxic heavy metal in them might leach into the ground, thereby making the soil and water dangerous to the environment and human health.

Furthermore, when these waste batteries are incinerated, the heavy metals can concentrate in the ashes or enter the atmosphere through stack emissions. When these ashes are disposed, the toxic metals can leach into ground water, surface water as well as the soil (May et al., 2018).

In many cities, unorganized, indiscreet, and unscientific rubbish dumping is a frequent disposal strategy that has a negative influence on the environment (Mahar et al., 2007). Almost all human activities produce garbage, and how this material is collected, handled, stored, and disposed of can be hazardous to public health and the environment. (Saxena et al., 2010). Electronic goods as well as used batteries, when dumped with municipal solid wastes raises the heavy metals concentration in the dumpsites.

Battery waste is one of the most notable hazardous waste. Batteries come in a variety of sizes and types depending on the appliances that require them, such as lead – acid batteries for automobiles (Orjiakor and Atuanya, 2015).

The wastes gotten from Automobile Battery Manufacturing Companies (ABMC) are known to emit a large percentage of heavy metals such as lead (Pb) into soil, and the physicochemical and heavy metal properties of the soil are affected as a result. Man – made wastes including automobile wastes, when introduced into the soil environment increases the level of trace element almost to an extent of threatening life and entire ecosystem (Oliveira and Pampulha, 2006). In many circumstances, wastes are taken up by plant roots and shoots, and then consumed by other higher creatures, including humans. Physicochemical qualities, on the other hand, play an important influence in soil quality, and these physical properties include soil texture, structure, colour and bulk density etc., while chemical properties includes Cation Exchange Capacity (CEC) and soil reaction, (pH) (McCauley et al., 2005).

When wastes contaminate the soil, the proportion of its constituents is negatively impacted, resulting in plant, animal, and human health problems. Several reports claim that pollution reduces soil microbial activity, however despite widespread use of batteries and their different effects on soil, there is little evidence on the impact of battery waste polluted soil. (Šmejkalová et al., 2003). Because Nigeria is a developing country with little or no policy on how to dispose of automotive batteries, such negative consequences go unrecognized. As a result, the research focuses on the effects of automotive battery waste on the soil's physicochemical properties. (Orjiakor et al., 2015).

2.6 SOIL

Soil is one of the most essential and basic natural resources, and it is important for the survival of humans (Song and Li, 2014). It is composed of water, organic matter, air and minerals. These composition and their proportion determines the soil physical properties; which includes structure, texture and porosity. Subsequently, these properties affect water and air movement in the soil, and as such the soil's ability to perform (McCauley et al., 2005).

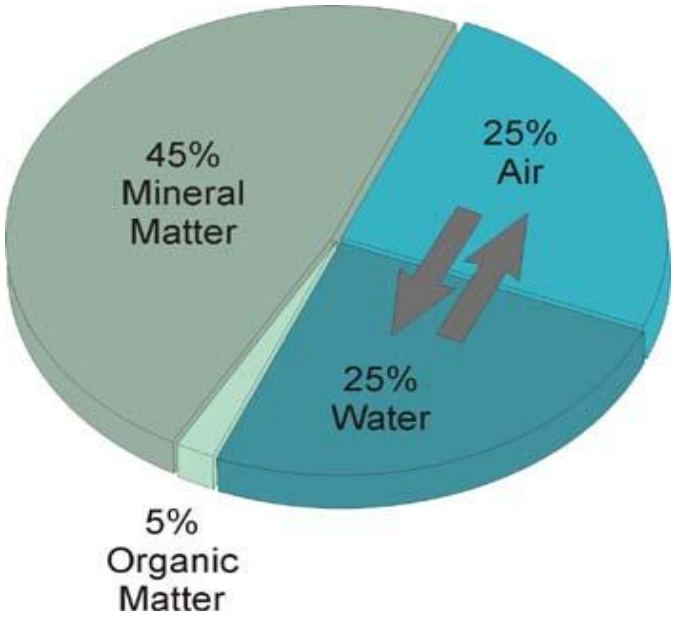


Figure 2. 2: Percentage composition of soil

2.6.1 SOIL STRUCTURE

Soil structure is important for soil function, plant and animal life support, and environmental quality management (Bronick and Lal, 2021). It is the arrangement and binding together of soil particles to form a larger lump, called "peds" or aggregates. The arrangement, shape and size of voids and solids, as well as the continuity of pores and voids, their ability to store and transport fluids and substances (inorganic and

organic), and their ability to support vigorous root growth and development, are all aspects of soil structure (Bronick and Lal, 2021).

2.6.2 SOIL POROSITY

Soil pores play a vital role in a variety of key soil activities (the air or water-filled spaces between particles). The size, number, and interconnectedness of pores are all influenced by the texture and structure of the soil (McCauley et al., 2005).

2.6.3 SOIL TEXTURE

Soil texture is one of the most essential physical features since it has such a big impact on many other physical properties. The texture of a soil is the proportion of three mineral particles; which are sand, clay and silt. These three particles are differentiated by their sizes and thus make up the fine mineral fraction (McCauley et al., 2005). Sandy, clay or loamy soil are determined by knowing the relative amount of the various particle sizes in the soil.

2.6.4 SOIL pH

The measure of hydrogen ions (H+) in the soil is the pH, which relates to the acidity or alkalinity of the soil. A low pH value corresponds to a high amount of H+, and vice versa. The pH scale runs from 0 – 14, with 7 being neutral, bellow 7 is acidic, and above 7 being alkaline i.e basic (McCauley et al., 2005).

2.7 HEAVY METALS

Heavy metals are major environmental pollutants, and their toxicity is becoming more of a concern for nutritional, ecological, environmental and evolutionary reasons (Nagajyoti et al., 2010). "Heavy metals" is a broad term that refers to a collection of metals and metalloids that have an atomic density larger than 4 g/cm3, or 5 times that of water (Walker, 2009). These heavy metals include lead (Pb), chromium (Cr), cobalt

(Co), cadmium (Cd), nickel (Ni), zinc (Zn), iron (Fe), arsenic (As), silver (Ag) as well as the platinum group elements (Nagajyoti et al., 2010). These metals can be classified as hazardous chemical substances since they cause various adverse effect especially to human health and the environment (Omar et al., 2019). Heavy metals are naturally occurring elements on the planet. They concentrate as a result of human activity and can infiltrate human, animal and plant tissues via nutrition, manual handling, and inhalation (Abosede, 2017).

Heavy metals are generally classified as essential and non – essential metals. The essential heavy metals such as manganese, zinc, strontium and iron are adequately needed by the human body to maintain its metabolism and assist in signalling and transportation (Alluri et al., 2007).

Each vital heavy metal has distinct ideal ranges that must be absorbed by humans at a proper and precise concentration, as too little or too much can produce negative side effects such as weariness, wound healing delays, and death. The non – essentials on the other hand are more potentially dangerous due to its characteristics to continuously appear and are difficult to remove from the environment, thereby causing it to accumulate in an organism (Omar et al., 2019).

2.7.1 SOURCES OF HEAVY METALS

Most of the automobile workshops in Nigeria consists of vulcanizers, panel beaters, spraying painter, mechanics and occasionally, car wash personnel. Solid, liquid and gaseous pollutants are generated as a result of the activities carried out by these workers, which affect the immediate surrounding (Osakwe, 2014). Of all these pollutants, the contamination of heavy metals in the surrounding presents great threat to human life and environment because of its toxicity.

Heavy metals have been thoroughly investigated, and international bodies such as the World Health Organization (WHO) examine their effects on human health on a regular basis. Acute heavy metal poisoning can harm the gastrointestinal (GI) and cardiovascular systems, central nervous system, as well as the kidneys, endocrine glands, lungs, liver, bones and endocrine glands. High levels of exposure to heavy metals has been connected to a variety of degenerative conditions affecting the same systems, as well as a higher risk of cancer in specific circumstances. (Arora, 2019).

Table 2. 1: Sources and toxicological effect of some heavy metals (Alluri et al., 2007)

HEAVY METAL	**SOURCES**	**EFFECTS**
Lead	Industries such as steel, mining, paints, automobiles and batteries. Also from pollutants arising from industrialization.	Kidney damage, vertigo, hyperactivity, nausea, encephalopathy, thyroid dysfunction, fatigue, degeneration of motor neurons, learning difficulties, schizophrenic-like behaviour, headache and vomiting.
Copper	Alcoholic beverages from copper brewery equipment, water pipes, instant gas hot water heaters, pesticides, copper jewellery, hormone pills, fungicides, insecticides, copper cooking pots,	Anaemia, mental disorders, hypertension, heart problem, cystic, fibrosis, inflammation and enlargement of liver, hyperactivity, insomnia,

	canned and frozen greens using copper to produce an ultra-green colour.	autism, stuttering, postpartum, psychosis.
Nickel	Zinc base casting, effluents of silver refineries, electroplating and storage battery industries.	Pulmonary fibrous, headache, cancer of lungs, dizziness, chest pain, dermatitis, rapid respiration, nausea and vomiting, cancer of the lungs, bone and nose.
Chromium	Textile and steel industry, automobiles.	Weakened immune systems, skin rashes, kidney and liver damage, acute renal failure, respiratory problems, haemolysis, pulmonary fibrosis, alteration of genetic material.
Mercury	Industries like paper and pulp, rubber processing, chloro-alkali, paints and fertilizers, batteries, fabric softeners, high intensity street lamps and fluorescent light tubes, adhesives, thermometers,	Kidney damage, birth defects, tremors, loss of vision or hearing, mental retardation, nausea, seizures, gingivitis, deafness, hypertonia,

	drugs, cosmetics and pharmaceuticals.	minamata diseases and deafness.
Cadmium	Electroplating, sewage sources and industrial mining. Cigarette smoking and in foodstuff.	Kidney damage, acute pulmonary effects, kidney cancer, liver and gastrointestinal tract.
Arsenic	Wood preservatives, mining industries and herbicides.	Damage to the skin, eye, liver, kidney damage and cancer.

2.7.2 HEAVY METAL CONTAMINATION IN SOIL

Contamination in soil can occur through sewage water used for irrigation, quarrying sites as well as industrial wastewater from hazardous waste disposal on soil. Nutritional deficiencies occurs when these heavy metals interact with the soil. (Gebreyesus, 2014). These heavy metals have the potential to alter soil matrices and thus metal transport. The usage, mining and manufacure of synthetic products (e.g. industrial waste, pesticides, batteries, paints, and land application of domestic or industrial sludge) can all lead to heavy metal pollution of agricultural and urban soils. Contaminated soils can be found in fields where wastewater or municipal sludge has been applied in the past, in or around mining waste piles and tailings, in industrial regions where chemicals have been deposited on the ground, automobile mechanic workshop and so on. The presence of hazardous metals in soil might stifle the biodegradation of organic pollutants (Maslin and Maier, 2000). Erosion, bushfires, and oil spoilage are types of land degradation that might affect heavy metal distribution on soil (Ohwoghere and Oghenero, 2012). Organic matter concentration,

cation exchange capacity, soil pH, soil texture, and interactions among the target elements are all factors that affect metal bioavailability and occurrence in the soil (Maslin and Maier, 2000).

2.7.3 CONTROL OF HEAVY METALS IN THE ENVIRONMENT

Heavy metals enters human food chain through bioaccumulation mechanism. These metals can easily enter into water bodies due to commercial usage, industrial waste-water, and agricultural runoff, household. Adsorption and bioremediation are treatment methods available for removal of toxic heavy metals from the soil (Vardhan et al., 2019).

2.8 LEACHATE

"Leachate is a polluted liquid emanating from the base of the land fill, which contains innumerable organic and inorganic compounds" (Papadopoulou et al., 2007). Concentrated leachate are produced from the improper collection, segregation and disposal practices of municipal solid waste (Kale et al., 2010). The chemical and biochemical processes responsible for the decomposition of waste materials as well as the nature of solid waste buried are factors that determine the composition of leachate (Maiti et al., 2016). Municipal solid waste leachates from uncontrolled landfills have become a major environmental hazard in millions of towns around the world.

2.9 FLOW THROUGH A PACKED BED

A tube, which is usually cylindrical and filled with active elements such as open foams, particles or structured inert is the fixed bed reactor. The particles in a packed or fixed bed are often rings, cylindrical or spherical in shape (Dixon and Partopour, 2020)

Fluid flow through a fixed bed of particles offers application in a number of processes in chemical industries. Examples of such applications includes adsorption, filtration, drying, ion exchange, heterogeneous catalysis, *etc* (Dolejš and Machač, 1995). This is because they can be used to store heat in chemical plants, chemical reactors, distillation process or a scrubber.

In most research work associated with packed bed, a lot of attention has been placed towards gross properties such as overall transfer coefficient and the pressure drop between the fluid and either the wall or the packing of particles (Mickley et al., 1965). Since the flow of fluids through beds that are composed of stationary granular particles is a common occurrence in the chemical industry, expression are thus necessary to predict the pressure drop across beds due to the resistance caused by the presence of these particles.

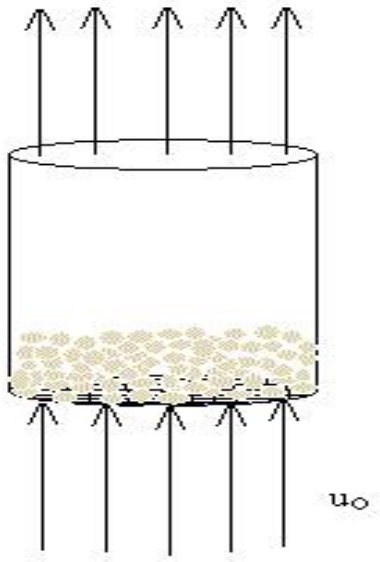


Figure 2. 3: A packed bed

In industries today, a lot of attention has been shown towards the packing of particles in a three – dimensional space. Packed beds finds application in separation process such as chromatography, the determination of permeability in porous media, heterogeneous catalysis, *e.t.c* (Gladkikh and Bryant, 2005).

In 1611, Kepler experimented on the packing of a bed. He speculated that to get the closest packing of a bed, one has to use the face centered cubic lattice in a three dimensional packing with an occupation coefficient of approximately 0.74. It was concluded that the density of a packed bed depends on the arrangement of the particles in the bed (Mohanty et al., 2016).

Thomas C. Hales gave the proof of Kepler's theory for a three dimensional packing (Hales, 2005). Since the particles of a packed bed are usually randomly arranged, the highest possible value of the occupation coefficient for a three dimensional closely packed mono dispersed spherical particle is approximately 0.64 (Jalali and Li, 2004).

2.10 MODELLING

Process modelling have seen their applications in the design and optimization of chemical, biological and physical processes. A model may be used to represent a system to be brought into use or to analyse a system that has been in existence. Models are used to predict future occurrence of that system.

Models can be classified as physical, analog, schematic and the mathematical models

2.11 DESIGN OF EXPERIMENT (DOE)

The behaviour of systems are studied using experimental designs. The experimental design, or design of experiment involves the planning and performing of a set of experiments in other to evaluate the effect of the system variables (Mäkelä, 2017). The estimation of interactions between the factors and the empirical models as well as

having the same amount of information in fewer experiments, are some of the advantages associated with design of experiments (Nair et al., 2014).

2.11.1 SELECTION OF INDEPENDENT VARIABLES

Various factors affect the response of a system and since it is almost impossible to include all of these variable into an experimental design due to economic reasons, it becomes necessary to identify variables with major effects. Using the one-factor-at-a-time approach or a two-level factorial designs are used in identify these variables (Nair et al., 2014).

2.11.2 TYPES OF DESIGN OF EXPERIMENT (DOE)

There are different designs which are available for conducting experiments. These designs are different to one another in terms of their selection of experimental points and the number of runs. The types of design of experiment includes the factorial design, Plackett – Burman design, Box – Behnken design and the Central Composite design.

Factorial design

The factorial experimental designs are those whose runs are a combination of levels of factors. They are geometrically constructed and vary all the factors simultaneously and orthogonally. Factorial designs collects its data at the vertices of a cube in the k – dimensions. Here, k is the number of factors that are being studied.

Plackett – Burman Design

This design was formerly developed as an easy route in determining the main factor effect for a multiple factor system (Plackett & Burman, 1946). The Plackett – Burman design only creates room of two levels for each of the k – control variables, just as we would have a 2k design. Where there is a large k, this design uses a much smaller

number of runs (Khuri & Mukhopadhyay, 2010). The “saturated design” as it is popular called has the number of parameters equal to the number of experiments in the first order RSM model, with the degree of freedom of such a design as equal to zero (Witek-Krowiak et al., 2014).

Box – Behnken Design (BBD)

In 1960, Box and Behnken developed a 3-level incomplete factorial design as an alternative approach to the labour extensive full factorial design. In order to effectively explain the linear, quadratic and interaction effects, a second order polynomial has to be used in the modelling box (Witek-Krowiak et al., 2014).

This design was created by Box and Behnken to reduce the number of experimental runs, especially in a quadratic model fitting. The experiment matrix were constructed by means of a two level factorial design (-1, 1) with incomplete block designs. In this experimental design, it was seen that there were no experimental points where all factors have extreme values and this proved necessary where undesired scenario might occur in extreme conditions. The Box – Behnken design is somewhat more labour efficient than the central composite design and way more efficient than the full factorial design (Box & Behnken, 1960).

According to Witek-Krowiak *et al.*, (2014), the Box – Behnken design has two major restrictions;

1. This design should not be used for fitting other equations than second order polynomials.
2. Its experimental factors has to be equal or higher than three.

Central Composite Design (CCD)

In 1951, Box and Wilson presented central composite design as an alternative to full-level factorial design. A central composite design is made up of 2 – level factorial design, a central point as well as an additional design which has its experimental points at a distance α from the centre (Myers et al., 1989). A higher quality prediction of linear and quadratic interaction effects of the various parameters that are affecting the process are often gotten using the central composite design (Witek-Krowiak et al., 2014).

According to Khuri and Mukhopadhyay (2010), the central composite design is the most used of all second orders and is made up of three portions;

1. The factorial portions, which is a complete (or a fraction of) 2^k factorial design whose factors' level are coded as -1, 1.
2. An axial portion, which consists of 2k points arranged so that two poimts are chosen on the axis of each control variable at a distance of from the design centre.
3. n_o centre points.

2.12 RESPONSE SURFACE METHODOLOGY

In 1950s, Box and Wilson first discussed about response surface methodology. It was applied in chemical experimentation, and generally included mathematical and statistical tools for the designing and analysing of response surface (Mäkelä, 2017). The research methodology method is based on the fit of different mathematical models which includes square polynomial functions, linear functions and others to obtained experimental results from designed experiment and also the verification of the model obtained by means of statistical techniques (Witek-Krowiak et al., 2014).

In Response surface methodology, the relationships between the dependent variables and the independent variable (factors) are generated using the data on experimental designs. To analyse the effects of the independent variables and their interactions on the responses, these models are used. The results gotten from RSM are usually presented as 2D contours and 3D plots (Nair et al., 2014).

CHAPTER THREE

MATERIALS AND METHODS

3.1 MATERIALS

3.1.1 REAGENTS AND RAW MATERIALS USED

Table 3.1 below shows a list of reagents and raw materials, their sources as well as uses, which are used in carrying out this study.

Table 3. 1: Raw materials and reagents

S/N	MATERIALS	SOURCE	USES
1	Uncontaminated soil samples	A field site at the University of Benin.	Our primary raw material, on which analysis are done.
2	Distilled water	The laboratory, Chemistry department, University of Benin.	For washing glassware and other apparatus.
3	Nitric acid (HNO_3)	The laboratory, Chemical engineering department, University of Benin.	Used in the digestion of soil sample.
4	Hydrochloric acid (HCl)	The laboratory, Chemical engineering department, University of Benin.	Used in the digestion of soil sample.
5	Lead (II) nitrate [$Pb(NO_3)_2$]	The laboratory, Chemical engineering department, University of Benin	Used in preparing stock solutions
6	Chloric acid (HClO)	The laboratory, Chemical engineering department,	Used in the digestion of soil sample.

		University of Benin.	

3.1.2 EQUIPMENT/APPARATUS

Table 3.2 below shows a list of equipment/apparatus and their uses, which are used in carrying out this study.

Table 3. 2: List of equipment/apparatus and their uses

S/N	APPARATUS	USES
1	Laboratory oven	Used in dying up of the soil samples when carrying out moisture content test.
2	Orbital shaker	Used to properly mix-up the soil samples with the acids.
3	Beaker	Used for holding liquid and solid samples.
4	Weighing balance	Used in weighing masses of samples during moisture content test and bulk analysis.
5	Atomic absorption spectrophotometer	Used to detect the presence of a metal in the soil sample as well as concentration levels.
6	Measuring cylinder	Used for measuring liquid.
7	pH meter	Used in the determining the pH of the soil sample
8	Crucible	Used in holding small mass of the soil sample
9	Mortar and pestle	Used in crushing the soil samples into finer particles
10	Sieves	Used in sieving the soil samples
11	Soil augers	Used in collecting the soil samples

3.2. METHODS

3.2.1 COLLECTION OF UNCONTAMINATED SOIL SAMPLES

Fresh uncontaminated soil samples were collected from a field site at the University of Benin, Benin City, Edo state. The soil samples were collected at random depth levels unto 4 holding vessels of about 70cm deep and filled up to 60cm mark.

3.2.2 PREPARATION OF THE POROUS BED

A cylindrical vessel of length 35cm with diameter of 20cm is opened at both ends and mounted on another vessel of same dimension, totalling the length of the bed to 70cm. The vessel is then filled with the uncontaminated soil sample to the 60cm mark.

3.2.3 PREPARATION OF Pb (II) ION SOLUTION

Stock solutions (1000 mg/L) of Pb (II) ions were prepared by dissolving 1.60g of Pb (II) nitrate in 1 Litre of distilled water in a 1000 ml standard flask.

3.2.4 CONTAMINATION OF SOIL SAMPLES

The uncontaminated soil samples in the 4 vessels were contaminated with 1 L each 100 mg/L of lead ion solution, which was prepared from the stock solution.

3.2.5 COLLECTION OF CONTAMINATED SOIL SAMPLES

The contaminated soil samples were collected from each of the four holding vessels using the soil augers at different points and depth levels of 25.86, 30, 40, 50 and 54.14 cm; representing the top soil, sub – soil and bottom soil respectively. The contaminated samples were collected at different time intervals of 7.03, 12, 24, 36 and 40.97 hours.

3.2.6 PREPARATION OF SOIL SAMPLES

The soil samples were air-dried at room temperature. The aim of air-drying the sample was to stop all form of chemical change on the soil sample. Upon complete drying, the soil samples was then crushed using the pestle and mortar into finer particles. After crushing, the soil samples was then sieved into finer particles using a 2 mm sieve. The sieved soil samples were then stored in a properly labelled sealed plastic bag at room temperature for 24 hours for further characterization.

3.2.7 CHARATERIZATION OF SOIL SAMPLES

3.2.7.1 Determination of bulk density

The determination of the bulk density of the contaminated soil were carried out according to the method employed by Blake and Hartge (2018). An empty 10ml measuring cylinder was weighed using a weighing balance. A dried mass of the contaminated soil sample was poured in the measuring cylinder till it got to the 10ml mark. The measuring cylinder + contaminated soil was weighed.

The bulk density in g/mL was calculated mathematically as follows;

$$Bulk\ density = \frac{W2-W1}{V} \quad (3.1)$$

Where;

W1 = Weight of cylinder in grams

W2 = Weight of soil sample + cylinder in grams

V = volume of measuring cylinder in ml

3.2.7.2 Determination of moisture content

5g of the soil sample was weighed using a weighing balance and place in the crucible. It was heated in an electric oven at 100^{o}C till a constant weight was gotten. The heated crucible of constant weight is then allowed to cool and re-weighed.

$$\%\ moisture\ content = \frac{W2-W3}{W2-W1}\ X\ 100\% \quad (3.2)$$

Where;

W1 = Weight of empty crucible in grams

W2 = Weight of crucible + sample before heating in grams

W3 = Weight of crucible + sample after cooling in grams

3.2.7.3 Determination of soil pH

1g of the soil sample was weighed using a weighing balance and placed in a 100 ml beaker. Distilled water was poured into the beaker holding the sample. The solution is then placed on a magnetic stirrer and allowed to stay for 2 hours. The solution is then filtered using the filter paper unto a conical flask. The pH of the filtrate is then tested using the pH meter.

3.2.7.4 Determination of soil porosity

The water – filled pore space or relative saturation is a method used in the determination of the porosity of the soil as carried out by Hao et al. (2006). 50 ml of water is weighed and poured into a beaker holding 150g of the soil sample. The soil porosity of calculated using the equation;

$$WFPS = \frac{W1/(Vt - \frac{W2}{D1})}{D2} \quad (3.3)$$

Where;

W_1 = Weight of water in grams

W_2 = Dry weight of soil in grams

D_1 = Density of soil in g/mL

V_t = Bulk volume

D_2 = Density of water in g/mL

3.2.7.5 Determination of Pb (II) concentration

The determination of the Pb (II) concentration level was carried out according to the method employed by Tüzen (2003). 0.5 g of the soil sample was heated in an electric oven for 6 hours at a temperature of about 90^{o}C. 8 ml of concentrated HCl and HNO_3 were added in a ratio of 3:1 to the soil sample. 3 ml of concentrated HClO was added to the solution. The solution was placed on a magnetic stirrer for 6 hours. The residue was filtered and diluted to 25 ml of deionized water. This was then taken to the atomic absorption spectrophotometer for test of Pb (II) concentration level.

3.2.8 CENTRAL COMPOSITE DESIGN OF EXPERIMENT

Table 3.3 shows the experimental design runs generated using central composite design model of Design Expert V13. X_1, X_2 and Y represents time (hrs), depth (cm) and heavy metal concentration (g/ml) respectively.

Table 3. 3: Experimental runs for central composite design (CCD)

		X1	X2	Y
Std	Run	Time (hrs)	Depth (cm)	Heavy metal concentration (g/ml)
6	1	40.9706	40	
2	2	36	30	
13	3	24	40	
5	4	7.02944	40	
1	5	12	30	
7	6	24	25.8579	
10	7	24	40	
8	8	24	54.1421	
11	9	24	40	
4	10	36	50	
9	11	24	40	
3	12	12	50	
12	13	24	40	

3.3 MODEL VERIFICATION

In forecasting the response for the transport process, the established mathematical mo del predictive capability was assessed by comparing the RSM model's predicted outcomes to the actual experimental data. The statistical indicators employed for the process includes; the coefficient of determination (R^2 value), the adjusted R^2 value, mean square error (MSE), root mean square error (RMSE), mean absolute error (MAE), standard error of prediction (SEP) and average absolute deviation (AAD). These statistical indices can be computed using equations 3.4 to 3.11.

$$R = \frac{\sum_{i=n}^{n}(x_{p,i}- x_{p,ave})(x_{a,i}- x_{a,ave})}{\sqrt{[\sum_{i=n}^{n}(x_{p,i}- x_{p,ave})^2]\,[\sum_{i=n}^{n}(x_{a,i}- x_{a,ave})^2]}} \quad (3.4)$$

$$R^2 = 1 - \frac{\sum_{i=n}^{n}(x_{a,i}- x_{p,i})^2}{\sum_{i=n}^{n}(x_{p,i}- x_{a,ave})^2} \quad (3.5)$$

$$Adjusted\ R^2 = 1 - [\left(1 - R^2\right) X \frac{n-1}{n-k-1}] \quad (3.6)$$

$$MSE = \frac{1}{n}\sum_{i=n}^{n}(x_{p,i} - x_{a,i})^2 \quad (3.7)$$

$$RMSE = \sqrt{\frac{1}{n}\sum_{i=n}^{n}(x_{p,i} - x_{a,i})^2} \quad (3.8)$$

$$SEP = \frac{RMSE}{x_{a,ave}} X\ 100 \quad (3.9)$$

$$MAE = \frac{1}{n}\sum_{i=n}^{n}\left|(x_{a,i} - x_{p,i})\right| \quad (3.10)$$

$$AAD = \frac{1}{n}\left(\sum_{i=n}^{n}\left(\frac{\left|x_{a,i}- x_{p,i}\right|}{x_{a,ave}}\right)\right) X\ 100 \quad (3.11)$$

3.4 OPTIMIZATION OF RESPONSES

Numerical optimization was used to improve the transport process and find the best response value. Finding a set of factor levels that fulfils the objectives established for each of the replies entailed doing this. The response was set at a minimum or maximum level, while the independent variables were maintained at their default levels. A weight was assigned to each objective to fit its own desirability function. The default setting was used for the goal, with an importance of three pluses (+++). The goals were combined into an overall desirability function which was maximized by the software.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 PHYSICO – CHEMICAL CHARACTERISTICS OF THE SOIL

Table 4.1 shows the physico – chemical characteristics of the uncontaminated soil sample.

Table 4. 1: Physico – chemical characteristics of sand

S/N	PARAMETER	VALUE
1	Bulk density	1.5 g/ml
2	Porosity (WFPS)	4.92 %
3	Moisture content	4 %
4	pH	5.97

From Table 4.1, the bulk density of the soil was found to be 1.5 g/ml, the water – filed pore space (Porosity) was found to be 4.92%, the moisture content was 4 % and the pH of the uncontaminated soil was 5.97..

The bulk density is a dynamic soil property, different to a particle's density in that a measure of bulk density includes all pore space. A bulk density of 1.5 g/ml is strongly influenced by the quantity and size of the pore spaces as well as the composition of the solid soil materials. Therefore, compared to a more compact soils, loose and porous soils will have lower bulk densities. Sandy soils often have greater bulk density values due to their lower total pore space and frequent low organic matter content. (Hao et al., 2006). Although we could say the bulk density of our soil (1.5 g/ml) is slightly high; this could be resulting from the compaction of the sand. The

soil's bulk density was not up to the critical bulk density value of 1.63 g/ml at which pressure drop through the soil is observed which makes flow of fluid difficult. As soil depth grows, organic matter decomposition, soil fauna activity, pore space distribution, and compression of soil trapped between expanding plant roots could all contribute to an increase in bulk density (Akinde et al., 2020).

The moisture content of 4% was obtained for the uncontaminated soil sample as reported in Table 4.1. This low value was gotten as a result of the present weather season (dry season) and thus will allow for the free flow of fluid down the soil. Moisture content of the sand is an indication of the amount of water present in the soil. The moisture content has been reported as having significant influence on the properties of the sand such as its bulk density and flow of fluid (Mäkelä, 2017).

The porosity (WFPS) of the soil was reported to be 4.92% as seen in Table 4.1. Agricultural activities, which could involve tillage or the wheels of heavy machinery compacting soils, can have a great effect on the soil's porosity. The water-filled pore space (WFPS), sometimes called ''relative saturation,'' expresses the volume of water in the soil relative to the total volume of pores. It ranges from 0% in a dry soil to 100% under saturated conditions. A WFPS value of 4.92% indicates that the soil sample is a very dry soil (Hao et al., 2006).

The pH value of 5.97 for the uncontaminated soil sample is with the normal range. A pH value of 5.97 will increase further after contamination of the soil, since lead contamination brings about increase in the acidic nature of soils. Nigerian soils especially in the forest and savannah regions are within a pH range of 5.70 – 6.50. This was taken as the normal pH range for ordinary soils that favour plant and micro-

organisms. The mean values of soil pH ranged from 5.88 to 9.31. may support crop cultivation (Udousoro et al, 2010).

4.2 MODELLING AND ANALYTICAL STUDY USING RESPONSE SURFACE METHODOLOGY (RSM)

The generated experimental runs using the central composite design model of experimental design under response surface for the determination of concentration levels for lead in a contaminated soil were analysed. Table 4.2 shows the responses of the actual values and the predicted values.

Table 4. 2: Experimental and predicted responses by RSM model

			RESPONSE **Heavy metal concentration (g/ml)**	
Run	**Time (hrs)**	**Depth (cm)**	**Actual**	**Predicted**
1	40.971	40	0.2000	0.2279
2	36	30	0.8000	0.7559
3	24	40	0.1400	0.0700
4	7.0294	40	0.0200	0.0671
5	12	30	0.6000	0.5423
6	24	25.85786438	0.9000	0.9565
7	24	40	0.0600	0.0700
8	24	54.14213562	0.0000	0.0185
9	24	40	0.0300	0.0700
10	36	50	0.0100	-0.0073
11	24	40	0.0600	0.0700
12	12	50	0.0100	-0.0209
13	24	40	0.0600	0.0700

Table 4.2 show that the concentration level of lead in the contaminated soil reduces going down the soil. It is also of key importance to note that the duration of contamination slightly affects the transport of the fluid (prepared lead solution) moving down the soil as would be seen later on during modelling.

4.3 DETERMINATION OF APPROPRIATE MODEL

4.3.1 Lack of fit test

In determining the best model that statistically shows the relationship between the response (heavy metal concentration) and the input variables (the independent variables), the linear, two – factor interaction, quadratic and cubic models were tested and the summary shown in Table 4.3.

Table 4. 3: Lack of fit test

Source	**Sum of**	**df**	**Mean**	**F-value**	**p-value**	**Remark**
Linear	0.3271	6	0.0545	32.07	0.0024	
2FI	0.3171	5	0.0634	37.31	0.0019	
Quadratic	**0.0131**	**3**	**0.0044**	**2.56**	**0.1929**	**Suggested**
Cubic	0.0113	1	0.0113	6.62	0.0618	Aliased
Pure Error	0.0068	4	0.0017			

As can be seen from the lack of fit summary table in Table 4.3, the p – value for linear model was seen to be 0.0024, two – factor interaction model was 0.0019, the quadratic model was 0.1929 and the cubic model was seen to be 0.0618.

The focus of the lack of fit test was ensuring that the selected model has a non - significant lack of fit. The quadratic model, having a p – value of 0.1929 was suggested. Usually, a model with a p – value > 0.05 is found to be non – significant and thus the model is suggested for use (Witek-Krowiak et al., 2014).

4.3.2 Model summary statistics

Table 4.4 illustrates the model summary statistics which shows the Standard deviation, R^2 values, the adjusted R^2 values, the predicted R^2 values and the prediction error sum of squares (PRESS) of each models.

Table 4. 4: Model summary statistics

Source	Standard deviation	R^2	Adjusted R^2	Predicted R^2	PRESS	Remark
Linear	0.1827	0.7306	0.6767	0.5077	0.6102	
2FI	0.1897	0.7386	0.6515	0.3310	0.8292	
Quadratic	**0.0533**	**0.9840**	**0.9725**	**0.9165**	**0.1035**	**Suggested**
Cubic	0.0601	0.9854	0.9650	0.4105	0.7306	Aliased

From Table 4.4, the linear model had an R^2 value of 0.7306 with a predicted R^2 value of 0.5077. The 2 – factor interaction model had an R^2 value of 0.7386 with a predicted R^2 value of 0.6515. The quadratic model had an R^2 value of 0.9840 with a predicted R^2 value of 0.9725. The cubic model had an R^2 value of 0.9854 with a predicted R^2 value of 0.9650.

Although the cubic model had a slightly better R^2 value than the quadratic model, but the model was aliased. A model is said to be aliased when the design points are not enough to estimate the model. This implies that certain parameters in the model cannot be independently computed as a result of the model containing more terms than the number of independent point in the design.

The prediction error sum of squares (PRESS) is another statistic that assesses a model's capacity for prediction. It gauges how accurately the experiment's model is likely to predict the outcome of a subsequent test. Similarly, the quadratic model with a PRESS value of 0.1035 is preferable. It can be concluded that the quadratic model best describes the relationship between the response and the independent variable. For a model with good prediction efficiency, the $-R^2$ value should be close to 1.0 (Nair et al., 2014).

4.3.3 Analysis of variance (ANOVA)

The model's regression analysis was performed and is given by Equation 4.1 in term of the actual factors.

$$Y = 4.37776 + 0.00848498\ (A) + -0.19016\ (B) + -0.000416667\ (AB) + 0.000269097\ (A^2) + 0.0020875\ (B^2) \quad (4.1)$$

Where;

Y = Concentration of lead in g/ml

A = Time in hrs

B = Depth in cm

The second order polynomial (Equation 4.1) was used to compute the predicted responses as presented in Table 4.2. A comparison of the predicted values with the values gotten from experimental analysis shows that a little deviation meant that the data are in a reasonable agreement.

The evaluation of fit of the statistical models for the responses and the statistical significance for the second order polynomial for the concentration of lead was

investigated by carrying out the analysis of variance (ANOVA) for the quadratic model as shown in Table 4.5.

Table 4. 5: ANOVA for Quadratic model

Source	**Sum of squares**	**Df**	**Mean**	**F-value**	**p-value**	**Remark**
Model	1.22	5	0.2439	85.98	< 0.0001	**significant**
A-Time	0.0258	1	0.0258	9.10	0.0195	
B-Depth	0.8797	1	0.8797	310.07	< 0.0001	
AB	0.0100	1	0.0100	3.52	0.1025	
A^2	0.0104	1	0.0104	3.68	0.0965	
B^2	0.3031	1	0.3031	106.85	< 0.0001	
Residual	0.0199	7	0.0028			
Lack of Fit	0.0131	3	0.0044	2.56	0.1929	**not significant**
Pure Error	0.0068	4	0.0017			
Cor. Total	1.24	12				

Table 4.5 suggests that the model equation, Equation 4.1 adequately describes the relationship between the responses and the independent variables, as the model was significant. For these results, the p – value of the model (< 0.0001), less than 0.05 indicated that the model terms are significant and can be used for predictive purposes. This implies that the change in the values of the actual physical factors represented by that model term could significantly affect the response under consideration. Apart from indicating if a model is significant or not, the p- values tells if a term in a model is significant as can be seen with A, B, AB, A^2 and B^2. Of all model terms, depth was found to be more significant with a p – value of < 0.0001 as against time with a p – value of < 0.0195. This implies that the change in depth could significantly affect the

concentration of lead. Model terms AB and A^2 were found to be non – significant to the model with p – vales > 0.05.

The Fisher test (F – values) shows the level of significance for the model terms but does not differentiate between the positive and negative effect of the model terms (Nair et al., 2014). The model F- value of 85.98 confirmed that the model was actually significant with a 0.01% chance that a model's F – value this large could occur due to noise. The "lack of fit" F – value of 2.56 implies that the lack of fit is not significant relative to pure error, which is desirable while the "lack of fit" p – values of 0.1929 implies that there is a 19.29 % chance that the "lack of fit" F – value could occur due to noise (Mäkelä, 2017).

4.3.4 Goodness of fit statistics

Other statistical factors, such as the coefficient of variance, the standard deviation, the adequate precision, e.t.c., were used to obtain the goodness of fit statistics between the experimental data and the model representing the concentration of lead as shown in Table 4.6.

Table 4. 6: Statistical information for ANOVA and goodness of fit statistics for RSM model

Std. Dev.	0.0533
Mean	0.2223
C.V. %	23.96
R^2	0.9840
Adjusted R^2	0.9725
Predicted R^2	0.9165
Adeq. Precision	27.0102

A standard deviation of 0.0533 was found to be relatively small when it is compared to the mean of observation, 0.2223. This indicates that individual data points did not deviate significantly from the mean. The coefficient of determination of the model (R^2) was seen to be 0.9840. For a good model fit, a high R^2 value is desired with the value close to unity as possible. Table 4.5 indicated that the model satisfactorily represented the relationship between the independent variables (time and depth) and the response (concentration of lead). It also gives an indication of consistency between the experimental and the predicted values. The adjusted R^2 values was seen as 0.9725 and was found to be enough to suggest the significance of the model. The predicted R^2 values of 0.9165 indicates that the model's predictive capacity for future outcomes is high. The Predicted R^2 of 0.9165 is in reasonable agreement with the Adjusted R^2 of 0.9725; i.e. the difference is less than 0.2 (Nair et al., 2014).

The coefficient of variance (C.V) is the standard deviation expressed as the mean. It indicates the degree of precision with which the experimental runs were performed. i.e., it evaluates the reliability and repeatability of the experiments. A coefficient of variance value of 23.96% is seen to be very high, since the C.V should not be greater than 10% for desired accuracy and reliability of experimental runs. The level of dispersion around the mean increases with the coefficient of variation and thus there is low reliability and accuracy of the experimental data.

Values of adequate precision greater than 4 are desired for the model. The value obtained was found to be 27.0102, showing that the model can be used to navigate the design space (Drury et al., 2015)

4.3.5 Performance Assessment of the predictive capacity of the RSM model

A performance evaluation was carried out to determine how well the RSM model predicted the response (concentration of lead). The predictive capability of RSM was assessed using statistical indicators such as correlation coefficient (R), coefficient of determination (R^2), adjusted R^2, mean square error (MSE), root mean square error (RSME), standard error of prediction (SEP), mean absolute error (MAE) and absolute average deviation (AAD) as shown in Table 4.7 for the concentration of lead.

Table 4. 7: Goodness of fit statistics for RSM model

PARAMETER	**RESPONSE VALUE**
R	0.9920
R^2	0.9700
Adjusted R^2	0.9640
MSE	0.0015
RMSE	0.0391
SEP (%)	17.58
MAE	0.0333
AAD (%)	14.98

The result presented in Table 4.7 show that the RSM had very good predictive capability. The predicted responses for RSM all had very high R, R^2 and adjusted R^2 values very close to 1. The response were also characterised by very low MSE, RMSE and MAE with low SEP and AAD which are indicative of models with high accuracy. This shows that there were very good fit between the RSM model predictions and the experimental values, thus confirming that the RSM had very good predictive capability.

4.3.6 Parity plot-

The actual and predicted values shown in Table 4.2 were plotted using Microsoft excel software to analyse the relationship between these values as can be seen in Figure 4.1. From the straight line, an evenly distributed points were seen near this line. This further confirms that the quadratic model could be employed as the significate model for predicting the response over the independent input variables.

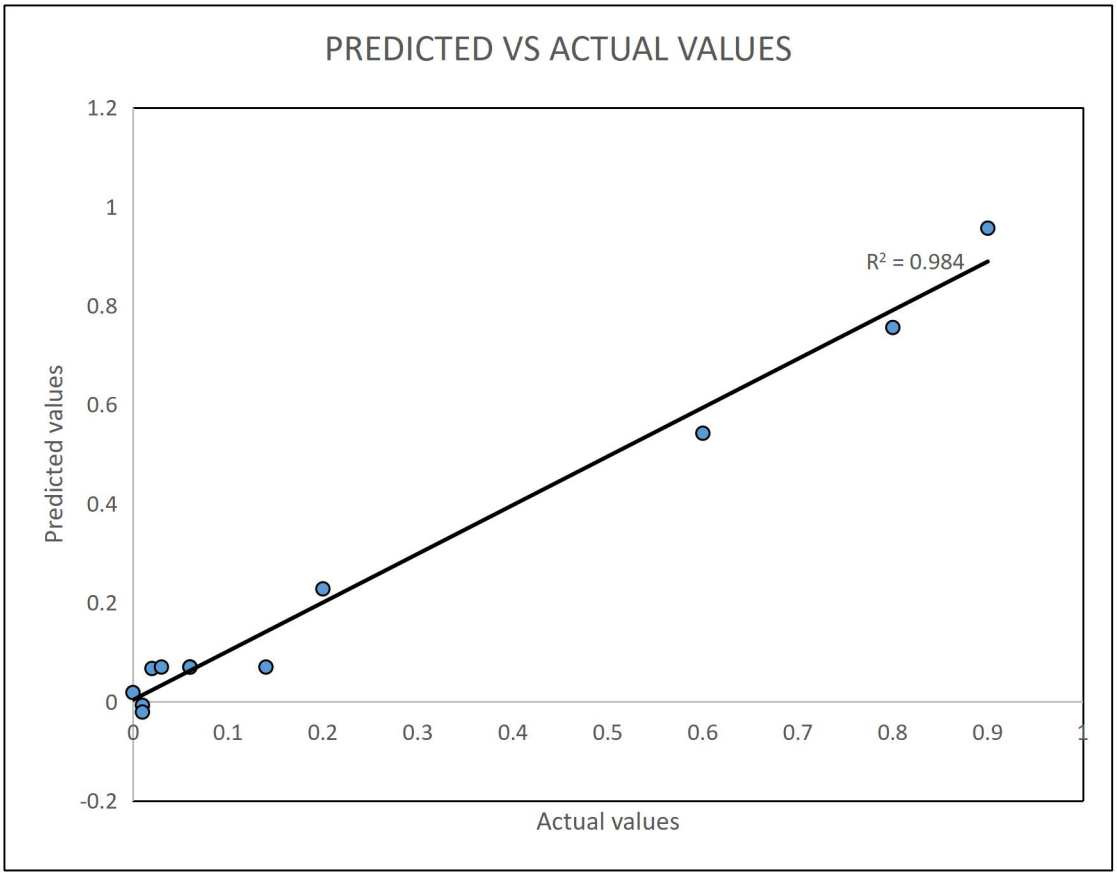


Figure 4. 1: Parity plot of predicted values against actual values of Pb (II) concentration from the RSM model

4.4 OPTIMIZATION OF THE TRANPORT PROCESS

Numerical optimization of the input factors and responses was carried out using the built – in optimization algorithm of the design expert software. The process was carried out to determine the levels of the input factors that yielded the optimum values of the responses. The input factors were constrained within the bounds shown in table below.

For the optimization process, the input factors (time and depth) were all set in range, while the concentration of lead was maximized after evaluating the model graphs and the solutions suggested by the numerical optimisation package, the best solution to the ,multi objective optimization was selected on the basis of its desirability.

Table 4. 8: Table of constraints for numerical optimization

Variables	Symbols	Goals	Lower limit	Upper limit	Lower weight	Upper weight	importance
	Input variables/factors						
Time (hrs)	A	In range	12	36	1	1	3
Depth (cm)	B	In range	30	50	1	1	3
	Response						
Heavy metal conc. (g/ml)	Y	Maximize	0	0.9	1	1	3

Table 4. 9: Summary of optimization result

s/n	Time (hrs)	Depth (cm)	Heavy metal conc. (g/ml)	StdErr (Heavy metal conc.)	Desirability	
1	**36**	**30**	**0.755918831**	**0.042108244**	**0.839909812**	**Selected**
2	35.99999943	30.08782727	0.748916656	0.041814135	0.832129618	
3	35.9999476	30.20170832	0.739884471	0.041437852	0.822093856	
4	35.99985404	30.31249603	0.731148933	0.041077313	0.812387703	
5	34.28992011	30.00000141	0.730438861	0.03776505	0.811598734	
6	34.19999546	30.00000868	0.729141983	0.037561635	0.810157758	
7	35.99995295	30.49376529	0.716970323	0.040500068	0.796633692	
8	33.24510551	30.00000265	0.715645785	0.035551912	0.795161984	
9	32.57494119	30.0000161	0.706465507	0.034301522	0.784961674	
10	25.49984594	30.0000053	0.624305074	0.027784012	0.693672305	
11	24.99274982	30.00000753	0.61945078	0.027687163	0.688278644	
12	24.19781667	30.00000687	0.612119935	0.027615174	0.680133261	
13	16.0418314	30.00000775	0.556550221	0.033263471	0.618389135	
14	15.89706785	30.0000033	0.555887574	0.033497634	0.61765286	

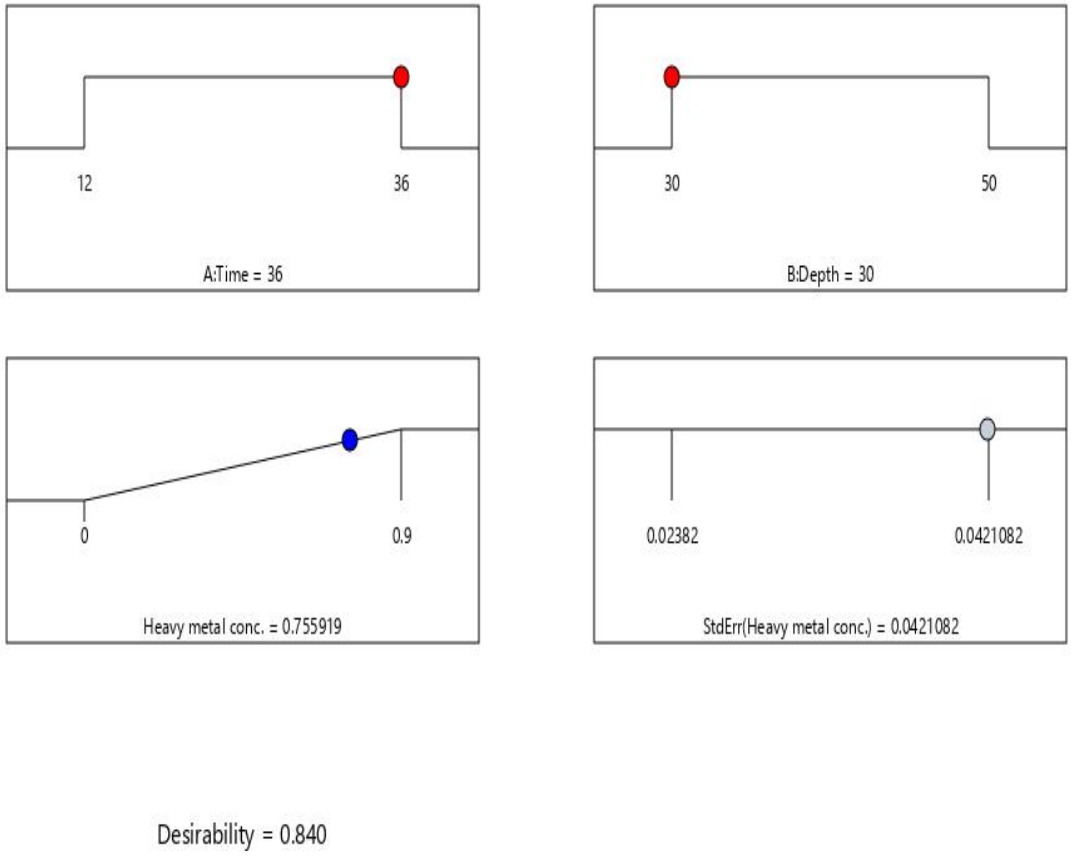


Figure 4. 2: Optimization result for the transport process

The optimization result of the transport process as shown graphically in Figure 4.2 and the summary of the results as represented in Table 4.9. The optimum result for the response was 0.7559g/ml for lead concentration. The optimal conditions of the input factors, depth and time was found to be 30cm and 36hrs respectively.

4.5 Response surface plots

In order to determine the optimal levels of the independent variables affecting concentration of Pb (II) in the contaminated vessels, three – dimensional (3D) response surface and contour plots were construed according to the regression model. The 3D plot in Figure 4.3 was generated using both variables (time and depth) within their experimental ranges. The resulting response surface shows the effect of depth and time against heavy metal concentration. The contour plot may be elliptical, rising ridges, saddle point, or circular point. Rising ridge plots shows that there is a significant interaction between the process factors.

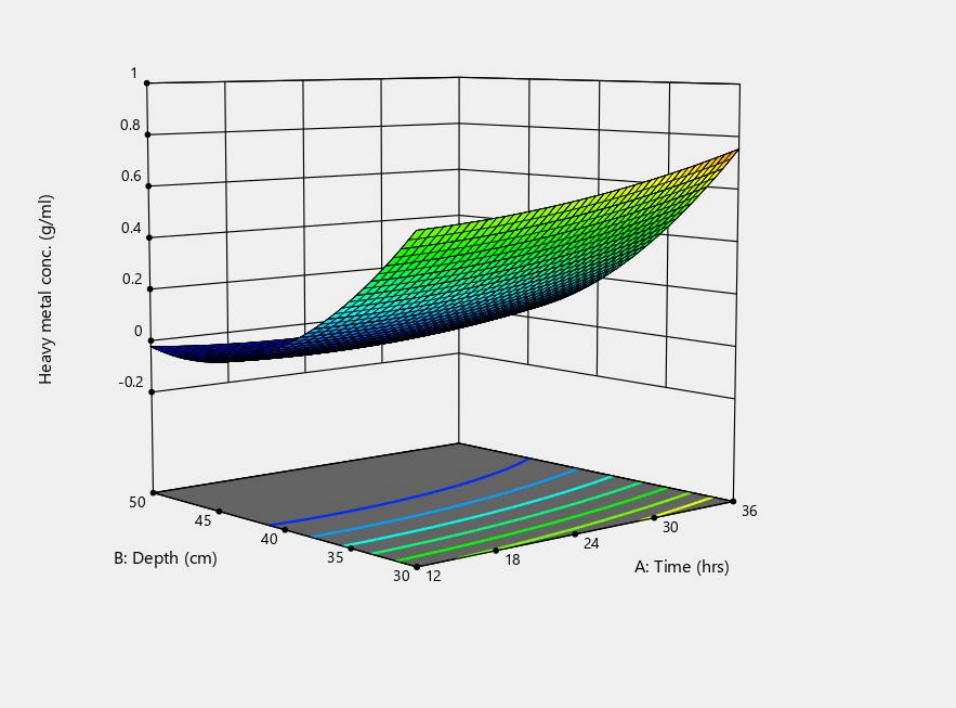


Figure 4. 3: 3D surface showing the relationship between the response (heavy metal concentration) and the independent variables (time and depth)

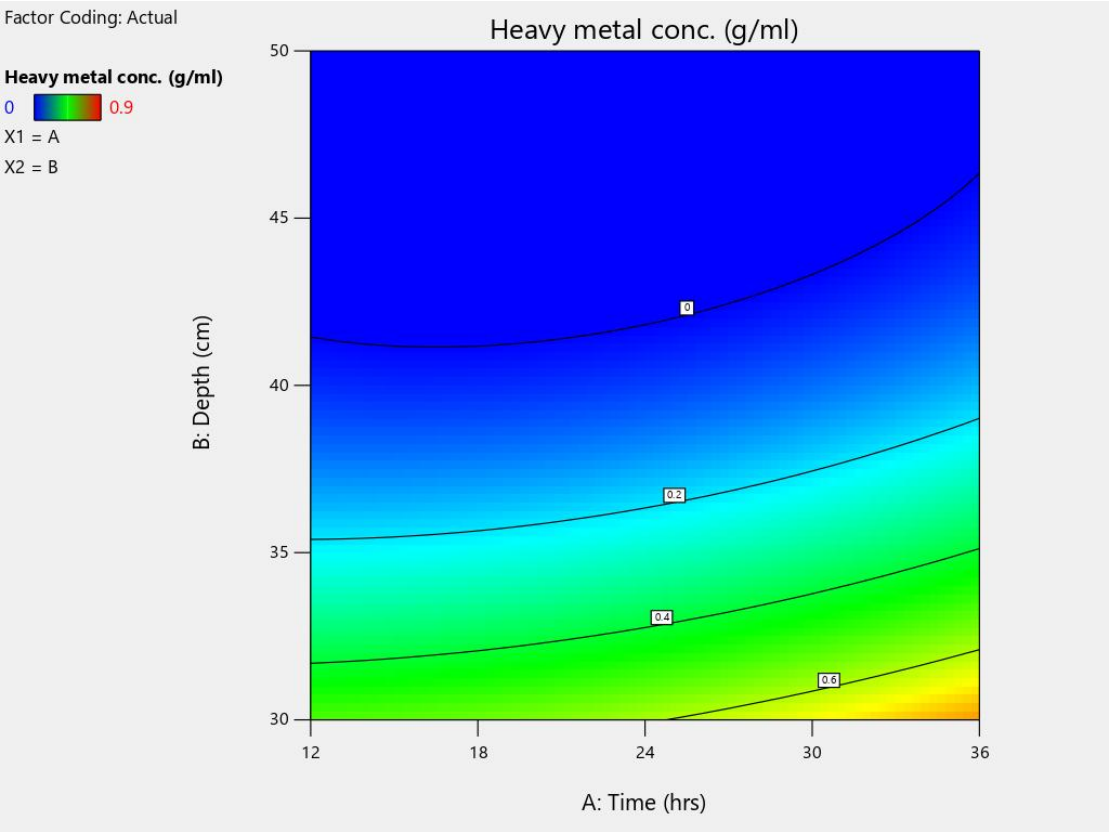


Figure 4. 4: Contour plot showing the relationship between the response (heavy metal concentration) and the independent variables (time and depth)

CHAPTER FIVE

CONCLUSION AND RECOMMENDATION

5.1 CONCLUSIONS

This research work investigated the transport of Pb (II) on a packed bed using response surface methodology (RSM) to analyse and predict the transport process. The study was carried on a packed bed. The following conclusion can be drawn from this investigation;

1. The air – drying, crushing and sieving of the soil samples using a 2mm sieve before physico – chemical analysis was carried out on them was done to remove all forms of rubbish from the soil and also to provide uniformity in particle size for evenly distribution of fluid.
2. The collected soil samples at different time and depth as generated by design expert clearly showed how fast the transport of fluid can be in soil at a determined depth with different time intervals.
3. The bulk density of 1.5 g/ml is slightly high, which resulted from the compactness of the soil. A moisture content of 4 % obtained from the uncontaminated soil sample was a low value since we are in the dry season. A pH value of 5.97 is within normal range and would further increase upon contamination since lead brings about the increase in the acidity of soil. The porosity (WFPS) of 4.92 showed that the soil is very dry.
4. The time factor had only a marginal effect on the concentration level of Pb (II) while an increase in depth showed a significant decrease in Pb (II) concentration. The optimum concentration level was found to be at 30cm deep, after 36 hrs of contamination. The findings from this study shows that the

depth of the soil is the predominant factor in the transport of Pb (II) on packed bed.

5.2 RECOMMENDATION

Based on the study carried out on the transport of heavy metal on soil, the following recommendations were made;

1. A study on the effect of various weather conditions as it affects transport of heavy metals in soil.
2. Since an automobile workshop is a station for Pb (II) contamination, soils in automobile mechanic battery workshop requires remediation to minimize soil pollution. These battery wastes can be recycled and properly disposed following the best scientific method.
3. Further studies should be carried out on various methods used in treatment of soil which have already been contaminated.
4. Further study should also be carried on ways of controlling soil pollution since pollution has now become a menace in the society.

REFERENCE

Abosede, O. A. (2017). Review on Heavy Metals Contamination in the Environment. *European Journal of Earth and Environment*, *4*(1), 1–6.

Adie, G. U., & Osibanjo, O. (2009). Assessment of soil-pollution by slag from an automobile battery manufacturing plant in Nigeria. *African Journal of Environmental Science and Technology*, *3*(9), 239–250.

Akinde, B. P., Olakayode, A. O., Oyedele, D. J., & Tijani, F. O. (2020). Selected physical and chemical properties of soil under different agricultural land-use types in Ile-Ife, Nigeria. *Heliyon*, *6*(9), e05090. https://doi.org/10.1016/j.heliyon.2020.e05090

Alloway, B. J., & Davies, B. E. (1971). Short Note: Heavy metal content of plants growing on soils contaminated by lead mining. *The Journal of Agricultural Science*, *76*(2), 321–323. https://doi.org/10.1017/S0021859600025697

Alluri, H. K., Ronda, S. R., Settalluri, V. S., Jayakumar Singh, B., Suryanarayana, V., & Venkateshwar, P. (2007). Biosorption: An eco-friendly alternative for heavy metal removal. *African Journal of Biotechnology*, *6*(25), 2924–2931. https://doi.org/10.5897/ajb2007.000-2461

Aronsson, P., & Perttu, K. (2001). Willow vegetation filters for wastewater treatment and soil remediation combined with biomass production. *Forestry Chronicle*, *77*(2), 293–299. https://doi.org/10.5558/tfc77293-2

Arora, R. (2019). Adsorption of heavy metals-a review. *Materials Today: Proceedings*, *18*(1), 4745–4750. https://doi.org/10.1016/j.matpr.2019.07.462

Blake, G. R., & Hartge, K. H. (2018). Bulk density. *Methods of Soil Analysis, Part 1: Physical and Mineralogical Methods*, *9*(11718), 363–375. https://doi.org/10.2136/sssabookser5.1.2ed.c13

Box, G. E. P., & Behnken, D. W. (1960). Some New Three Level Designs for the Study of Quantitative Variables. *Technometrics*, *2*(4), 455–475. https://doi.org/10.1080/00401706.1960.10489912

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

Bronick, C. J., & Lal, R. (2005). Soil structure and management: A review. *Geoderma*, *124*(1–2), 3–22. https://doi.org/10.1016/j.geoderma.2004.03.005

Bullock, K. R. (1994). Lead/acid batteries. *Journal of Power Sources*, *51*(1–2), 1–17. https://doi.org/10.1016/0378-7753(94)01952-5

Di Bonito, M. (2008). Sewage Sludge in Europe and in the UK. Environmental Impact and Improved Standards for Recycling and Recovery to Land. *Environmental Geochemistry: Site Characterization, Data Analysis and Case Histories*, 251–286. https://doi.org/10.1016/B978-0-444-53159-9.00011-5

Dixon, A. G., & Partopour, B. (2020). Annual review of chemical and biomolecular engineering computational fluid dynamics for fixed bed reactor design. *Annual Review of Chemical and Biomolecular Engineering*, *11*(1), 109–130. https://doi.org/10.1146/annurev-chembioeng-092319-075328

Dolejš, V., & Machač, I. (1995). Pressure drop during the flow of a Newtonian fluid through a fixed bed of particles. *Chemical Engineering & Processing: Process Intensification*, *34*(1), 1–8. https://doi.org/10.1016/0255-2701(94)00566-4

Drury, C., Paquet, V., & Kelly, H. (2015). Experimental Design and Analysis. *Evaluation of Human Work, Fourth Edition*, 37–60. https://doi.org/10.1201/b18362-13

Fakunle, M. A., Adegoke, J. A., & Enemali, J. O. (2021). Determination of the Spread of Heavy Metal from Ori-Ile Battery Waste Dumpsite Using Electrical Resistivity Method. *Annals of West University of Timisoara - Physics*, *63*(1), 26–39. https://doi.org/10.2478/awutp-2021-0003

Ferronato, N., & Torretta, V. (2019). Waste mismanagement in developing countries: A review of global issues. *International Journal of Environmental Research and Public Health*, *16*(6). https://doi.org/10.3390/ijerph16061060

Gaines, L. (2014). The future of automotive lithium-ion battery recycling: Charting a sustainable course. *Sustainable Materials and Technologies*, *1*(2), 2–7. https://doi.org/10.1016/j.susmat.2014.10.001

Gebreyesus, S. T. (2014). Heavy Metals in Contaminated Soil: Sources & Washing through Chemical Extractants. *American Scientific Research Journal for Engineering, Technology, and Sciences (ASRJETS)*, *10*(1), 54–60. http://asrjetsjournal.org/

Gladkikh, M., & Bryant, S. (2005). Prediction of imbibition in unconsolidated granular materials. *Journal of Colloid and Interface Science*, *288*(2), 526–539. https://doi.org/10.1016/j.jcis.2005.03.029

Gupta, N., Khan, D. K., & Santra, S. C. (2012). Heavy metal accumulation in vegetables grown in a long-term wastewater-irrigated agricultural land of tropical India. *Environmental Monitoring and Assessment*, *184*(11), 6673–6682. https://doi.org/10.1007/s10661-011-2450-7

Hales, T. C. (2005). A proof of the Kepler conjecture. *Annals of Mathematics*, *162*(3), 1065–1185. https://doi.org/10.4007/annals.2005.162.1065

Hao, X., Ball, B. C., Culley, J. L. B., Carter, M. R., & Parkin, G. W. (2006). Chapter 57: Soil density and porosity. *Soil Sampling and Methods of Analysis*, *June*, 743–760.

Jackson, A. P., & Alloway, B. J. (1991). The transfer of cadmium from sewage-sludge amended soils into the edible components of food crops. *Water, Air, and Soil Pollution*, *57–58*(1), 873–881. https://doi.org/10.1007/BF00282950

Jalali, P., & Li, M. (2004). An estimate of random close packing density in monodisperse hard spheres. *Journal of Chemical Physics*, *120*(2), 1138–1139. https://doi.org/10.1063/1.1631911

Kale, S. S., Kadam, A. K., Kumar, S., & Pawar, N. J. (2010). Evaluating pollution potential of leachate from landfill site, from the Pune metropolitan city and its impact on shallow basaltic aquifers. *Environmental Monitoring and Assessment*, *162*(1–4), 327–346. https://doi.org/10.1007/s10661-009-0799-7

Khuri, A. I., & Mukhopadhyay, S. (2010). Response surface methodology. *Wiley Interdisciplinary Reviews: Computational Statistics*, *2*(2), 128–149. https://doi.org/10.1002/wics.73

Kuchhal, P., & Sharma, U. C. (2019). Battery waste management. *Environmental Science and Engineering*, *5*(March), 141–155.

Kushnir, D. (2015). Lithium Ion Battery Recycling Technology 2015: Current State and Future Prospects. *Environmental Systems Analysis*, 56. http://publications.lib.chalmers.se/records/fulltext/230991/local_230991.pdf

Lannelongue, J., Cugnet, M., Guillet, N., & Kirchev, A. (2017). Electrochemistry of thin-plate lead-carbon batteries employing alternative current collectors. *Journal of Power Sources*, *352*, 194–207. https://doi.org/10.1016/j.jpowsour.2017.03.129

Li, C., Zhou, K., Qin, W., Tian, C., Qi, M., Yan, X., & Han, W. (2019). A Review on Heavy Metals Contamination in Soil: Effects, Sources, and Remediation Techniques. *Soil and Sediment Contamination*, *28*(4), 380–394. https://doi.org/10.1080/15320383.2019.1592108

Mahar, R. B., Liu, J., Yue, D., & Nie, Y. (2007). Landfilling of pretreated municipal solid waste by natural convection of air and its effects. *Journal of Environmental Science and Health - Part A Toxic/Hazardous Substances and Environmental Engineering*, *42*(3), 351–359. https://doi.org/10.1080/10934520601144659

Maiti, S. K., De, S., Hazra, T., Debsarkar, A., & Dutta, A. (2016). Characterization of Leachate and Its Impact on Surface and Groundwater Quality of a Closed Dumpsite – A Case Study at Dhapa, Kolkata, India. *Procedia Environmental Sciences*, *35*, 391–399. https://doi.org/10.1016/j.proenv.2016.07.019

Mäkelä, M. (2017). Experimental design and response surface methodology in energy applications: A tutorial review. *Energy Conversion and Management*, *151*(August), 630–640. https://doi.org/10.1016/j.enconman.2017.09.021

Masindi, V., & Muedi, K. L. (2018). Environmental Contamination by Heavy Metals. *Heavy Metals*. https://doi.org/10.5772/intechopen.76082

Maslin, P., & Maier, R. M. (2000). Rhamnolipid-enhanced mineralization of phenanthrene in organic-metal co-contaminated soils. *Bioremediation Journal*, *4*(4), 295–308. https://doi.org/10.1080/10889860091114266

May, G. J., Davidson, A., & Monahov, B. (2018). Lead batteries for utility energy storage: A review. *Journal of Energy Storage*, *15*, 145–157. https://doi.org/10.1016/j.est.2017.11.008

McCauley, A., Jones, C., & Jacobsen, J. (2005). Basic Soil Properties. *Soil and Water*, *1*(1), 1–12. http://landresources.montana.edu/SWM/PDF/Final_proof_SW1.pdf

Mickley, H. S., Smith, K. A., & Korchak, E. I. (1965). Fluid flow in packed beds. *Chemical Engineering Science*, *20*(3), 237–246. https://doi.org/10.1016/0009-2509(65)80034-3

Mohanty, R., Mohanty, S., & Mishra, B. K. (2016). Study of flow through a packed bed using discrete element method and computational fluid dynamics. *Journal of the Taiwan Institute of Chemical Engineers*, *63*, 71–80. https://doi.org/10.1016/j.jtice.2016.03.025

Muchuweti, M., Birkett, J. W., Chinyanga, E., Zvauya, R., Scrimshaw, M. D., & Lester, J. N. (2006). Heavy metal content of vegetables irrigated with mixtures of wastewater and sewage sludge in Zimbabwe: Implications for human health. *Agriculture, Ecosystems and Environment*, *112*(1), 41–48. https://doi.org/10.1016/j.agee.2005.04.028

Myers, R. H., Khuri, A., & Carter, W. H. (1989). Response surface methodology: 1966-l988. *Technometrics*, *31*(2), 137–157. https://doi.org/10.1080/00401706.1989.10488509

Nagajyoti, P. C., Lee, K. D., & Sreekanth, T. V. M. (2010). Heavy metals, occurrence and toxicity for plants: A review. *Environmental Chemistry Letters*, *8*(3), 199–216. https://doi.org/10.1007/s10311-010-0297-8

Nair, A. T., Makwana, A. R., & Ahammed, M. M. (2014). The use of response surface methodology for modelling and analysis of water and wastewater treatment processes: A review. *Water Science and Technology*, *69*(3), 464–478.

https://doi.org/10.2166/wst.2013.733

Ohwoghere Asuma, Oghenero. (2012). Acoustic velocity properties of Danian limestone section exposed at the Curfs quarry, Southeastern Netherlands. *Journal of Geology and Mining Research*, *4*(4), 43–50. https://doi.org/10.5897/jgmr11.021

Oliveira, A., & Pampulha, M. E. (2006). Effects of long-term heavy metal contamination on soil microbial characteristics. *Journal of Bioscience and Bioengineering*, *102*(3), 157–161. https://doi.org/10.1263/jbb.102.157

Omar, S., Muhamad, M. S., Te Chuan, L., Hadibarata, T., & Teh, Z. C. (2019). A Review on Lead Sources, Occurrences, Health Effects, and Treatment Using Hydroxyapatite (HAp) Adsorbent Made from Fish Waste. *Water, Air, and Soil Pollution*, *230*(12). https://doi.org/10.1007/s11270-019-4312-9

Onoyinka Afolayan, A. (2017). Lead, Cadmium and Iron Concentrations in <i>Zea Mays</i> Grown Within the Vicinity of Ori-Ile Battery Waste Dumpsite, Olodo, Ibadan, Nigeria. *American Journal of Bioscience and Bioengineering*, *5*(5), 92. https://doi.org/10.11648/j.bio.20170505.11

Orjiakor, P. I., & Atuanya, E. I. (2015). Effects of automobile battery wastes on physicochemical properties of soil in Benin City, Edo State. *Global Journal of Pure and Applied Sciences*, *21*(2), 129. https://doi.org/10.4314/gjpas.v21i2.5

Orjiakor, P. I., Atuanya, E., Mbata, T. I., Umar, A. F., & Eze, C. N. (2015). Effects of Automobile Battery Wastes on Microbial Qualities of the Soil. *Society for Experimental Biology of Nigeria*, *15*(3), 118–122.

Osakwe, S. (2014). Heavy metal contamination and characteristics of soils from automobile workshops in Abraka, Delta State, Nigeria. *International Journal of Natural Sciences Research*, *2*(4), 48–58.

Palizban, O., & Kauhaniemi, K. (2016). Energy storage systems in modern grids—Matrix of technologies and applications. *Journal of Energy Storage*, *6*(2015), 248–259. https://doi.org/10.1016/j.est.2016.02.001

Papadopoulou, M. P., Karatzas, G. P., & Bougioukou, G. G. (2007). Numerical modelling of the environmental impact of landfill leachate leakage on groundwater quality - A field application. *Environmental Modeling and Assessment*, *12*(1), 43–54. https://doi.org/10.1007/s10666-006-9050-x

Plackett, R. L., & Burman, J. P. (1946). The Design of Optimum Multifactorial Experiments Author (s): R. L. Plackett , and J. P. Burman. Published by : Biometrika Stable URL : http://www.jstor.org/stable/2. *Biometrika*, *33*(4), 305–325.

Saxena, S., Srivastava, R. K., & Samaddar, a B. (2010). Sustainable Waste Management Issues in India. *The IUP Journal of Soil and Water Sciences*, *III*(1), 72–90.

Šmejkalová, M., Mikanová, O., & Borůvka, L. (2003). Effects of heavy metal concentrations on biological activity of soil micro-organisms. *Plant, Soil and Environment*, *49*(7), 321–326. https://doi.org/10.17221/4131-pse

Song, Q., & Li, J. (2014). Environmental effects of heavy metals derived from the e-waste recycling activities in China: A systematic review. *Waste Management*, *34*(12), 2587–2594. https://doi.org/10.1016/j.wasman.2014.08.012

Stoveland, S., Astruc, M., Perry, R., & Lester, J. N. (1979). Comparison of flameless atomic absorption for the analysis of the metallic content of sewage sludge with flame atomic absorption and colorimetric methods. *Science of the Total Environment, The*, *13*(1), 33–45. https://doi.org/10.1016/0048-9697(79)90015-9

Tüzen, M. (2003). Determination of heavy metals in soil, mushroom and plant samples by atomic absorption spectrometry. *Microchemical Journal*, *74*(3), 289–297. https://doi.org/10.1016/S0026-265X(03)00035-3

Udousoro, I. I., & Umoren, I U and Asuquo, E. D. (2010). Survey of some heavy metal concentrations in selected soils in South Eastern parts of Nigeria . *World Journal of Applied Science and Technology*, *2*(2), 139–149.

Vaccari, M., Vinti, G., & Tudor, T. (2018). An analysis of the risk posed by leachate from dumpsites in developing countries. *Environments - MDPI*, *5*(9), 1–17.

https://doi.org/10.3390/environments5090099

Vardhan, K. H., Kumar, P. S., & Panda, R. C. (2019). A review on heavy metal pollution, toxicity and remedial measures: Current trends and future perspectives. *Journal of Molecular Liquids*, *290*, 111197. https://doi.org/10.1016/j.molliq.2019.111197

Walker, S. (2009). What is a "Heavy Metal" machine? *Manufacturing Engineering*, *142*(2), 97331.

Wang, X., Gaustad, G., & Babbitt, C. W. (2016). Targeting high value metals in lithium-ion battery recycling via shredding and size-based separation. *Waste Management*, *51*, 204–213. https://doi.org/10.1016/j.wasman.2015.10.026

Winslow, K. M., Laux, S. J., & Townsend, T. G. (2018). A review on the growing concern and potential management strategies of waste lithium-ion batteries. *Resources, Conservation and Recycling*, *129*(October 2017), 263–277. https://doi.org/10.1016/j.resconrec.2017.11.001

Witek-Krowiak, A., Chojnacka, K., Podstawczyk, D., Dawiec, A., & Pokomeda, K. (2014). Application of response surface methodology and artificial neural network methods in modelling and optimization of biosorption process. *Bioresource Technology*, *160*, 150–160. https://doi.org/10.1016/j.biortech.2014.01.021

Zeng, X., Li, J., & Singh, N. (2014). Recycling of spent lithium-ion battery: A critical review. *Critical Reviews in Environmental Science and Technology*, *44*(10), 1129–1165. https://doi.org/10.1080/10643389.2013.763578

Zhang, W. L., Yin, J., Lin, Z. Q., Shi, J., Wang, C., Liu, D. B., Wang, Y., Bao, J. P., & Lin, H. B. (2017). Lead-carbon electrode designed for renewable energy storage with superior performance in partial state of charge operation. *Journal of Power Sources*, *342*(2699), 183–191. https://doi.org/10.1016/j.jpowsour.2016.12.061

Zhang, X., Xie, Y., Lin, X., Li, H., & Cao, H. (2013). An overview on the processes and technologies for recycling cathodic active materials from spent lithium-ion

batteries. *Journal of Material Cycles and Waste Management*, *15*(4), 420–430. https://doi.org/10.1007/s10163-013-0140-y

Ziraba, A. K., Haregu, T. N., & Mberu, B. (2016). A review and framework for understanding the potential impact of poor solid waste management on health in developing countries. *Archives of Public Health*, *74*(1), 1–11. https://doi.org/10.1186/s13690-016-0166-4

APPENDIX

APPENDIX A

Preparation of Pb (II) stock solution;

Molecular weight of Pb $(NO_3)_2$ = 331.2 g/mol

Molar mass of Pb = 207.2 g/mol

The mass of Pb in Pb $(NO_3)_2$ is;

$$= \frac{molecular\ weight\ of\ \text{Pb (NO3)2}}{molar\ mass\ of\ Pb}$$

$$= \frac{331.2\frac{g}{mol}}{207.2\frac{g}{mol}} = 1.6g$$

Bulk density;

$$Bulk\ density = \frac{W2 - W1}{V}$$

Where;

W1 (weight of cylinder) = 130.3g

W2 (Weight of soil sample + cylinder in grams) = 145.3g

V (volume of measuring cylinder in ml) = 10ml

$$Bulk\ density = \frac{W2 - W1}{V}$$

$$= \frac{145.3 - 130.3}{10} = 1.5\frac{g}{ml}$$

Moisture content;

$$\%\ moisture\ content = \frac{W2 - W3}{W2 - W1}\ X\ 100\%$$

Where;

W1 (weight of empty crucible) = 22.5g

W2 (weight of crucible + sample before heating) = 27.5g

W3 (weight of crucible + sample after cooling) = 27.3

$$= \frac{27.5 - 27.3}{27.5 - 22.5} \, X \, 100\% = 4\%$$

Porosity (Water filled pore space);

$$WFPS = \frac{W1/(Vt - \frac{W2}{D1})}{D2}$$

Where;

W_1 (weight of water) = 49.2g

W_2 (dry weight of soil) = 150g

D_1 (bulk density of soil) = 1.5 g/ml

V_t (bulk volume) = 110 ml

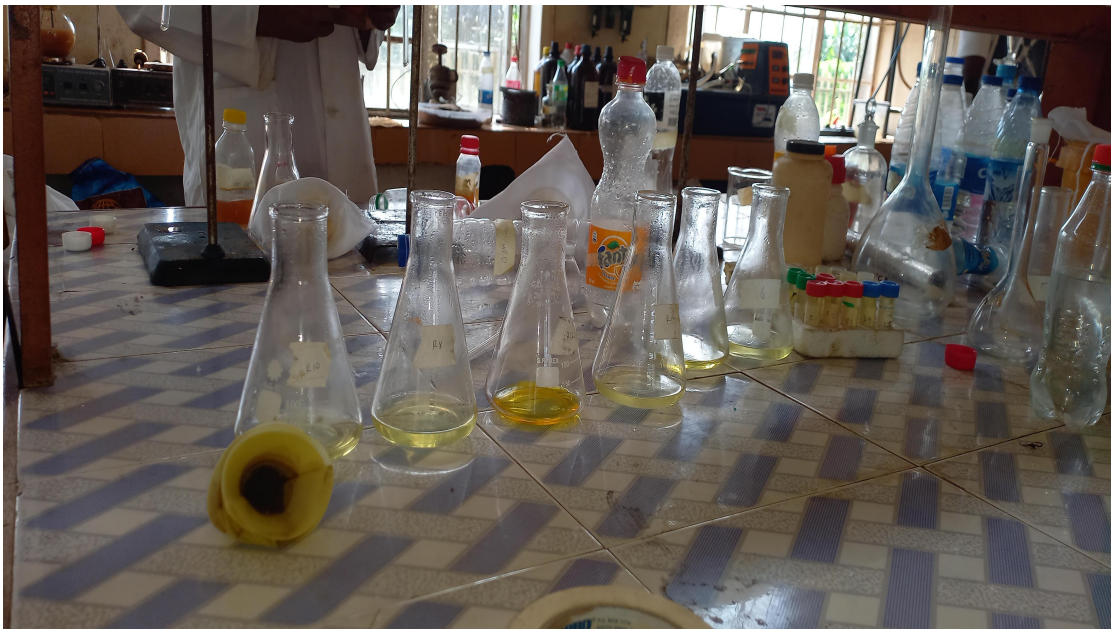
D_2 (density of water) = 1 g/cm^3

$$= \frac{49.2/(110 - \frac{150}{1.5})}{1} = 4.92\%$$

APPENDIX B

A packed bed

Soil samples



Filtration after the digestion of the soil samples

Atomic adsorption spectrophotometer