**ADDIS ABABA INSTITUTE OF TECHNOLOGY (AAIT)**

**SCHOOL OF CHEMICAL AND BIO ENGINEERING**

**ENVIRONMENTAL ENGINEERING STREAM**

# Removal of Lead Metal Ion from Paint Industries Wastewater by Mango and Avocado Seed Waste

**By:**

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**February, 2024**

**Addis Ababa, Ethiopia**

**Addis Ababa University**

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# Removal of Lead Metal Ion from Paint Industries Wastewater by Mango and Avocado Seed Waste

*A Thesis Submitted to the School of Graduate Studies of Addis Ababa University for the Partial fulfillment of the requirements of the Degree of Masters of Science in Environmental Engineering Stream.*

**By:** Tseganesh Kegne

**Thesis Advisor: -** Belay Weldeyes (Prof. Dr.-Ing)

**September, 2023**

**Addis Ababa, Ethiopia**

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Approved by the Examining Board

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Internal Examiner Signature Date

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External Examiner Signature Date

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Chairperson Signature Date

**DECLARATION**

I, hereby, declare that the find out about entitled “Removal of Lead Metal Ion from Paint Industries Wastewater by Mango and Avocado Seed Waste” is my unique work and has no longer been used through others for any different necessities in any different university and all sources of the substances used for this thesis have been correct acknowledged.

Name: Tseganesh Kegne

Signature ______________

Date of Submission ________________

This thesis has been approved for:

Prof. Dr. –Ing. Belay Weldeyes

Signature ______________

Date ________________

**ABSTRACT**

*In this study, the effectivity of Mango and Avocado Seed Waste as an adsorbent an inexperienced science in the removal of lead metal ion from paint industry wastewater is analyzed. The adsorbent was once characterized the use of physico-chemical residences such as moisture content, ash content, volatile matter and iodine number. The surface morphology of mango and avocado seed adsorbent was once characterised with the aid of SEM, FTIR and BET. Experimental consequences confirmed that mango and avocado seed adsorbent may want to operate successfully inan extensive vary ofexperimentalconditions.Thewastewatersamples ha vebeen physicochemically characterized earlierthan andafter remedy inaccordance to well-known system the usage of mango and avocado seed adsorbent. Batch adsorption experiments have been performed to consider the impact of contact time, pH and adsorbent dose of adsorbate had been studied, and the adsorption isotherms and kinetics of on Pb (II) elimination have been determined. To set up optimal adsorption conditions, Design Expert version 13 Software was once used. To decide the ultimate setting, a central composite design under response surface methodology to be used. The most elimination effectivity of $Pb^{2+}$ions through mango and avocado seed adsorbent used to be got most advantageous pH 5.5, foremost adsorbent dose of 1.25g, and the most advantageous contact time of 120 min; in these highest quality stipulations the elimination effectivity was once 99.5%. The effects have been additionally verified that the adsorption method follows Langmuir isotherm model with a higher sorption fit and supported for the monolayer adsorption of Pb+2ions on mango and avocado seed adsorbent. The kinetic model of this learn about indicates a pseudo-second order kinetic model with top correlation coefficient. Based on the outcomes obtained, the mango and avocado seed adsorbent produced from Mango and Avocado Seed waste has a suitable functionality in elimination of the lead metal ions from the Paint industry wastewater.*

**Key words:** *Paint wastewater, Mango and Avocado Seed Adsorbent, Lead metal ion, response surface methodology, optimal conditions.*

**ACKNOWLEDGEMENTS**

First of all, my exclusive thanks go to the almighty God for enhance me to done my study. I am indebted to the precious remark of my thesis guide Belay Weldeyes (Prof. Dr. -Ing) for his non-stop follow-up, advice, and positive comments. I would additionally like to thank my households and buddies for their guide and encouragement throughout working my thesis work. I additionally would like to thank Nefas Silk Paint Company, Addis Ababa Institute of Technology, Adama Science and Technology University, Bahirdar Institute of Technology as nicely as Ethiopian Construction Design and supervision Works Corporation Laboratory Staffs for their guide imparting me with the vital facts for my study.

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| | |
|---|---|
| AC | Activated Carbon |
| ADLI | Agricultural Development Led Industrializations |
| ANOVA | Analysis of Variance |
| AOAC | Association of Official Analytical Chemist |
| AP | Adequate Precision |
| APHA | American Public Health Authority |
| ASTM | American Standard Test Method |
| AWWA | American Water Work Association |
| BET | Branauer, Emmett, and Teller |
| BOD | Biological Oxygen Demand |
| CCD | Central Composite Design |
| COD | Chemical Oxygen Demand |
| CV | Coefficient Variation |
| DOE | Design of Experiments |
| EEPA | Ethiopia Environmental Protection Authority |
| EPA | Environmental Protection Agency |
| FTIR | Fourier Transform Infrared |
| GAC | Granular Activated Carbon |
| GDP | Gross Domestic Product |
| GFAAS | Graphite Furnace Atomic Absorption Spectrometer |
| GTP | Growth and Transformation Plan |
| IN | Iodine Number |
| MC | Moisture Content |
| NSPF | Nefas Silk Paints Factory |
| PAC | Powdered Activated Carbon |
| RSM | Response Surface Methodology |

| | |
|---|---|
| SEM | Scanning Electron Microscope |
| TSS | Total Suspended Solid |
| UNWWDR | United Nations World Water Development Report |
| USEPA | United States of Environmental Protection Agency |
| VC | Volatile Content |
| WHO | World Health Organization |

**CHAPTER ONE**

# 1. INTRODUCTION

## 1.1 Background

The launch of heavy metals in to the surroundings through industrial effluents has ended up an international trouble at some point of the present day years. The fast improvement of arrange of industrial things to do and technology discharged heavy metals in to the surroundings which enormously affected the surroundings and human fitness due to their toxicity, bioaccumulation, and bio-augmentation in the meals chain and persistence in nature (Tessema, Adugna, and Kamaraj 2020). Heavy metals like arsenic, chromium, lead, cadmium, copper, mercury, nickel, and silver are amongst contemporary effluents' most extensively recognized toxins. However, Pb (II) ions are mainly frequent heavy metals determined in paint industries wastewater. Heavy metals are no longer biodegradable and have a tendency to be collected in organisms and purpose several ailments and problems Heavy metals like arsenic, chromium, lead, cadmium, copper, mercury, nickel, and silver are amongst contemporary effluents' most extensively recognized toxins. However, Pb (II) ions are mainly frequent heavy metals determined in paint industries wastewater. Heavy metals are no longer biodegradable and have a tendency to be collected in organisms and purpose several ailments and problems (Shafiq, Alazba, and Amin 2018). To get rid of heavy metals from industrial effluent, precipitation, ion exchange, coagulation, electron dialysis, etc. are the most regularly used technologies (Abou El-Maaty 2014). These technologies have several hazards such as incomplete metal ion removal, excessive power and reagent costs, and poisonous sludge (Yi et al. 2015). However, adsorption strategies seem greater pleasing due to their simplicity, ease of use, excessive efficiency, and comparatively cheap elimination of heavy metals from wastewater. Another gain of adsorption over different methods were functionality to deal with wastewater pollution at low concentrations (Yusuff, Popoola, and Anochie 2021).

Adsorption procedure the use of activated carbon, extensively used as adsorbent, is amongst the most positive strategies for heavy metals' elimination from waste streams. It is presently the quality accessible technology for the elimination of natural and inorganic pollutants. Commercially on hand activated carbon is nevertheless pricey and purpose unique issues to the environment, such as the non-biodegradable nature of silica gel (Shafiq, Alazba, and Amin 2018).

Although it is substantially used in the cure of water and wastewater, activated carbon is a pricey material, and therefore the manufacturing of low-fee selections have been the focal point of researchers in the remaining few years. In the final decades, there have been a perfect vogue for the use of less expensive absorbents and one of a kind research have established that natural agents have excessive elimination ability for divalent heavy metallic ions (Bernard E, Jimoh A, and Odigure JO 2013). Materials domestically accessible in massive portions such as natural materials, agricultural waste or industrial by-products can be utilized as inexpensive adsorbents. Some of these substances can be used as adsorbents with little processing. Conversion of these substances into activated carbon, which can be used as an adsorbent for water purification, would enhance financial value, assisting industries to limit the fee of waste disposal and imparting a practicable choice to activated carbon (Kurniawan et al. 2006). Some preceding research have suggested the manufacturing of adsorbent from agricultural residues and different substances for removing of Pb (II) ions from wastewater, for instance, banana steam (Ogunleye et al. 2014), tamarind wood (Singh et al. 2008), almond shell (Parthasarathy and Narayanan 2014), winemaking waste (Alguacil et al. 2018), and pine cone (Momčilović et al. 2011). This choice sorbent cloth is picked out primarily based on its doubtlessly content material of cellulose, pectin, hemicellulose and lignin and due to its abundance as waste fabric from juice enterprise or fruit stall (Othman, Mohd-Asharuddin, and Azizul-Rahman 2013).

The technology of massive quantities of by-products, such as seeds, peels, and rotten fruits, from fruit juice processing and oil processing industries poses sizeable challenges in phrases of their remedy and disposal. Improper administration of these meals wastes can lead to uncontrolled decay, contributing to international warming and fitness dangers (Tesfaye et al. 2022). This learns about objectives to tackle the elimination of Pb (II) ions from Nefas Silk Paint Industry effluent in Addis Ababa, Ethiopia, by using making use of mango and avocado seed waste as an adsorbent. Mango and avocado are extensively used via juice processing industries, oil industries, and small juice merchandising homes as foodstuff. Consequently, a sizeable quantity of waste is generated from these industries and frequently disposed of on land, contributing to environmental pollution. By the usage of these waste substances as adsorbents, there are twin benefits: minimizing the disposal prices for fruit juice and oil processing industries, consequently decreasing environmental pollution, and including fee to wastewater therapy through the adsorption of heavy metal ions.

## 1.2 Problem Statement

The hassle of untreated industrial wastewater discharge is especially extreme in Addis Ababa, the place a giant element of giant and medium-scale manufacturing industries are located. It has been suggested that 90-96% of industries in Addis Ababa discharge their wastewater barring desirable therapy immediately into close by water bodies. This lack of cure amenities is ordinary in the paint manufacturing sector, which is dispersed for the duration of distinctive components of the city, such as residential and industrial areas such as the Nefas Silk Lafto sub-city and Akaki Kality sub-city. Some of these industries are additionally discovered in regional states, however they lack fantastic waste discharge mechanisms and contemporary cure flowers to deal with their effluents correctly (Berihun and Solomon 2017).

Within the paint industry, wastewater is generated mainly from cleansing operations involving mixers, reactors, and blenders, packing machines, and floor (M A Aboulhassan et al. 2014). The untreated effluents comprise several pollution that can be detrimental to human fitness when they exceed permissible limits. Paint components, such as binders, pigments, solvents, and additives, make contributions to wastewater pollution. Pigments, each natural (azo, anthraquinone) and inorganic (white lead, lead chromates, cadmium yellow), furnish color, opacity, and gloss. Among these components, heavy metals pose a widespread challenge as they are noticeably toxic, carcinogenic even at low concentrations, and non-biodegradable (Ahenda, Wangeci, and Nyang'au 2020). Improper discharge of Pb (II) metal into the surroundings has been regarded to purpose destruction of neighborhood aquatic ecosystems. Lead, in particular, is an exceptionally poisonous metal that can reason environmental degradation and fitness problems (Kaur and Sharma 2017). Excessive consumption of lead has destructive results on the human body, affecting a number of structures such as the kidney, liver, worried system, reproductive system, and gastrointestinal system. Lead is identified as one of the most hazardous heavy metals, and its presence in the surroundings can have extreme penalties for each the ecosystem and human well-being (Wang et al. 2021).

The extent of wastewater being discharged from industries is growing daily, whilst the quantity of wastewater being handled has been reducing annually. This highlights the urgency and significance of introducing cheap therapy strategies that make use of domestically handy uncooked materials (Yemisi, Aiyesanmi, and Adebayo 2020).

Conventional applied sciences for the elimination of Pb (II) metal ions can be expensive. Hence, there is a want to discover cheap, renewable, non-polluting, and biodegradable alternatives. Fruit juice and oil processing industry waste, such as mango and avocado seeds, are presently regarded environmental pollution as they lack acknowledged utilization. Finding a choice use for these waste substances by way of remodeling them into an adsorbent for the elimination of Pb (II) metal ions would now not solely have financial fee however additionally make contributions to a cleaner and safer environment. Integrating the waste substances from fruit juice and oil processing industries, specifically mango and avocado seeds, as an adsorbent for getting rid of Pb (II) metal ions from paint industry effluent may want to set up a new, simple, and low-priced cure technological know-how in Ethiopia.

### 1.3 Research Questions

1. What is the effectiveness of mango and avocado seed waste-based adsorbents in removing of lead metal ion from paint industries' wastewater, and how does their overall performance evaluate to traditional adsorbents?
2. What are the most suitable running stipulations for the removal of lead metal ion from paint industries' wastewater by way of mango and avocado seed adsorbents, and how do these prerequisites have an effect on the adsorption performance?
3. What is the long-term balance and reusability of mango and avocado seed waste-based adsorbents for the removal of lead from paint industries' wastewater?

### 1.4 Objectives

#### 1.4.1 General Objective

The main objective of this study is Removal of Lead Metal Ion from Paint Industries Wastewater by Mango and Avocado Seed Waste

#### 1.4.2 Specific Objectives

1. Preparation and Characterization of Mango and Avocado seed wastes as an adsorbent for removal of lead metallic ion.
2. Characterization of untreated and treated Nefas Silk paint industry wastewater primarily based on wastewater parameter.
3. Evaluation of efficiency and performance of adsorbent for removal of lead metal ion from Nefas Silk paint industry wastewater.

4. Optimization of removal efficiency, pH, Contact time and adsorbent dosage for the removal of Pb (II) from Nefas Silk paint industry wastewater by Mango and Avocado Seed adsorbent.
5. Determination of adsorption models of the adsorbent by different isotherm and kinetic models.

### 1.5 Significance of the Study

The discovering of this lookup will assist to elevate cognizance about the have an effect on of paint industry heavy metal lead toxicity on surroundings especially in humans' health. To use agriculturewastesorindustrialby-products(mangoandavocadoseeds)togenerate
adsorbent material as less expensive domestically made for the removal of $Pb^{+2}$ metal ion from painting industry wastewater and to reduce solid waste for safety of the environment. The records thatwill occur from findoutabout will assist the different researchersto inspect the cl oth for comparable purpose.Itwill additionally be capable to decorate theuseof costefficient neig hborhood materials to decorate sustainable development. It additionally encourages the use of neighborhood applied sciences for financial stimulus, growth, improvement and job creation

### 1.6 Scope and Limitation of Study

The scope of this research about includes evaluating the adsorption capability of mango and avocado seed waste for Pb(II) metal ion removal from paint industry effluent. The lookup consists of optimizing working conditions, characterizing the adsorbent materials, evaluating them with traditional adsorbents, and assessing the elimination efficiency. However, barriers exist in phrases of generalizability to different locations, scalability to industrial settings, Collection of waste materials, elimination effectivity for different pollutants, and useful resource constraints. Considering each the scope and obstacles presents a balanced appreciation of the research's doable implications.

### 1.7 Expected Output/Outcome

The predicted effects of this lookup consist of evaluating the adsorption capability of mango and avocado seed waste for removing Pb (II) metal ions from paint industry wastewater, optimizing the working stipulations for most elimination efficiency, characterizing the adsorbent materials, evaluating them with traditional adsorbents, assessing the normal elimination efficiency, examining the monetary viability and sustainability of the process, creating a lower priced therapy technology, and offering guidelines for implementation. The lookup targets to generate expertise on the attainable of mango and avocado seed waste as a sustainable and low in cost answer for wastewater treatment, addressing environmental pollution and promotion cleaner practices for industries in Ethiopia.

# CHAPTER TWO

# 2. LITERATURE REVIEW

## 2.1 Research Gap Analysis

A complete overview of the literature on fruit waste and industrial derivative adsorbents exhibits necessary findings involving the therapy of Pb (II) metal ions from aqueous solutions. Researchers usually hire batch adsorption strategies below a range of experimental stipulations to look into components such as particle size, most adsorption capacity, modification, removal efficiency, and focused pollutants. Analyzing the statistics introduced in the literature allows comparisons between distinct adsorbents and affords insights into their reliability for Pb (II) metal ion elimination beneath unique conditions. This overview additionally helps become aware of expertise gaps and areas the place similarly lookup is needed. Additionally, the results of experimental parameters like pH, contact time, and adsorbent dosage on the adsorption manner are mentioned in the literature, which can make a contribution to the improvement of greater positive elimination strategies for Pb (II) metal ions in paint industry wastewater. Recent research spotlight the effectivity of fruit waste adsorbents for Pb (II) metal ion removal, underscoring their conceivable in addressing the elimination wishes of paint industry wastewater.

### 2.1.1 Studies Related to the Use of Fruit Wastes as an Adsorbents to Remove Lead Metal Ion

From Table (1) below lead removal from aqueous solution by means of fruit waste adsorbents. Due to the elevated launch of Pb (II) ions in the environment. (Olu-owolabi 2012) Utilized mango stone and cocoa pod waste to do away with lead from wastewater. The mango stone and cocoa pod waste had been now not handled to emerge as activated carbon. The authors carried out the experiments at pH: 4, metal concentration: 100mg/L contact time: 40 min., temperature: room temp. Best in fit isotherm model Langmuir and great suit kinetic model used to be Pseudo-2$^{nd}$-order. (Kanjilal et al. 2015) Experimented on the elimination of lead from industrial wastewaters the use of Mango seed integuments wastes. The pH of the options used to be different from 3 to 9 and the optimum pH value was once mentioned pH 5. Different temperatures in the range of 20- 70° C had been examined and the perfect temperature used to be executed at 30° C. The equilibrium time of 118.7 min was once bought when 1.62 g/L of adsorbents have been introduced to 49.79 ppm of lead solutions. The Langmuir isotherm and and Dubinin–kaganer–radush kevich model described the adsorption technique well. Mango seed integuments wastes had most lead removal effectivity of 75.23%. (Moyo, Pakade, and Modise 2017) Utilized NaOH and EDTA handled Mangifera indica seed shells to put off lead metal ion. The equilibrium time is said to be 30 min, pH: 5.2, Metal concentration: 130–400 mg\l, and NaOH and EDT handled mangifera indica seed shells waste had most lead adsorption capacities of 59.25 and 306.33, respectively. The kinetic research confirmed that the experimental statistics geared up into pseudo-second-order and the Langmuir isotherm great described the adsorption process. According to the change approaches and quantity of chemical used to be used, the technique does no longer seem to be price effective. (Njuguna 2016) Was determined the adsorption ability of 9.69 mg/g for the removal of Pb (II) the usage of Mangifera indica Kernel Ash as adsorbent. The authors referred to that the optimal pH used to be observed to be 6, Metal concentration: 20 mg\l, Contact time: 60min., Temperature: 25-450C, Best Fit Isotherm Model used to be Freundlich and about 97.62% of lead was once removed. (Murungi and Hassanali 2016) Examined sulpheric acid modified avocado seed as adsorbent to dispose of lead from wastewater. The change was once accompanied by means of thermo-chemically handled at a temperature of a 150 ºC for 24 hours. Each product used to be then washed with distilled water to eliminate the extra acid, filtered and stored in sodium bicarbonate answer NaHCO3 (1 %) in a single day to take away the acid residue. Finally, every handled adsorbent was once dried at one 105 ºC to a steady weight. After equilibrium time of 60 min the most adsorption capability was once pronounced to be 271.2 mg/g. At the most advantageous pH of 6 about 99.2% used to be eliminated with a lead awareness of 50 mg/l. The experimental facts geared up the Freundlich isotherm model with R2 value of 1. The kinetic research confirmed that pseudo-second-order model described the adsorption system best. When massive portions of fruit-waste used to be concerned .To the satisfactory of the author’s knowledge, the literature does now not consist of any statistics about the usage of Mango and Avocado Seed Waste collectively as an adsorbent to take away contaminants from wastewater and extra especially no learn about has been suggested regarding the use of mango and avocado seed waste as an adsorbent for the removal of Pb (II) metal ions from Paint industry wastewater.

Adsorbents differ in how efficiently they sequestrate heavy metal ions due to the fact the adsorption procedure is below the impact of distinct experimental conditions. For instance, the pH of the answer has a giant effect on the adsorption capability of the adsorbent. It is additionally linked to the surface charge of the adsorbents. The preliminary metal concentration and adsorbent dosage additionally have a plain have an impact on metal sequestration. According to the literature, contact time is every other experimental situation that desires to be regarded in the adsorption process. Normally, the adsorption charge is fast at the establishing of the scan and receives slower till the equilibrium time is reached. When the adsorption reaches the equilibrium time, it skill that the energetic web sites on the surface of the adsorbent are saturated. This method is quicker in some adsorbents than others. Some physical deformations in the shape of the adsorbent have been found via growing the temperature. In this regard, most of the researchers have carried out their experiments at ambient temperature. Although a range of research are performed in adsorption area, quite a few troubles and barriers want to be investigated.

All in all, our grasp of the physical and chemical interactions between metal ions and the surface of the bio-sorbent beneath unique operational and experimental prerequisites permits us to handle the difficult troubles at the back of the adsorption process. Development in figuring out of active functional groups which are accountable for the adsorption method is additionally required. This work is vital due to the fact it will facilitate the resolution of terrific fruit waste adsorbents which will supply environment friendly adsorption interplay between the contaminant and the surface of the chosen material. A lot of amendment strategies have been used on the adsorbents to facilitate the exchange and metal uptake process, however the value of the changes wants to be regarded as an essential issue. The fee implication is a vital aspect in relation to the commercialization of a reasonable water remedy technique on an industrial scale. The existing lookup hypothesizes that utilizing notably environment friendly fruit waste adsorbents will be a fee effective, possible and natural way to take away contaminants from contaminated wastewater.

A evaluation of the literature displays that Mango and Avocado seed waste has now not been evaluated as an adsorbent for the elimination of Pb (II) metal ions from Paint industry wastewater and greater specifically no find out about has been pronounced regarding the use of Mango and Avocado seed waste as an adsorbent to remove Pb (II) ions from aqueous solutions. This lookup consequently represents a contribution to the lookup area. The use of Mango and Avocado seed waste has numerous advantages: each fruit waste adsorbents are inexpensive and biodegradable, they have a porous surface, and they are in a position to dispose of Pb (II) ions from contaminated water rapidly and effectively. The predominant benefit of the use natural uncooked substances as adsorbents is that the utilization of chemical compounds for the duration of the water therapy procedure is minimized. In contrast, chemical redress are commonly pricey and the opportunity of releasing undesirable by-products from chemically handled adsorbents into water might also create a want for in addition remediation procedures. The existing find out about examined the effectivity of Mango and Avocado seed waste for the elimination of lead in low concentrations from paint industry wastewater. The results of experimental elements such as preliminary pH, contact time, and adsorbent dosage, had been investigated. The got experimental facts had been then validated the use of extraordinary isotherm and kinetic model to inspect the adsorption technique of Pb (II) metal ions onto the surface of the adsorbents. This lookup verified that Mango and Avocado seed waste are particularly wonderful as economical, biodegradable and environmentally easy adsorbents for the removal of Pb (II) from paint industry wastewater.

Table 1: Adsorption of pb (II) ions from aqueous solutions by different Fruit waste or industrial by product adsorbents.

| Adsorbent | Particle Size | Target Pollutants | Optimum Experimental Conditions | Modification | Best Fit Isotherm Model | Best Fit Kinetic Model | Maximum Adsorption Capacity (mg/g) or (mmol/Kg) | Removal % | Ref. |
|---|---|---|---|---|---|---|---|---|---|
| Mango stone and cocoa pod waste | 40 mesh | Pb | pH:4, Metal concentration: 100mg/L, Contact time: 40min., Temperature: room temp. | | Langmuir | Pseudo-2nd-order | - | - | (Olu-owolabi 2012) |
| Mango seed integuments | 110 μm | Pb | PH:7, Metal Concentration: 49.79g/L, Contact time: 118.7min, Temperature: 30$^0$C | NaOH | Langmuiran d Dubinin–kaganer–radushkevich | - | - | 75.23 | (Kanjilal et al. 2015) |
| Mangiferaindica seed shells | 90–425 µm | Pb | PH:5.2, Metalconcentration:130-400mg\l, Contact time: 30min., Temperature: room temp. | NaOH and EDTA | Langmuir | Pseudo-2nd-order | 59.25 and 306.33 | - | (Moyo, Pakade, and Modise 2017) |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Mangiferaindica Kernel Ash | - | Pb | pH:6, Metalconcentration:20mg\l, Contact time: 60min., Temperature:25-45$^0$C | - | Freundlich | - | 9.69 | 97.62 | (Njuguna 2016) |
| Avocado seed | - | Pb | PH: 6, Metal concentration: 50 mg\l, Contact time: 60min., Temperature:25-45$^0$C | $H_2SO_4$ | Freundlich | Pseudo-2$^{nd}$-order | 271.2 | 99.2 | (Murungi and Hassanali 2016) |

## 2.2 Ethiopian Paint Industries

The first paint system enterprise in Ethiopia has been located in 1960s with overseas investors. With the growth in the development of everlasting housing structures, the portray industry, which includes many players, is additionally developing in the country. Consequently, the want for ornamental and protecting paints has risen. This state of affairs derives the boom in the ornamental paints segment. Till 1990s, there had been solely two domestically operated paint factories. Currently there are 54 paint manufacturing industries working in Addis Ababa which are privately owned with the aid of Ethiopian and non- Ethiopian entrepreneurs. The important neighborhood producers are Nefas Silk Paint Factory, Modern Building Industries (DILl Paint Factory), Zemilli Paint Factory, Rainbow Paint Factory, KADISCO Paint Factory, and Addis Paint Factory.

Ethiopian Paint enterprise zone is greater expressed as a method and packaging industry. The greatest product section by using quantity is estimated to be the architectural and ornamental paints segment. Included in this class are family paints, such as indoors and exterior aqueous (latex) paints and indoors and exterior non-aqueous (oil) paints. Import paints cowl 20 % to 25 % of Ethiopian architectural and ornamental paint demand (Measho and Denu 2017)(Beyene 2019).

Nefas Silk Paints Factory (NSPF) is the oldest Paints Factory in Ethiopia which used to be centered in 1967 as a personal company. NSPF produces water based totally and oil-based paints, every with greater than 53 types of colors regularly. Apart from these two simple types, it additionally produces quartz, adhesives, antirust, varnishes and different associated products. It has a doable manufacturing potential of 32 million liters of paints per annum and produces extra than 1500 kinds of paints and paint associated merchandise (Beyene 2019). The manufacturing facility produces most of 87000 liters of paint per day and discharges its 2000 liters waste at once on the drainage barring treating untreated wastewater had been discharging into the Akaki River because its establishment. The river continues to go with the flow into the most important Aba Samuel River (Takele 2018). Paint wastewater is one of the most complexes, tough and sturdy industrial effluent, having excessive chemical oxygen demand (COD), total suspended solids (TSS) and heavy metals. The excessive chemical oxygen demand (COD), total suspended solids (TSS) and heavy metal quantity of the paint effluent normally ranged between 3,000 – 3,500mg/L and6,000 – 6,500 mg/L and 0.1 –15.5 mg/L respectively (M. A. Aboulhassan et al. 2006) (Tsegaye 2011).

### 2.2.1 Paint Industry Wastewater

Paint manufacturing industries makes use of giant portions of water and chemicals, and hence, produces massive quantity of wastewater. According to one, paint manufacturing industries, worldwide, use about 75–85 million gallons per day out of which solely about 4% of it is recycled. Nearly 70% of this wastewater is discharged untreated in the natural water bodies whilst about 25% receives evaporated (Nair K, Manu, and Azhoni 2021). Paint industries are amongst these industries that discharge effluent containing heavy metals. Paint is usually regarded as a combination of pigment, binder, solvent and additives. Paint classification can be made on many one of a kind bases; one handy technique is to classify paints based totally on their predominant solvent for waste copy and disposal. Using this approach, paints can be labeled as water based, natural solvent based totally or powder (dry) and barring solvent. The principal waste that paint enterprise need to manipulate is dominantly gear cleansing wastes, which makes up 80% of the waste generated in paint manufacture (Shazly, Hasanin, and Kamel 2010). An ordinary plant produces each solvent-based and water-based paints. The strategies for each sorts of paints are usually similar, though the components vary. Water-based paints are normally composed of water, pigments, resins, extenders (to prolong drying time), ammonia, dispersant, antifoam additives, polyvinyl alcohol emulsion, and a preservative. Solvent-based paints are normally composed of a solvent, pigments, extenders, resins, plasticizers, and drying oils (Lorton 1988).

### 2.2.2 The Characteristics of Paint Industries Wastewater

Paint a uniformly dispersed combination having a viscosity ranging from a skinny liquid to a semi-solid paste consisting of

i. Drying oil, artificial resin or binder
ii. Solvent or thinner and
iii. Organic or inorganic pigment.

Characteristics of Alkyd paint or Oil based totally paint and Latex paint or Water primarily based paint. Alkyd paints include oil and solvents which are toxic and flammable. Cleaning of portray tools requires the use of solvents which have the equal hazardous residences as alkyd paint (Effects, Service, and Prevention 1998). Latex paints commonly consist of natural and inorganic pigments and dyestuffs, extenders, cellulosic and non-cellulosic thickeners, latexes, emulsifying agents, anti-foaming agents, preservatives, solvents and coalescing marketers (Moulay Abdelazize

Aboulhassan et al. 2014). In general, paint effluents are alkaline and have excessive BOD, COD, heavy metals, suspended solids and colored substances (Shazly, Hasanin, and Kamel 2010).

### 2.2.3 Environmental Impacts of Paint industry Wastewater

Paint industries pollute the surroundings via effluent discharge, gasoline emission and waste disposal in the shape of natural and inorganic substances. All the three types of pollution discharged via a paint industry; the effluents are by way of some distance the most great due to its heavy metallic compositions. The heavy metals have cumulative consequences over the years; the presence of these heavy metals in the ecosystems has multiplied as an end result of extend in industrialization process. Health issues such as genetic mutation, deformation, cancer, kidney troubles etc., have been attributed to air pollution via heavy metals (Chidozie and Nwakanma 2017).

The paint wastewaters are characterized by way of along with sizable natural matter, excessive salinity, sulfate rich and excessive suspended solid. Untreated or allegedly handled paint industrial effluents incorporates variable quantities of heavy metals such as arsenic, lead, nickel, cadmium, copper, mercury, zinc and chromium, which have the doable to contaminate plants developing below such irrigation. These heavy metals have a marked impact on the aquatic plant life and fauna which thru bio-magnification enter the meals chain and eventually have an effect on the human beings as well. Heavy metal pollution is an ever-increasing trouble of our oceans, lakes and rivers (Woldeamanuale 2017).

### 2.2.4 Impact of Lead

Pb (II) is labeled as a non-essential widespread poisonous metallic ions and main environmental fitness problems, which influences a couple of physique structures together with the hematologic, neurologic, gastrointestinal, renal and cardiovascular structures (Rezaei, Pourang, and Moradi 2022). Lead can additionally harm the kidney, liver and reproductive system, fundamental cell techniques and intelligence functions. The poisonous signs are anemia, insomnia, headache, dizziness, and irritability, weak spot of muscles, hallucination and renal damages(Agarwal and Chaudhry 2015). Lead compounds have been labeled by using the International Agency for Research on Cancer (IARC) as Group 2A cancer causing agents (likely to motive human cancer) and as possibly human cancer agents via the US Environmental Protection Agency (EPA). Lead receives get entry to the physique via both ingestion, inhalation of arousal, or contact with pores and skin of lead-containing materials. Exposure to lead motives genotoxic outcomes such as chromosome aberration, mutation, DNA breakage, and DNA synthesis inhibition (Ibrahem et al. 2020). Lead (II) pollution, in particular, poses a risk to organic systems. More so due to the fact lead (II) being the most poisonous heavy metallic pollutant after cadmium and mercury, it is greater probably to be encountered in industrial effluents than both of the different two metals, as it is extra versatile in its industrial purposes than both of the two metals. For this reason, an increasing number of greater stringent legislations are being positioned upon industries to limit metallic discharge into the surroundings thru industrial influents. The industries are, as a consequence, required to put in force extra bold effluent remedy practices in order to conform to required heavy metallic requirements (Renu, Agarwal, and Singh 2017).

In Ethiopia, for tremendous industrial air pollution control, there are environmental requirements in vicinity that decide the allowable limits for a number of pollution in effluents discharged to inland waters. Specifically, the Emission Limit Value (ELV) for lead, in accordance to Ethiopian standards, is set at 0.5 mg/L (EPA FDRE 2003). This ability that industrial effluents discharged into inland waters need to now not exceed this restriction for lead concentration.

### 2.2.5 Standards of Paint Effluent Discharge

Paint effluent comprise excessive variety of heavy metals and organic pollutants so the elimination of these poisonous pollutants from effluent earlier than discharging to the surroundings and from uncooked water earlier than public use is vital for safety of human fitness and environment. However, in the wake of current industrialization and quick urbanization the first-class of groundwater has emerge as an growing problem due to illness with the aid of a variety of poisonous chemicals. Therefore, widespread is developed by means of the countrywide environmental safety authority and world fitness agency in accordance the neighborhood circumstance and environmental requirement is fundamental for every country. Table (2) beneath provides the requirements of paint effluent discharge from WHO (2015), US- EPA (2006) and EEPA (2003) (Takele 2018) .

Table 2**:** The Maximum Contaminated Level (MCL) Standards, for Paint Effluent Discharge

| Parameter | Unit | WHO (2015) | US-EPA (2006) | EEPA (2003) |
|---|---|---|---|---|
| pH | - | 6.5-8.5 | 6.5-8.5 | 6.5-8.5 |
| Temperature | $^{O}C$ | - | - | 40 |
| Turbidity | NUT | 5 | 15 | 25 |
| $BOD_5$ | mg/L | 15 | 23 | 50 |
| COD | mg/L | 40 | 120 | 150 |
| Total suspended solid | mg/L | 30 | 50 | 50 |
| Pb | mg/L | 0.04 | 0.05 | 0.5 |

### 2.2.6 Technologies Used to Remove Heavy Metals from Wastewater

#### 2.2.6.1 Chemical Precipitation

Chemical precipitation is a normally used traditional system for elimination of heavy metal ions from contaminated water due to the fact of its effortless use and less expensive nature. In this process, chemical reagents react with metal ions to shape insoluble precipitates, which can be separated by using filtration. Precipitation of metals is acquired via the addition of chemical reagents like alum, lime and limestone. The predominant negative aspects of chemical precipitation are the requirement of an extra quantity of chemical reagents for the remedy of heavy metals, manufacturing of sludge to a giant quantity, and excessive value for disposal of sludge (Chakraborty et al. 2020).

#### 2.2.6.2 Membrane Technology

The use of membranes for wastewater therapy and elimination of heavy metals recuperation have attracted great interest in many industries. The system entails flowing the answer beneath strain thru a splendid porous membrane and extracting permeate or easy water go with the flow of the membrane at atmospheric pressure (Mohd Noor et al. 2019). The dangers of this approach are that it is steeply-priced (Agarwal and Chaudhry 2015).

#### 2.2.6.3 Ion exchange

Ion-exchange approaches have been broadly used to dispose of heavy metals from wastewater due to their many advantages, such as excessive remedy capacity, excessive elimination effectivity and quickly kinetics. The ion change technique is an operative medium in eradicating heavy metals from wastewaters through a reversible chemical reaction, finished by means of the ions trade in the resin. Various resins can be used with many heavy metals for any particular purpose. Many researchers have hooked up that zeolites showcase suitable cation trade capacities for heavy metal ions beneath one of a kind experimental conditions. The negative aspects of ion trade manner are now not all ion trade resin is appropriate for metal elimination and the manner desires excessive capital fee (Chakraborty et al. 2020).

#### 2.2.6.4 Solvent extraction

Solvent extraction is an effective approach used basically for getting better /separating metal ions from aqueous solution having greater concentrations to gain excessive pure solutions. The precept of solvent extraction is that when a steel ion answer is contacted with a solvent, the metal ion is allotted between the two phases. The drawback of this technique is that the massive quantity of solvent of the extracted section ought to be refreshed in a pricey stripping step. It can also now not be recommended to undertake this approach to take away heavy metals whose awareness is very much less as the restoration value will be very excessive (Rao et al. 2010).

#### 2.2.6.5 Coagulation and Flocculation

Coagulation is the common water cure science which is broadly utilized in the ingesting water treatment. It is fascinating to learn about the feasibility of coagulation/flocculation science to deal with the heavy metal in water for the pollution control. In the coagulation/flocculation process, the chemicals, specifically coagulants or flocculants, are delivered into water to play an essential position in the elimination of heavy metals. These chemical substances ought to be roughly categorized into three categories, inorganic-based coagulant, and organic- primarily based flocculent and hybrid materials, in accordance to their chemical composition (Tang et al. 2016).

#### 2.2.6.6 Electrodialysis

Electro-dialysis (ED) is a membrane separation which ionized species in the answer are moved ignore via an ion alternate membrane through the usage of an electric powered potential. The membranes are skinny sheets of plastic substances with anionic or cationic characteristics. When an answer comprising, ionic species strikes thru the cellphone compartments, the anions switch to the anode and the cations to the cathode, crossing the anion alternate and cation-exchange membranes. It used to be observed that possible of an ED cellphone is nearly free on the sort of ions and solely depends on the running instances and the shape of cell. Despite its limitation, ED affords benefits for the remedy of wastewater encumbered with heavy metals such as the successful to generate a relatively targeted movement for recuperation and the denying of unpleasing filth from water. However, this techniques the disposal of hazardous wastes, and ought to detect business enterprise that will redeem and salvage metals from the sludge (Boontham and Babel 2018).

#### 2.2.6.7 Adsorption

Adsorption is described as the mass transport of materials from both gasoline or liquid nation to a stable interface, which receives connected by way of bodily and/or chemical interactions. It is a mechanism the place molecules pass out of the answer and, thereby get attached to the floor of the chemical via bodily and chemical bonding. Adsorption differs from absorption in that adsorption is based totally on floor whereas, absorption is based totally on volume. A notion recognized as "sorption' is used for each absorption and adsorption whereas desorption refers to the contrary of adsorption (Ugwu et al. 2020). Owing to its ease of operation and large vary of applications, adsorption is viewed as a complete water therapy and reclamation technique. Therefore, the approach has received interest for the therapy of industrial wastewater, in most cases owing to the lower priced and bulk availability of bio-adsorbents, metal selectivity, handy metal recovery, greater heavy metal uptake, Regenerative, and there is no era of poisonous sludge in this cure (Shafiq, Alazba, and Amin 2018) (Kaur and Sharma 2017) (Devanna, Begum, and Chari 2019).

### 2.3 Adsorption Phenomena

Adsorption is the occupation of the floor and pores (if any) of a substance (solid, liquid or gas) via molecules of every other substance as an end result of some appealing forces between the adsorbing floor and the substance adsorbed. This will become viable solely when the substance to be adsorbed is in contact with the adsorbing surface. The adsorbing floor is known as the adsorbent whilst the adsorbed substance is known as the adsorbate. The chemical equilibrium which represents the adsorption of molecules on a floor is as follows:

$$A + B \rightleftarrows AB$$

Where, A is the adsorbate, B is the adsorbent and AB is the product of the adsorption process. For adsorption of compounds on activated carbon, which is a reversible reaction, molecules proceed to accumulate on the floor of the carbon till the fee of the ahead response (adsorption process) is equal to the charge of the backward response (desorption process). At this point, equilibrium country is attained and no in addition accumulation of the adsorbate on the adsorbent floor occurs. Hence, adsorption stops. This equilibrium nation allows relationship acknowledged as adsorption isotherm (Okoye 2010).

Various inexpensive adsorbents, derived from agricultural waste, industrial by-product, natural material, or modified biopolymers, have been these days developed and utilized for the elimination of heavy metals from metal-contaminated wastewater. The attachment of atoms or molecules of adsorbate on the floor of solids and drinks can also be via two sorts of forces, bodily or chemical. Depending upon the sorts of forces worried in adsorption, it may also be divided into two types, bodily adsorption or physio sorption and chemical adsorption or chemisorption (Takele 2018).

**a) Physical Adsorption (Physio sorption)**

The quantity of physio sorption decreases swiftly as temperature is raised and is commonly very small above the integral temperature of the adsorbed specie. Due to the susceptible pressure concerned in physio sorption, the activation power is low, now not extra than 42kJ/mol. The charge of physio sorption is very high however the procedure is non-specific. Generally, the manner of bodily adsorption starts as an adsorbate molecule is transported from the bulk adsorbate section to the floor of the adsorbent. Next, the molecule then diffuses into the pore and then bodily bonds with the surface. Heat is commonly evolved, making adsorption an exothermic process. In the first step, the bulk adsorbate circulation ought to be intimately blended with the adsorbent to promote proper contact between the two components. In the 2d and 0.33 stages, the awareness gradient between the quantity of adsorbate existing in the bulk adsorbate flow and that inside the micro-pore presents the riding pressure for adsorption (Okoye 2010).

**b) Chemical Adsorption (Chemisorption)**

In chemisorption, adsorption happens solely in the vicinity the place chemical bonding between adsorbent and adsorbate such as ionic and covalent bonds are running on the grounds that chemisorption is pretty precise and can solely be finished with the aid of the opportunity of chemical bonding formation. The chemical bonding between each adsorbent and adsorbate leads to the enthalpy of the chemisorption to be inside 200 to four hundred kJ/mol. Chemisorption is strongly associated to the floor place and temperature, as it will have an effect on the adsorption effectivity (Zaimee, Sarjadi, and Rahman 2021).

### 2.3.1 General Adsorption mechanism

The classical mechanisms of adsorption are divided into three stages. In general, the major steps worried in adsorption of pollution on strong adsorbent are:

1. Diffusion of adsorbate to adsorbent floor takes place diffusion of adsorbate on the adsorbent floor by way of intermolecular forces between adsorbate and adsorbent. (Transfer of the metal ion from bulk answer to the outer floor of the adsorbent.)

2. Migration into pores of adsorbent entails migration of adsorbate into pores of adsorbent (Internal mass switch by using pore diffusion from outer floor of adsorbent to the internal floor of porous structure.)

3. Monolayer build-up of adsorbate on the adsorbent when the adsorbate ‘s particles are disbursed on the floor and crammed up the extent of pores, particles of adsorbate are constructing up the monolayer of reacted molecules, ions and atoms to the lively websites of adsorbent (Adsorption of adsorbate onto the lively web sites of the pores of adsorbent). The typical charge of adsorption is ruled through both movie formation or intra particle diffusion or each as the remaining step of adsorption are very quickly as in contrast to the different two steps (Takele 2018) (Raouf MS and Raheim ARM 2016).

### 2.3.2 Factor affecting adsorption performance

***a) Effect of Adsorbent dose***

The adsorbent dosage is a vital parameter due to the fact this determines the ability of an adsorbent. The elimination of metal ions increases with an increase in the adsorbent dosage. Ushakumary (2013) investigated Cd (II), Pb (II), Zn (II), Cr (III) and Cu (II) adsorption the usage of milled adsorbents of mango peel and Alisma plantago aquatic. His end result confirmed that the adsorption of metallic ions multiplied with the adsorbent dosage. Hence, with an adsorbent dosage above 0.4gm/100ml, equilibrium used to be reached. The metal elimination share thus, will increase with the growing quantity of adsorbent dosage (Ugwu et al. 2020).

### b) Effect of initial concentration

The charge of Adsorption relies upon on the preliminary attention of solution. Previous research on adsorption confirmed that the fee of adsorption will increase at a decrease concentration. Ushakumary (2013) said greater fee of adsorption for Cd (II), Pb (II), Zn (II), Cr (III) and Cu (II) the usage of milled adsorbents of mango peel and Alisma plantago aquatica when the attention was once low. This is due to the fact when the attention was once high, saturation of adsorption web sites came about which left most metal ions un-adsorbed. Hence, at decrease concentration, the fee of adsorption expanded due to the availability of a large surface region of the adsorbent (Ugwu et al. 2020).

### c) Effect of solution pH

The pH value of the metal solution performs an important function in heavy metal adsorption. It contributes so an awful lot in adsorption capacity. The pH impacts the conduct of the aqueous solution as nicely as the factors of attachment for the surface. The pH impact is established on the adsorbent surface charge. The pH contributes to the adsorbent surface charge, ionization workable and distribution of metal ions. For a negatively charged adsorbent surface, at a reduced pH, the negatively charged surface is neutralized by way of the H+ ions which are found in giant number, and in flip minimize the impediment to diffusion with a multiplied adsorption rate. Previous research confirmed that at decrease pH values, the adsorption effectivity decreases whilst it will increase at greater pH (Ugwu et al. 2020). The adsorptive ability of metal cations will increase with growing pH of the sorption system, however no longer in a linear relationship. On the different hand, too excessive pH cost can reason precipitation of metal complexes, so it must be averted in the course of experiments. For one of a kind adsorption mechanism of metal ions, the optima pH is different. It is stated that the greatest pH value is 5–9 for copper adsorption with the aid of timber ash and 4–5 for uranium. pH results (i.e., preliminary pH value and the pH shift and control) on the elimination of Cu2+, Cd2+ and Pb2+ from unbuffered aqueous solution via non-viable timber ash, it is observed that most effective pH value for Pb (II) and Co (II) ion uptake is 5.0 (Tsegaye 2011).

*d) Effect of contact time*

For adsorption to be complete, equilibrium between the adsorbent and the solute of the answer need to be attained. Thus, a unique time is required for the interactions of the equilibrium in order to make sure that the adsorption is achieved. The time required for the equilibrium to be attained is regarded as the contact time. Several authors have studied the impact of contact time on adsorption. Their effects confirmed that the charge of adsorption of metal ions will increase with time, after a sure time, a most excellent value was reached after which no extra elimination of metal ion takes place. The quantity of metal ion adsorbed at the contact time was a reflection of the most adsorption capability carried out with the aid of the adsorbent beneath the running prerequisites (Ugwu et al. 2020).

*e) Effect of temperature*

Temperature can have an effect on the adsorption ability of the adsorbent relying on the sorts of adsorbents used. Temperature can exchange the adsorption equilibrium depending on whether or not the technique is exothermic or endothermic. The impact of temperature on adsorption charge is such that it alters the molecular interplay and the solubility of the adsorbate. In the vary of 15–40 °C, the most equilibrium adsorption ability for Pb (II), Ni (II), Co (II) and Cr (VI) ions by way of the wooden ash used to be reached at temperature of 25 °C. The limit in ability at greater temperature between 25 and 40 °C printed that the tactics of adsorption for these metal ions with the aid of ash are exothermic. Reduce of adsorption capability at greater temperature may additionally be due to the injury of energetic binding web sites in the biomass (Tsegaye 2011).

*f) Effect of Particle Size*

The particle measurement is an essential parameter in adsorption process. The smaller the particle sizes of the adsorbent, the greater its adsorption rate. As the particle dimension decreases, the adsorption increases. This is due to the fact the surface area will increase as the particle measurement decreases (Ugwu et al. 2020).

*g) Effects of mixing rate*

The mixing charge enhances the adsorption of metal ion in the solution by using minimizing the mass switch resistance and affecting the bodily shape of the adsorbent. As mixing rate elevated from 0 to 200, the adsorption potential additionally increased. The adsorption improved due to the extra turbulence which enhances the metal ion diffusion into the surface of adsorbent (Takele 2018).

## 2.4 Adsorbents

### 2.4.1 Adsorbent Classification

Adsorbents can be typically categorized in 5 categories: (1) herbal substances such as sawdust, wood, fuller's earth or bauxite; (2) herbal substances handled to improve their buildings and houses such as activated carbons, activated alumina or silica gel; (3) manufactured substances such as polymeric resins, zeolites or alumino silicates; (4) agricultural stable wastes and industrial by-products such as date pits, fly ash or purple mud; and (5) bio sorbents such as chitosan, fungi or bacterial bio- mass. Another Simplified classification, can be used as follows: conventional and non-conventional adsorbents. The listing of conventional business adsorbents consists of activated carbons, ion-exchange resins (polymeric natural resins) and inorganic substances such as activated aluminas, silica gel, zeolites and molecular sieves (which are formally now not zeolites). Only four sorts of regularly occurring adsorbents have dominated the business use of adsorption: activated carbons ≫ zeolites ≫Silica gel > activated aluminas. The listing of non-conventional adsorbents consists of activated carbons acquired from agricultural stable waste and industrial by-products, natural substances such as clays, industrial by-products such as crimson mud, bio sorbents such as chitosan, and miscellaneous adsorbents such as alginates (Crini et al. 2019).

### 2.4.2 Characteristics of Adsorbent

Adsorbent is a stable substance that normally adsorbs gas, liquid or dissolved substance. They have to have excessive abrasion resistance, excessive thermal balance and small pore diameters, which effects greater uncovered surface area and consequently excessive ability for adsorption. The adsorbents have to additionally have a wonderful pore shape that permits quick transport of the gaseous vapors. A few adsorbent substances have been tried in the previous to take a look at their probabilities and techno-economic feasibility as de-fluoridating specialists. Activated alumina, activated carbon, activated alumina covered silica gel and so on more than a few adsorbent substances stated in literature. In current years, the use of clay substances to substitute commercially reachable adsorbents has attracted lots interest due to their low cost, availability, excessive surface area, lack of toxicity and plausible for ion change Their special residences together with excessive precise surface location and surface chemistry, a range of surface and structural properties, chemical and mechanical stabilities provide these substances a large vary of purposes (Crini et al. 2019). Characteristics of a desirable adsorbent;

a) The adsorbent ought to be on hand locally.

b) The price of the adsorbent have to be economic

c) The substances need to now not provide any different facet effect.

d) The technique of operation should be easy

e) The substances have to be effectively suitable via the users (Raouf MS and Raheim ARM 2016).

Table 3: Advantages and Disadvantages of Adsorbents.

| **Adsorbent** | **Advantages** | **Disadvantages** |
|---|---|---|
| Activated carbon | High surface area | High cost |
| Bio-sorbents | High adsorption capacity | High market cost |
| Agricultural and industrial by-products | Available in abundance | Sorption properties depend on origin |
| Bentonite | High surface area, high cation exchange capacity and low cost. | Needs modification for adsorption of anions. |
| Zeolite | High ion exchange capacity and surface area. | Complex sorption mechanism |

### 2.4.3 Adsorbent Surface Modification Method

Surface amendment of low- cost adsorbent is diagnosed an eye-catching method for enhancement of pollutant removal. Modification can be performed through adsorbing overseas natural compound on the surfaces of carbons. There are two techniques accessible to alter adsorbent such as physical and chemical modification.

i. ***Physical Modification Method***

Surface area and the pore volume of the adsorbent may be enhanced by physical modification; the most common method of physical modification is heating treatment, in which the low-cost adsorbent is treated in an inert atmosphere at high temperature. The significant disadvantage of this method is the decomposition of surface oxygen base functional groups, which are thermally unstable (Takele 2018)

ii. ***Chemical Modification Method***

Surface modification of the surface of the low-cost adsorbent is possible through reaction with an acid and base. Based on this fact the method divides in to major categories such acid surface modification and base surface modification. Chemical modification using base and acid in this method the preparation of activated carbon, the lingo cellulosic precursor and of the low-cost adsorbents are treated primarily with a chemical agent, such as NaOH, KOH or $ZnCl_2$, $H_3PO_4$, $H_2SO_4$ and $HNO_3$ by impregnation or physical mixture and the resulting precursor is carbonized at temperatures between 400 and 800°C under a controlled atmosphere. (Takele 2018).

## 2.5 Mango and Avocado Seed Waste in Ethiopia

Ethiopia's wide range of agro climatic conditions and soil types make it suitable for the production fruits, bananas, avocados, citrus fruits, mangoes, mandarin, papayas, guava, grapes, asparagus etc., are produced in Ethiopia. Around 47 thousand hectare of land is under fruit production in Ethiopia. Mango that contributed about 12.61 % and avocado 17.26% of fruit areas (Gultie and Sahile 2013) (Etefa, Forsido, and Kebede 2022).

### 2.5.1 Mango Seed Waste

Mango (Mangifera indica) is a perennial crop of the household Anacardiaceous. It is grown virtually all over tropical and sub-tropical areas of the world (Rai et al. 2020). Mango is the 2nd most vital fruit crop subsequent to banana in Ethiopia. It included about 19,497.92 hectares (ha) of 119,908.57 ha whole blanketed location with the aid of fruit which is 16.21%. A complete of 1,337,049.26 quintals of mango used to be produced in the 2018/19 manufacturing season with a productiveness stage of 68.57 quintals per ha (Tarekegn and Kelem 2022). According to the records got from the MoTI, Food institute file of 2008 EC, there are about 12 energetic medium and large-scale fruits processing corporations working in Ethiopia. Most of these corporations use mango fruit as uncooked cloth though, Ethiopian has a lot of fruits types, the fruits processing corporations in most cases use mango as uncooked cloth for in addition processing. From sixteen groups working mango fruit as uncooked substances are 7 stare fruits industry, 3D juice factory, Amine juice manufacturing facility and Sadura juice enterprise (Abdi 2019). PETRAM Maaza Mango Juice PLC hooked up 2014, The Company's mango juice processing plant is placed in Sebeta Town, and the manufacturing capability of this plant is 4,000 bottles/hour (International and Forum 2016). Around 20 percent of mango are processed for merchandise such as puree, nectar, leather, canned slice and chutney, juices, fruit bars, and pies. The mango seed represents about 20 percent of the complete weight of fruit, whilst the kernel is 45-85 percent of the seed (Ojha et al. 2019). After pulp extraction from fruit (meso carp part), peel and kernel are discarded as waste and turning into a supply of pollution ; they account for 35-60% of the fruit, relying on the variety (Puligundla et al. 2014),(Marcos et al. 2020). Actual figures on the extent of mango waste generated commercially are no longer simply available. Therefore, the utilization of mango by-products particularly mango seed may additionally be an in your price range way to minimize the hassle of waste disposal from mango manufacturing (Kittiphoom 2012). The current exercise has been contributed to the utilization on of the quite common, less expensive and thrown away waste mango seeds as adsorbent for the elimination of Pb from aqueous and synthetic solutions (Ji et al. 2002).

### 2.5.2 Avocado Seed Waste

Avocado (Persea Americana) is a tree, categorized in the Lauraceae family. The avocado tree is now cultivated in tropical and subtropical climates at some point of the world (Bhaumik et al. 2014). Avocado is a tropical crop with extra than 6 million tons produced annually. These days the crop is produced in countless international locations the place Ethiopia stands the tenth main producer and sixth most essential purchaser in the world (Faris 2016). In Ethiopia, currently, 84,793.7 tons of avocado was once produced on an estimated region of 19,758.75 ha of land with a productiveness of 4.2 tons/ha. And Oromia vicinity shares 34% place insurance and manufacturing contributing 34.6% in Ethiopia (Jalata 2021). Although lots of avocado manufacturing is fed on fresh, many avocado meals (drinks, guacamole, sauces, etc.) and beauty (shampoo, pores and skin creams, oils, etc.) merchandise are additionally accessible in the market. Avocado cultivation and processing generate massive portions of waste products, primarily peels and kernels, which signify between 18% and 13% of fruit sparkling weight. The avocado oil processing enterprise generates by-products like skin, rotten/over matured fruit, pulp and seeds.

These wastes are disposed to the surroundings as of no cost which creates environmental and social impact, therefore, coping with and utilization of these by-products are very vital to fight such issues (Tesfaye et al. 2022). Thus there is solely few agro-processing plant that underpin on avocado, and it has already ceased its undertaking of mixing avocado to produce pasta and macaroni. But some Cosmetic Industry has launched producing of hair pomade with the aid of the usage of avocado as uncooked material. Avocado processing is curiously restricted to juice making the place cafés, eating places and juice homes takes the leads in delicacies practice (Faris 2016). In 2019, Trading Organic has hooked up the enterprise Sunvado, avocado manufacturing facility processing excessive quality, and natural avocado oil. Guidelines on managing and revaluing the by-products from oil processing are being developed to amplify the sustainability of the agro- industrial park in Yirga Alem and Sunvado's manufacturing line (Challenge and Partnership 2019). The fruit of the avocado is notably bump off in the meals industry. However, its seed that represents the 10-13 % of the fruit can be viewed as an agricultural waste, which is discarded except similarly applications. Several choice makes use of have been proposed for this natural waste inclusive of its use as an adsorbent and as a precursor for the synthesis of carbon-based adsorbents for the elimination of precedence pollution from water (Pastore and Bitonto 2019).

### 2.6 Adsorption Isotherm Models

Sorption isotherm can be referred to as the system of the interplay of adsorbate ions on the adsorbent's surface. In the literature, quite a number isotherm equations exist, which can be used to analyses the applicable experimental parameters. However, one of the commonplace adsorption isotherm models, which is frequently employed for the single solute system, is the Langmuir (Langmuir, 1916) and Freundlich isotherm (Freundlich, 1906). These fashions are greater viable in explaining the affiliation between the extent of adsorbed material at equilibrium, q, in mg/g and the concentrations of the last adsorbate in the bulk solution at equilibrium, C, in mg/l (Jaafar and Alatabe 2021) (Abas et al. 2013).

#### *a. Langmuir isotherm model*

The assumption of the Langmuir isotherm is based totally on the reality that the attainment of equilibrium is executed when there is saturation of the adsorbent by means of the monolayer adsorbate substances. The Langmuir adsorption model is the most frequent model used to quantify the quantity of adsorbate on an adsorbent as a feature of partial stress or attention at a given temperature (Chen 2015).This equation expressed by means of relation linearized shape of the Isotherm is:

$$\frac{C_e}{Q_e} = 1 + \frac{1}{q_m KL} + \left(\frac{1}{q_m}\right) C_e \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

The Langmuir isotherm is shown thus:

$$Q_e = q_m \frac{KLC_e}{1 + KLC_e} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

Where, Qe is the volume of the adsorbed adsorbate per unit mass of the adsorbent (mg/g), Ce is the adsorbate equilibrium awareness (mg/l), KL is a consistent which is associated to the affinity current between the adsorbate and the adsorbent and qm is the saturation capability of the monolayer which is expressed theoretically. The Langmuir separation thing RL, which is a vital attribute component of this isotherm is calculated by way of the usage of the relation: (Ngakou, Ngomo, and Anagho 2018).

$$RL = \frac{1}{1 + CoKL} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

Where Co is the preliminary attention of lead, whilst KL and qm are the Langmuir consistent and the most adsorption capability respectively.

***b. Freundlich isotherm model***

The Freundlich equation or Freundlich adsorption isotherm is an adsorption isotherm, which a curve is pertaining to the attention of a solute on the surface of an adsorbent, to the attention of the solute in the liquid with which it is in contact. In 1909, Freundlich gave an empirical expression representing the isothermal version of Adsorption of an extent of gas adsorbed through unit mass of strong adsorbent with pressure. This equation is recognized as Freundlich Adsorption Isotherm or Freundlich Adsorption equation. This model is particular with equation

$$qe = K = KfCe^{1/n} \rightarrow \ln qe = \ln Kf + \frac{1}{n} \ln Ce \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4)$$

Kf and n in the equation are the regarded as the Freundlich constants, the place n offers the favorability of the adsorption approach and Kf is the adsorption capacity. Kf and n can be decided by using plotting ln qe versus ln Ce. In this equation, qe (mg/g) is quantity of absorbed material in absorbent surface, K, n in association are adsorption capability (Sreeremya 2017).

### 2.7 Adsorption Kinetics model

The best potential of grasp the experimental facts from batch kinetic find out about is to get a notion about stay lead concentration in liquid segment at equilibrium time. Even though there are numerous models such as heterogeneous diffusion model (also acknowledged as pore and diffusion model), pore diffusion model and homogeneous surface diffusion models are drastically used in batch adsorption, alternatively the mathematical complexity have constrained utilization for sensible purposes. At present, the applicability of pseudo-first-order model, pseudo-second-order model, Weber and Morris intra particle diffusion model, and Elovich's equation are most typically investigated in order to describe adsorption kinetics data. The adsorption of the lead from wastewater in this find out about used to be employed through the use of pseudo- first-order and pseudo-second-order kinetic models (Boontham and Babel 2018).

#### ***a. Pseudo-First Order Kinetic Model***

The first order kinetic models usually take the form;

$$\frac{dq_1}{dt} = k_1 \frac{dq_1}{dt} + (q_e - q_t) \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots..\dots\dots\dots\dots\dots\dots \quad (5)$$

Where qe and qt are the sorption capacities at equilibrium and at time t, respectively (mg/g) and k1 is the charge regular of first order charge adsorption, (1/min). After integration and making use of boundary conditions, qt = zero to qt = qt at t = zero to t = t. The built-in structure of equation (5) become

$$\frac{k_1 t}{2.303} log = log(qe - qt)\ 2 \dots\dots\dots\dots\dots\dots.\dots\dots\dots\dots.\dots\dots\dots\dots\dots\dots\dots (6)$$

#### ***b. Pseudo-Second Order Kinetic Model***

If the rate of sorption is a 2$^{nd}$ order mechanism the 2$^{nd}$ order kinetic rate equation is expressed as

$$\frac{dq_1}{\mathrm{dt}} = k_2(\mathrm{qe} - \mathrm{qt})2 \dots\dots\dots\dots\dots\dots\dots\dots\dots.\dots\dots\dots\dots\dots\dots\dots\dots.\dots\dots (7)$$

Where qe and qt are the sorption capacities (mg/g) at equilibrium and at time t, respectively and $k_2$ is the rate constant of pseudo-second order sorption, g/mg. min). For the boundary conditions, qt=0 to qt at t=0 to t. The built-in shape of Equation 7 gives:

$$\frac{1}{(\mathrm{qe}-\mathrm{qt})}=\frac{1}{\mathrm{qe}}+k_2\mathrm{t} \ldots\ldots\ldots\ldots\ldots (8)$$

Equation 8 can be rearranged to get:

$$\frac{\mathrm{t}}{\mathrm{qt}}=\frac{1}{k_2\mathrm{qe}^2}+\frac{1}{\mathrm{qe}}\mathrm{t} \ldots\ldots\ldots\ldots\ldots (9)$$

Where, t is the contact time (min), qe (mg/g) and qt (mg/g) is the quantity of the solute adsorbed at equilibrium and at any time, t respectively. Equation (9) does no longer have the hassle of assigning a positive qe. If pseudo-second order kinetics is applicable, the plot of t/qt in opposition to t of Equation (9) ought to supply a linear relationship, from which qe and k can be decided from the slope and intercept (Chen 2015)

# CHAPTER THREE

# 3. MATERIAL AND METHODS

## 3.1 Preparation and Characterization of Mango and Avocado seed wastes as an adsorbent for removal of $Pb^{2+}$.

### 3.1.1 Materials

In this lookup work, the fundamental uncooked substances used for the adsorbent are mango and avocado seeds. These seeds are sourced as a waste product from fruit processing industries or juice merchandising houses, which are effectively accessible in Ethiopia. Laboratory equipment's (plastic bags, plastic try, knife, sieves, beakers, erlenmeyer flasks, pipettes, measuring cylinder, volumetric flasks, filter paper, crucible, desiccators, etc.) and Laboratory Instruments analytical balance (model Adam AE 9XC954), muffle furnace (model BIOBASE JKKZ-4-10GJ), Drying Oven (model ALFA), grinding machine (modelPn-MFC9OD), pH meter(model Thermo-scientific), Scanning Electron Microscope (SEM) and Fourier Transform Infrared spectroscopy (FTIR).

### 3.1.2 Methods

#### 3.1.2.1 Preparation of Raw Sample (MAS) from Mango and Avocado Seed Waste

Mango and avocado seeds have been sourced from nearby fruit juice providers in Addis Ababa. The accumulated seeds have been cautiously washed to dispose of filth particles and impurities, first with faucet water. Then they had been reduce into small portions and washed by using DDI water earlier than sun-dried for one day to dispose of extra moisture, accompanied by means of drying in an oven at 105°C for 12hrs. Subsequently, the dried seeds have been overwhelmed and handed thru a 250-μm sieve to attain a fantastic powder. To make sure homogeneity, the mango and avocado seed powders have been combined 1:1 ratio thoroughly. The ensuing mixture, referred to as Mango and Avocado Seeds (MAS) powder, was once saved in hermetic plastic luggage for in addition experimental evaluation.

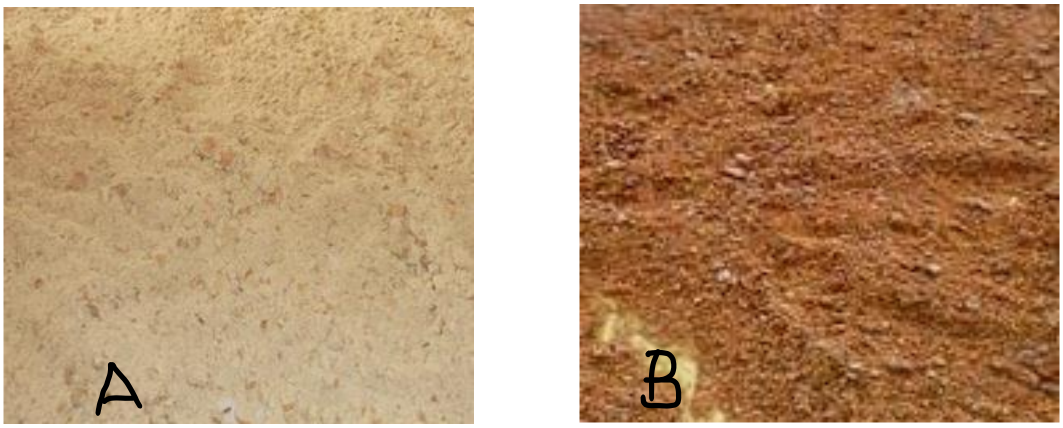



Figure 1: The Photograph image of (A) Powder of ground Mango seeds, (B) powder of Avocado seeds

### 3.1.2.2 Characterization of Raw Sample (MAS)

The proximate analysis (moisture, volatile matter, ash, and iodine number) shall be determined with American Standard Test Method Methods (ASTM).

***a. Moisture content:***

The moisture content material dedication observed the ASTM (D2867-70) method. For the determination of moisture content, a small quantity of MAS powder used to be weighed and spread evenly in a petri dish. The dish used to be then positioned in an oven at a temperature vary of 105-110°C for a period of 1.5 hours. Throughout the heating process, the petri dish remained uncovered. After heating, the petri dish was once eliminated from the oven and allowed to cool in a desiccator. Once totally cooled, the dried powder used to be weighed. The moisture content material used to be calculated the use of the applicable equation supplied by,

$$MC\% = \frac{(B - F) * 100}{(B - G)} \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (3.1)$$

Where, B is weight of Petri dish + authentic sample, F is weight of Petri dish + dried powder and G is weight of Petri dish.

***b. Ash content determination:***

The ash content material willpower observed the ASTM (E 1755-01) method. A 1g dry sample (C) was once positioned in a porcelain crucible and then transferred to a preheated muffle furnace set at a temperature of 600°C. The furnace was once left on for a period of 4 hours. Subsequently, the crucible containing the sample used to be transferred to a desiccator and allowed to cool. The weight loss discovered used to be recorded as the ash content material of the MAS sample. The share ash content material was once then calculated the usage of the equation supplied in,

$$\text{Ash Content\%} = \frac{(D - B) * 100}{(C - B)} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3.2)$$

Where, B is empty crucible weight, C is weight of MAS sample and D is MAS sample weight with the crucible after ash

***c. Volatile matter content:***

The volatile matter content of material dedication observed the ASTM (E 872-82) method. 2g of sample used to be taken in cylindrical crucible closed with a lid. It used to be then heated to 925˚c for precisely 7 minutes in a muffle furnace. Then the crucible used to be cooled in a desiccator and weighted by using the usage of digital stability which was once touchy to 0.0001gm. Volatile count number content material used to be decided from the equation,

$$\text{VM\%} = \frac{[(B - F) - M(B - G)] * 100}{[(B - G)(100 - M)]} \ldots\ldots\ldots.\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots. (3.3)$$

Where, B is Mass of crucible, lid and sample earlier than heating, F is Mass of crucible, lid and contents after heating, G is Mass of empty crucible & lid and M is % of moistures determined

***d. Iodine Number:***

The excellent of the completed adsorbent is measured through its capacity to adsorb a liquid (iodine). Iodine variety calculations which correspond to the quantity of milligrams iodine one gram of adsorbent can adsorb. Iodine wide variety is the most vital parameter used to symbolize adsorbent performance. It is the widespread measure for liquid segment applications. This was once carried out in accordance to the ASTMD (4607-94) method. The iodine wide variety is described as the milligrams of iodine adsorbed with the aid of 1.0g of MAS when the iodine attention of the filtrate is 0.02 N (0.02mol L-1). The iodine wide variety is the X/M calculated by using the Equations,

$$\frac{X}{M} = \frac{(N_I * 126.93 * V_I) - \left[\frac{V_I + V_{HCl}}{VF}\right]}{M_{MAS}} * \frac{(N_{Na2S2O3} * 126.93) * V_{Na2S2O3}}{M_{MAS}} \quad \ldots (3.4)$$

Where: NI is the iodine solution normality, VI is the delivered extent of iodine solution, VHCl is the brought volume of 5% HCl, VF is the filtrate volume used in titration, NNa2S2O3 is the sodium thiosulfate solution normality, VNa2S2O3 is the fed on volume of sodium thiosulfate solution and MMAS is the mass of Raw Sample (MAS).

**3.1.2.3 Preparation of Adsorbent (MASA) from Mango and Avocado Seeds (MAS) Powder**

The dried mango and avocado seed samples, bought from the preceding section, will bear a burning technique to produce ash. The pretreated MAS powder will be cautiously positioned in crucibles and subjected to a furnace at 600°C for a length of 4 hours. After the process, the ensuing ash will be washed the use of distilled water to take away soluble components, accompanied with the aid of oven drying. To make sure uniformity and put off massive particles, the ash will be surpassed via a sieve. Finally, the mango and avocado seed adsorbent (MASA) will be saved in hermetic plastic containers for similarly characterization, with storage maintained in a desiccator to preserve it’s fantastic.

***Yield***

The complete yield was once decided after sample processing in raw material mass through moist oxidation techniques and loss ignition. The yield of MASA is calculated as the share weight of the resultant Ash divided via the weight of dried MAS.

$$\text{Yield \%} = \left(\frac{WA}{WO}\right) * 100\% \ldots \ldots (3.5)$$

Where: WA is the dry weight (g) of final Ash and WO is the dry weight (g) of precursor before ashing.

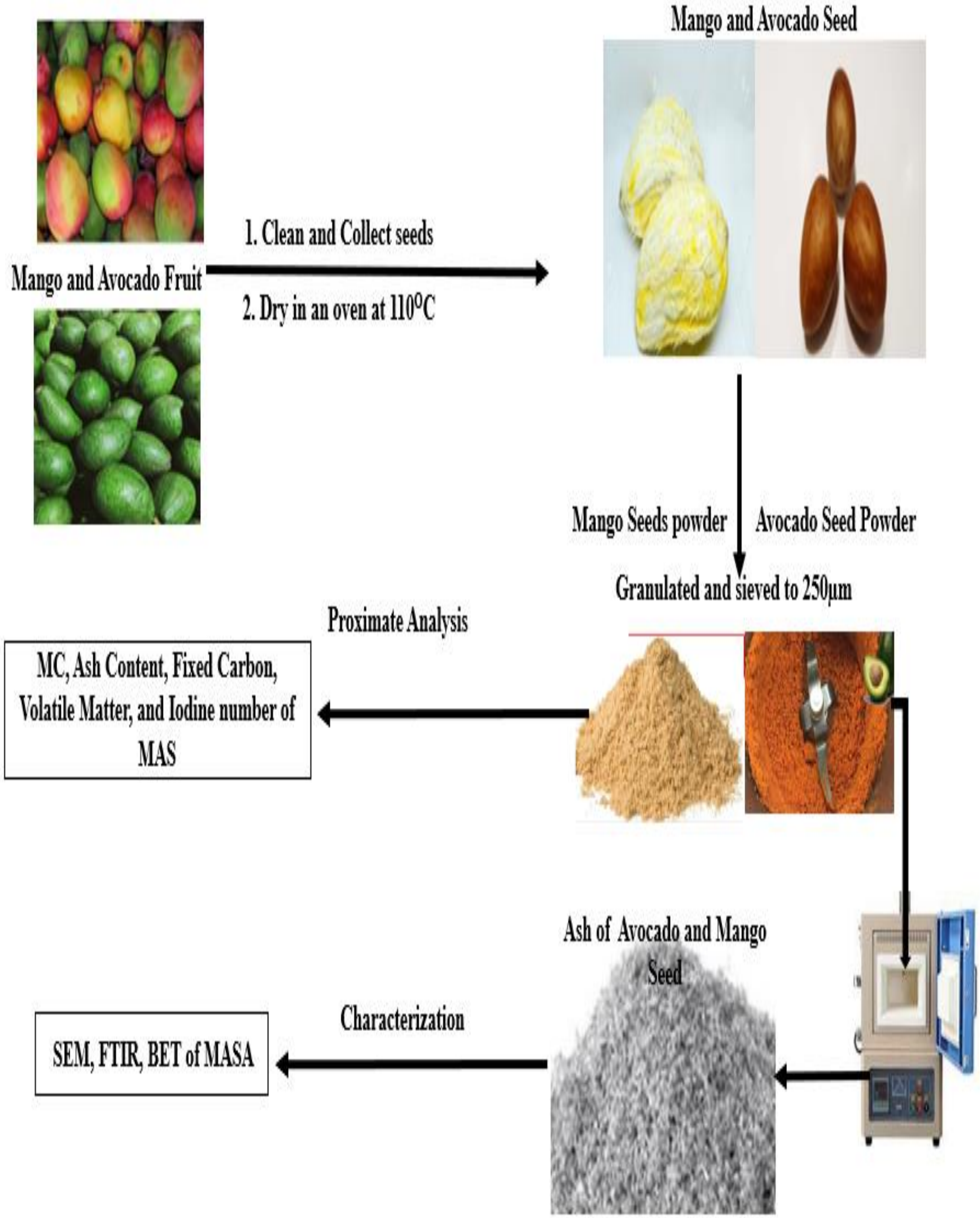



Figure 2: Preparation of MAS and MASA Adsorbent from raw fruit waste materials

#### 3.1.2.4 Physicochemical Characterization of Adsorbent MASA

The physicochemical characteristics of adsorbent will look at the use of the following techniques: The surface area, pores size and pores volume used to be measured thru the Brunauer, S., Emmett, P., Teller,E. (BET) equation model (Nova Station C ©1994-2010, Quanta chrome, model 11.0) BiT (Bahir Dar Institute of Technology, Ethiopia). The physical properties of adsorbents, as nicely as their elemental composition, have been measured with a Scanning Electron Microscope (SEM) (ASTU, Adama Science and Technology University, Ethiopia). The surface functional group that extensively make a contribution in the stronger adsorption effectivity of the adsorbent will investigated over 400–4000cm−1 ranges the usage of FTIR (Fourier Transform Infrared spectroscopy) approach (Ojeme et al. 2019).

## 3.2 Characterization of untreated and treated Nefas Silk paint industry wastewater based on wastewater parameter.

### 3.2.1 Materials

***Equipment and Instrument***

Laboratory equipment's (beakers, erlenmeyer flasks, pipettes, measuring cylinder, volumetric flasks, filter paper, thermometer, etc.) and Laboratory Instruments, Drying Oven (model ALFA), pH meter (model Thermoscientific), fridge (model LIEBHERR), Incubator, Graphite furnace Atomic Absorption Spectrophotometer (GFAAS) model Analytikjena novAA400P.

***Chemicals/reagents***

These chemicals, listed in Table (4) below, had been of analytical reagent grade and have been procured from one of a kind chemical shops in Addis Ababa, Ethiopia. Using wonderful chemical substances ensures the accuracy and reliability of the experimental outcomes got at some stage in the lookup process. It is necessary to make certain that the chemical compounds used in the find out about are of analytical reagent grade to keep the high-quality and consistency of the experimental procedures. By the usage of standard-grade chemical compounds and adhering to the gorgeous protocols, researchers can make certain accuracy, reproducibility, and validity in their findings.

Table 3: Chemicals/reagents and their specification

| Reagent | Chemical Formula | FW ($gmol^{-1}$) | Purity (%) | Uses |
|---|---|---|---|---|
| Nitric acid | $HNO_3$ | 63.01 | 69.72% | Preserve the painting wastewater samples |
| Sodium hydroxide | NaOH | 40.0 | 99 | pH adjustment |
| Hydrochloric acid | HCl | 36.46 | 36 | |
| Lead nitrate | $Pb(NO_3)_2$ | 331.2 | 99.95 | Lead standards for Calibration of GFAAS |
| Distilled water | - | - | >5.0µS | Washing raw materials, preparation and dilution of solutions |

### 3.2.2 Methods

#### 3.2.2.1 Collection and Processing of Nefas Silk Paint Industry Effluent

The Effluent Sample accumulated from Nefas Silk Paint Industry close to Addis Ababa, Oromia Region Gelan city. From equalization tank. The accrued sample will be at once transported to the laboratory enable to settle the solids for 1h and evaluation inside 24h. The paint wastewater effluent samples have been gathered randomly in June, July and September, 2022 in the afternoon session from Nefas Silk paint manufacturing facility from equalization tank. The sampling approach used to be executed through gathering the wastewater the usage of composite sampling. Polythene bottles of 5L have been used to acquire the portray wastewater samples. The bottles totally cleaned with hydrochloric acids, washed with tape water to render free acids, washed with distill water twice, once more rinsed with the water sample to be amassed and stuffed up the bottle with the sample leaving solely a small air hole at the top. The sample bottles had been Stoppard. Each of the samples Wastewater was once accumulated at the output point of every of the one chosen site. Care was once taken now not to introduce blunders all through sampling and storage the place illness ensuing from improperly cleaned sampling gadgets and sample containers. Sampling Equipment's have been cleaned earlier than sampling and at the stop of sampling, sampling tools labeled referring to the Sampling factor and date of sampling. Distill water is used for rinsing. In waste water sampling; care was once made to minimize modifications in the chemistry of the samples. To maintain the natural chemistry of the samples, protection strategies such as pH control, refrigeration and defending from mild used to be performed. Loss of metals through absorption or precipitation in sample containers used to be prevented by using acidifying the sample suitable the use of concentrated HNO3 acid. The equipment's used to withdraw waste water sample from equalization tank have been selected to preserve physical or chemical ameliorations of the sample to a minimal and to maintain sample Integrity. Devices used for accumulating waste water samples each for physicochemical and metals evaluation have been made of plastic APHA (2017) approach (E.W. Rice, R.B. Baird 2017).

Sample Preservation is made by using including 1.5 ml of concentrated HNO3 per liter of sample as cited in environmental sampling and evaluation for metals. The whole samples container used to be as it should be labeled, recognized and wonderful from every different for similarly separation in the laboratory.

#### 3.2.2.2 Physicochemical Characterization of Nefas Silk Paint Industry Wastewater

Characterization of the physicochemical parameter learn about is very necessary to get genuine concept about the excellent of wastewater and we can evaluate consequences of distinct physicochemical parameter values with widespread values. The strategies and the strategies comply with for collection, preservation, evaluation and interpretation primarily based on America public association standard techniques for estimation of wastewater. The heavy metal Pb (II) and physicochemical characteristics (BOD5, COD, TSS, Turbidity, pH, and Temperature) of the effluent earlier than and after adsorption will be characterized the usage of the APHA (2017) technique (E.W. Rice, R.B. Baird 2017)(Ghadirian 2013) and performed at Ethiopian Construction Design & Supervision Works Corporation at Water Quality Laboratory (ECDSWCWQL).

i. ***pH****:* The pH of the wastewater sample was once decided via APHA 4500-H+ B technique via the usage of Thermoscentific pH-meter calibrated with buffer standard solution of pH 4, 7 and 9.2 used to be used to decided pH. The probe of the meter used to be dipped into beaker of 50ml effluent sample, and the pH mode known as up. The fee displayed used to be taken as the proper pH value.
ii. ***Turbidity:*** The Turbidity was once decided through the APHA 2130 B. method. Using a laboratory-model nephelometer, or calibrate the devices in accordance to manufacturer's guidelines with formalin primary standard or appropriate secondary standard. Run at least one popular in every instrument vary to be used. Make sure the nephelometer offers steady readings in all sensitivity tiers used. Gently agitate sample. Wait till air bubbles disappear and pour sample into cell. When possible, pour well-mixed sample into cell and immerse it in an ultrasonic tub for 1 to 2 s or practice vacuum degassing, inflicting whole bubble release. Read turbidity immediately from instrument display. Calibrate non-stop turbidity

video display units for low turbidities by way of finding out turbidity of the water flowing out of them.

iii. ***Total Suspended Solid (TSS):*** The Total Suspended Solid was once decided by way of the APHA 2540 D method. Porcelain crucible used to be dried in an oven at 1000c for 2hr to acquire an acknowledged steady weight W1. A 50ml quantity of the paint effluent sample used to be brought into the crucible and the crucible heated in an oven at 1000C till the effluent pattern vaporized. It used to be cooled in desiccators and reweighed to achieve W2. The Total Suspended Solid used to be calculated the usage of the equation:

$$\text{Total Suspended Solid (TSS)\%} = \frac{\text{W2} - \text{W1}}{50} * 100 \ldots\ldots\ldots\ldots\ldots (3.6)$$

iv. ***Chemical Oxygen Demand (COD):*** It is decided the usage of the APHA 5220 B method, Treatment of samples with COD of >50 mg O2/L: Blend sample if critical and pipet 50.00 mL into a 500-mL refluxing flask. For samples with a COD of >900 mg O2/L, use a smaller element diluted to 50.00 mL. Add 1 g HgSO4, a number of glass beads, and very slowly add 5.0 mL sulfuric acid reagent, with mixing to dissolve HgSO4. Cool whilst mixing to keep away from feasible loss of risky materials. Add 25.00 mL 0.04167M K2Cr2O7 solution and mix. Attach flask to condenser and flip on cooling water. Add final sulfuric acid reagent (70 mL) thru open give up of condenser. Continue swirling and mixing whilst including sulfuric acid reagent. Cover open give up of condenser with a small beaker to forestall overseas material from coming into refluxing combination and reflux for 2 h. Cool and wash down condenser with distilled water. Reflux condenser and dilute combination to about twice its extent with distilled water. Cool to room temperature and titrate extra K2Cr2O7 with ferrous ammonium sulfate, the usage of 0.10 to 0.15 mL (2 to 3 drops) ferroin indicator. Although the extent of ferroin indicator is no longer critical, use the identical extent for all titrations. Take as the cease factor of the titration the first sharp color alternate from blue-green to reddish brown that persists for 1 min or longer. The COD attention is then calculated based totally on the titration volume.

$$\text{Chemical Oxygen Demand (COD)} = \frac{(\text{A} - \text{B}) * \text{M} * \text{B} * 8000}{\text{mL sample}} \ldots (3.7)$$

where: A mL ferrous ammonium sulfate used for blank, B mL ferrous ammonium sulfate used for sample, M molarity of ferrous ammonium sulfate, and 8000 milli-equivalent weight of oxygen 1000mL/L.

**v.** ***Biological Oxygen Demand ($BOD_5$)*****:** It decided with the aid of the APHA 5210 B. Transfer preferred working extent of supply water to a suitably sized bottle (glass is preferred). Check to make sure that the dissolved oxygen awareness is at least 7.5 mg/L earlier than the usage of water for BOD tests. If not, add DO by means of shaking bottle or via aerating with organic-free filtered air. Add 1 mL every of phosphate buffer, MgSO4, CaCl2, and FeCl3 solution/L to organized supply water. Mix entirely and convey temperature to 20 ± 30C. Prepare dilution water right now earlier than use until dilution water blanks show that the water is suited after longer storage times. If the dilution water blanks exhibit a DO depletion increased than 0.20 mg/L, acquire a pleasant water with the aid of enhancing purification or use water from some other source. Do now not add oxidizing agents or expose dilution water to ultraviolet mild in tries to convey the dilution clean into range. Bring samples to 20 ± 30C earlier than making dilutions. Using the dilution water organized as in, the above make at least three dilutions of organized sample estimated to produce a residual DO of at least 1.0 mg/L and a DO uptake of at least two mg/L after a 5-d incubation. Add 5-4 mixture natural parts (5000) gorgeous quantities of seed suspension and nitrification inhibitor. Dilute to last degree with dilution water. Mix properly however keep away from entraining air. Siphon combined dilution into an appropriate range of BOD bottles, taking care no longer to let solids settle in the cylinder or flask for the duration of transfer. Determination of preliminary DO: Use the azide change of the iodometric technique (Section 4500-O.C) to decide preliminary DO on all sample dilutions, dilution water blanks, and, the place appropriate, seed controls. Replace any displaced contents with enough diluted sample or dilution water to fill the bottle, stopper all bottles tightly, and water seal earlier than opening incubation. After getting ready dilution, measure preliminary DO inside 30 min. Prepare a more bottle for preliminary DO willpower for every sample dilution. Incubate at 200C ± 10C the stoppered and sealed BOD bottles containing favored dilutions, seed controls, dilution water blanks, and glucose-glutamic acid checks. Exclude mild to keep away from boom of algae in the bottles all through incubation. Determination of remaining DO: After 5 d ± 6 h of incubation, decide DO in all sample dilutions, and in all blanks and tests as the azide change of the titrimetric method.

Calculations:

1) For every take a look at bottle having 2.0 mg/L minimum DO depletion and at least 1.0 mg/L residual DO, calculate BOD as follows:

$$BOD5, \frac{mg}{L} = \frac{(D1 - D2) - (S)Vs}{P} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3.8)$$

Where: D1= DO of diluted sample immediately after preparation, mg/L,

D2= DO of diluted sample after 5 d incubation at 20°C, mg/L,

S = oxygen uptake of seed, Δ DO/mL seed suspension added per bottle (S= 0 if samples are not seeded),

Vs= volume of seed in the respective test bottle, mL, and

P= decimal volumetric fraction of sample used; 1/P dilution factor.

2) If DO depletion is much less than two mg/L and sample attention is a hundred percent (no dilution without for seed, nutrient, mineral, and buffer solutions), true seed-corrected, DO depletion may additionally be said as the BOD even if it is much <2.0 mg/L.

3) When all dilutions end result in a residual DO < 1.0, pick out the bottle having the lowest DO attention (greatest dilution) and report:

$$BOD5, \frac{mg}{L} > \frac{(D1 - D2) - (S)Vs}{P} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3.9)$$

In the above calculations, do no longer make corrections for DO uptake by way of the dilution water clean at some point of incubation. This correction is useless if dilution water meets the clean criteria stipulated. If the dilution water does no longer meet these criteria, ideal corrections are difficult; do now not file consequences or, as a minimum, mark them as now not meet quality control criteria.

**vi. *Lead metal ion determination :*** It determined by the APHA 3113 B

It determined by the APHA 3113 B. Concentration of heavy metals such as (Pb) was once decided the usage of Graphite Atomic Absorption Spectrophotometer (GFAAS). All instrumental measurements have been carried out the usage of the respective hallow cathode lamp of target metal at 283.3nm wavelength, Silt width 1.2nm, Current 2mA and different working stipulations (Berihun and Solomon 2017).

## 3.3 Evaluation of efficiency and performance of adsorbent for removal of lead metal ion from Nefas Silk paint industry wastewater.

### 3.3.1 Materials

***Equipment and Instrument***

Laboratory equipment’s (beakers, erlenmeyer flasks, pipettes, measuring cylinder, volumetric flasks, filter paper (whatman No.1), thermometer, stoppered reagent bottles, mechanical shaker, etc.) and Laboratory Instruments, pH meter(model Thermo-scientific), Graphite furnace Atomic Absorption Spectrophotometer (GFAAS) model Analytikjena novAA400P.These chemicals, listed in Table (4) above, have been of analytical reagent grade and had been procured from specific chemical shops in Addis Ababa, Ethiopia. Using wonderful chemical compounds ensures the accuracy and reliability of the experimental consequences received for the duration of the lookup process. It is vital to make certain that the chemical compounds used in the study about are of analytical reagent grade to hold the pleasant and consistency of the experimental procedures. By the use of standard-grade chemical substances and adhering to the excellent protocols, researchers can make sure accuracy, reproducibility, and validity in their findings.

### 3.3.2 Methods

#### 3.3.2.1 Adsorption Experiments

Batch adsorption experiments would be carried out in a collection of stoppered plastic shaking bottles (250 ml) on a mechanical shaker at 150 rpm, a hundred ml of wastewater containing recognized awareness of Pb ion at room temperature (25+/- 10C) and weighed quantity (0.5-2 g) of adsorbent and the wastewater pH (2-9) will be adjusted to the favored value by means of including 0.1M HCl or 0.1M NaOH for a prescribed time (30-120 min.) to acquire the equilibrium. The options have been filtered via the usage of whatman No.1 filter paper and the concentrations of Pb ion had been decided by means of GFAAS (model Analytikjena novAA400P) method. The results contact time (30–120 min), solution pH (2–9), and adsorbent dose (0.5–2g) will be studied. Blank options (distilled water) will be dealt with in a similar fashion (without wastewater sample) and the recorded attention with the aid of the stop of every operation was once taken as the preliminary one.

Percentage removal of lead from wastewater used to be computed the usage of the following equation:

$$\% \text{ Removal} = \frac{((\text{Ci} - \text{Cf}))}{\text{Ci}} * 100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots. (3.10)$$

Where, Ci is initial Lead concentration (mg L-1) and Cf is equilibrium Lead concentration (mgL-1). This shows the amount of Lead adsorbed by the MASA from the wastewater. The lead removal capacity of the adsorbent was computed using the following equation:

$$\text{q} = \frac{((\text{Ci} - \text{Cf}) * \text{V})}{\text{m}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots. (3.11)$$

Where, Ci = initial lead concentration (mg L-1) and Cf = equilibrium lead concentration (mg L-1), V = volume of lead solution (L), and m = weight of MASA (adsorbent) in grams (g). This shows the amount of lead adsorbed per gram of the MASA.

### 3.4 Optimization of removal efficiency, pH, Contact time and adsorbent dosage for the removal of Pb (II) from Nefas Silk paint industry wastewater by Mango and Avocado Seed adsorbent.

#### 3.4.1 Methods

##### 3.4.1.1 Experimental Design and Optimization

In this study, observe experimental layout based on the value-added product for wastewater treatment, Response Surface Methodology (RSM) was once used to enhance a mathematical model to find out about the influences of the response's primary operative parameters. The study about found the results of the major operative parameters on the adsorption of lead the use of MASA adsorbent. In this regard, the procedure will model and optimized by way of thinking about three parameters: contact time, pH, and adsorbent dose, every measured at three tiers the use of a central composite Design (CCD). CCD is recognized as one of the principal graph strategies in RSM. This mathematical model will used to construct a second-order model (quadratic model), and is traditional for technique optimization. Design Expert® software program model 13.0.5.0 (Stat –Ease, Inc.) will used to assemble the mathematical model. A quadratic polynomial model Equation (3.12) was once used to correlate the response and independent variables (operational factors).

$$Y = \beta_0 + \sum_{i=1}^{K}(\beta_0 X_i) + \sum_{i=1}^{K}(\beta_{ii} X_i^2) + \sum_{i=1}^{K-1}\sum_{i=1}^{K}(\beta_{ij} X_i X_j) + \varepsilon \ldots\ldots (3.12)$$

Where Y is the predicted response model (Pb2+ removal percentage), βo is the constant Coefficient, βi is the coefficient of the linear term, βii is the interactive coefficient, βij is the coefficient of the quadratic term, k is the number of experimental factors, Xi and Xj are the coded values of the experimental factors and ε is an error associated with the model:

CCD requires three types of trials, i.e., 2k factorial trials, 2k axial trials and nc center point trials, where k is number of factors studied in the experiment. Where each point defines a unique set of values of experimental trials for the three factors (k = 3) tested in an experiment. The ranges and levels of the experimental parameters are shown in Table (5). The total number of experiments are determined using the following equation: Based on CCD options on Design

Expert® software version 13.0.5.0 (Stat –Ease, Inc.) by Face Centered Central Composite Design (FCCCD).

$$N = 2k + 2k + nc \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots (3.13)$$

Where, k is the number of independent variables, and nc is the number of repetitions of experiments at the center point. In this study, the values of N, k, and nc were 20, 3 and 6, respectively.

Table 4: Selected experimental factors with study levels according to Face-centered Central Composite Design (FCCD)

| **Factors** | **Variables** | **Unit** | **Levels** | | | |
|---|---|---|---|---|---|---|
| | | | **Low** | **High** | **-alpha** | **+alpha** |
| A | MASA dose | gm | 0.5 | 2 | 0.5 | 2 |
| B | Contact time | min | 30 | 120 | 30 | 120 |
| C | pH | _ | 2 | 9 | 2 | 9 |

Analysis of variance checked the model accuracy and the enter parameters' outcomes on the response variable thru a statistical contrast of the P-value and F-value of the regression coefficient at a 95% confidence interval. The coefficient of determination (R2), the adjusted coefficient of determination (R2adj), adequate precision (AP), and the coefficient variation (CV) had been used to examine the fitness quality of the developed model. Three-dimensional response surface plots displayed the interplay between impartial elements and their respective impact on the response variable.

## 3.5 Determination of adsorption models of the adsorbent by different isotherm and kinetic models.

### 3.5.1 Methods

#### 3.5.2.1 Adsorption Isotherms and Kinetics Models

***A. Adsorption Isotherm Models***

The equilibrium relationship between adsorbent and adsorbate are described by means of adsorption isotherm, generally the ratio between the extent adsorbed and that closing in solution at a constant temperature at equilibrium (Mbadcam et al. 2011). In this paper, the Langmuir Isotherm and the Freundlich Isotherm have been investigated.

**The Langmuir isotherm theory** assumes monolayer adsorbent distribution over a homogeneous adsorbent surface. The Langmuir isotherm is introduced in the following equation:

$$\frac{C_e}{Q_e} = \frac{C_e}{q_m} + \left(\frac{1}{KLqm}\right) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3.14)$$

Where qm is the most quantity of metal ion adsorbed capacity (mg/g), Qe is the quantity of metal ion per unit mass of adsorbent at equilibrium (mg/g), KL is a constant related to the binding energy of adsorption, and the other constants can be estimated by plotting Ce versus Qe. A plot of Ce vs. Ce/Qe should be linear, if the data are described by the Langmuir isotherm. The value of qm is determined from the slope and the intercept of the plot. It is used to derive the maximum adsorption capacity and KL is determined from the original equation and it represents the intensity of adsorption.

The Langmuir separation factor RL, which is an essential characteristic factor of this isotherm is calculated by using the relation:

$$\mathrm{RL} = \frac{1}{1 + \mathrm{CoKL}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3.15)$$

Where Co is the initial concentration of lead, while KL and qm are the Langmuir constant and the maximum adsorption capacity respectively

**The Freundlich isotherm** is based on multilayer adsorption on the heterogeneous surface of the adsorbent containing an unequal number of energies. It is not limited to a monolayer adsorption, but also it is applied for multilayer adsorption. The Freundlich isotherm is an empirical equation describing heterogeneous surface adsorption. The Freundlich isotherm is commonly presented as shown in the following equation:

$$\mathrm{qe} = \mathrm{Kf}\,\mathrm{Ce}^{1/n} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3.16)$$

Where kf is the Freundlich constant related to adsorption capacity (mg/g) and n is the Freundlich exponent (dimensionless). By taking the logarithmic function of equation (3.16), it is simplified to the following equation:

$$log\ qe = log\ Kf + \frac{1}{n} log\ Ce \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3.17)$$

Where Qe is the amount of Pb+2 ions adsorbed per unit weight of adsorbents (mg/g), Ce is the equilibrium concentration in solution (mg/l), and Kf and 1/n are the Freundlich constants. Kf and n are the indicators of the adsorption capacity and adsorption intensity, respectively. The ability of Freundlich model to fit the experimental data was examined. For this case, the plot of log (Ce) Vs log (qe) was employed to generate the intercept and the slope values to determine Kf and n respectively.

***B. Adsorption Kinetic Models***

The kinetics of sorption describes the solute uptake rate, which in flip governs the residence time of sorption reaction. It is one of the essential traits in defining the effectivity of sorption. In order to inspect the controlling mechanism of adsorption procedures such as mass transfer and chemical reaction, the pseudo-first-order and pseudo-second order equations had been utilized to mannequin the kinetics of Lead adsorption onto Mango and avocado seed adsorbent.

**Pseudo-first-order kinetics model** is also known as Largergren model, proposed in 1898 (Mbadcam et al. 2011). Linear equation of pseudo-first-order kinetics is as follows:

$$\text{Log}\ (\text{qe} - \text{qt}) = \text{Log}\ \text{qe} - \left(\frac{k_1}{2.303}\right)\text{t} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3.18)$$

Where qe (mg g-1) is adsorption capacity at equilibrium, qt (mg g-1) is the adsorption capacity at time t, and K1 (min-1) is the rate constant of pseudo first order. The values of log (qe – qt) have been linearly correlated with t. The plot of log (qe – qt) versus t have to provide a linear relationship from which k1 and qe can be decided from the slop and intercept of the plot, respectively.

**Pseudo-second order kinetic** assumes that chemisorption control the adsorption rate (Abas et al. 2013).Linear equation of pseudo-second-order kinetics is as follows:

$$\frac{\text{t}}{\text{qt}} = \frac{1}{k_2\text{qe}^2} + \left(\frac{1}{\text{qe}}\right)\text{t} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3.19)$$

This equation is applied to obtain K2 (g.mg-1min-1), the second-order rate from the plots t vs. t/qt. If pseudo-second order kinetics is applicable, the plot of t/qt against t of Equation (3.19) should give a linear relationship, from which qe and k can be determined from the slope and intercept.

# CHAPTER FOUR

# 4. RESULT AND DISCUSSION

The following chapter offers end result of laboratory evaluation made for uncooked MAS and adsorbent MASA characterization, paint waste water characterization earlier than and after treatment; learn about of outcomes of parameters such as pH, dose of MASA and contact time on Lead ion elimination capability of MASA from Nefas Silk Paint Factory waste water and findings of different scientific information generated from this study. The paint waste water loaded with lead metal is then treated with MASA and the overall performance of the MASA is measured with the aid of various the parameters to optimize these elements which have an effect on the overall performance of MASA for particular metal ion.

## 4.1 Preparation and Characterization of Mango and Avocado seed wastes as an adsorbent for removal of lead metal ion.

### 4.1.1 Adsorbent Characteristics

#### 4.1.1.1 Proximate Analysis of Raw Adsorbent MAS

The Proximate Analysis of MAS have been decided by means of general technique and introduced in the Table (6) under and Comparison of comparative inexpensive adsorbent and Commercial AC. Iodine range is an integral parameter used to symbolize adsorbent performance. It is a measure of the micro pore content material of the adsorbent and is got with the aid of the adsorption of iodine from a solution through the adsorbent sample. The end result confirmed that the organized uncooked adsorbent has very excessive Iodine variety 10.34%, associated to the end result acquired from Commercial AC (Bello, Adegoke, and Akinyunni 2017), Banana Stalks Activated Carbon (Ogunleye et al. 2014), Activated fluted pumpkin seed shells (Chime, Onyema, and Ejikeme 2016) and Wood Apple Fruit Shell (Ashtaputrey and Ashtaputrey 2020). Iodine adsorption is an easy and rapid method to decide the adsorptive ability of MASA, additionally regarded as iodine variety frequently mentioned in mg/g (typical vary 600 mg/g to 1100 mg/g). It has been hooked up that the iodine quantity offers an estimate of the surface area in m2/g, and is associated to the porosity traits of the MASA. A decrease iodine wide variety can be ascribed to the presence of pores narrower than 1.0 nm. It have to be mentioned Wood Apple fruit shell activated carbons (WAAC300) confirmed the excessive cost of iodine quantity implying greater surface area. Thus, the MASA produced in this find out about are having greater effectivity for use in water treatment. Very low moisture content material (3.59%), Low moisture helps in combustion, whereas excessive moisture hampers ignition and reduces the combustion temperature. This adversely influences the response products of combustion and great of combustion. The release and combustion of volatiles are essential elements to be considered, Volatile depend is due to presence to natural compounds current in the uncooked cloth the excessive risky content material prevents whole combustion and the combustion is quickly and challenging to manage (Pathak, Mandavgane, and Kulkarni 2017). MASA has very low volatile matter (5.77%). The ash content material indicates the quantity of inorganic substituent existing in the adsorbent. Therefore, the organized uncooked adsorbent is environment friendly as it's proven with the aid of more than a few proximate evaluation parameters. The MASA, however, had decrease percent yield 7.13.

Table 5: Proximate Analysis of MAS, Comparison of comparative low-cost adsorbent and Commercial AC

| **Low-Cost adsorbent** | **Moisture Content (%)** | **Ash Content (%)** | **Volatile matter (%)** | **Iodine number mg/g)** | **Ref** |
|---|---|---|---|---|---|
| MASA | 3.59±0.0086 | 7.13± 0.1357 | 5.77± 0.0004 | 1034± 0.6371 | This Study |
| Activated Fluted Pumpkin Seed Shells | 6.60 | 2.0 | 28.0 | 411.40 | (Chime, Onyema, and Ejikeme 2016) |
| Banana Stalks | 2.79 | 5.12 | 12.48 | 6.73 | (Ogunleye et al. 2014) |
| Wood Apple Fruit Shell | 5.42 | 1.75 | 36.90 | 898.0 | (Ashtaputrey and Ashtaputrey 2020) |
| Canna Indica Seed Activated Carbon | 5.40 | 5.0 | 26.70 | 797.50 | (Tessema, Adugna, and Kamaraj 2020) |
| Commercial AC | 6.67 ± 0.07 | 7.10 ± 0.01 | 17.50 ± 0.03 | 200.36 ± 0.30 | (Bello, Adegoke, and Akinyunni 2017) |

Values are mean ± standard deviation of three replicates.

### 4.1.1.2 Physicochemical Characterization of Adsorbent MASA

***BET Surface Area and Pore Volume***

Table 6: The BET surface areas and pore characteristics of prepared adsorbent MASA.

| **Adsorbent** | **Correlation coefficient ($R^2$)** | **Sample mass (g)** | **C constant** | **Surface Area ($m^2/g$)** | **Pore Volume (cc/g)** | **Pore Diameter (nm)** |
|---|---|---|---|---|---|---|
| MASA | 0.994333 | 0.1 | 2.636 | 287.467 | 7.058e-02 | 2.648 |
| **Surface Area Data** | | | | | | |
| Multi Point BET | | | 2.875e+02 m²/g | | | |
| NLDFT cumulative surface area | | | 5.856e+01 m² /g | | | |
| **Pore Volume Data** | | | | | | |
| NLDFT method cumulative pore | | | 7.058e-02 cc/g | | | |
| **Pore Size Data** | | | | | | |
| NLDFT pore Radius (Mode) | | | 1.324e+01 Å=1.32nm | | | |

Results of BET evaluation in Table (7) above printed that the surface area, pore volume and pore diameter of MASA. Surface area and porosity are two extensive physical properties that have an impact on the quality of adsorbents. Surface area dimension may also be the most normally used skill to characterize porous materials. Since the surface area coincides to the roughness of the particle exterior and its porous internal. The surface area of the chosen adsorbent used to be very excessive 287.467 m2/g associated to the end result acquired from fruit peel waste (Pathak, Mandavgane, and Kulkarni 2017), bottom ash (Gorme et al. 2010) and Coal Fly Ash (Misran et al. 2019). The massive surface area of absorbent is one of the most essential elements in a bio-adsorbent study. According to the IUPAC classification, we can study that MASA have mesoporous (diameter 2-50nm) (Matthias Thommes*, Katsumi Kaneko, Alexander V. Neimark, James P. Olivier and Sing 2013). The BET Equation:-

$$\frac{1}{\mathrm{W}\left(\left(\frac{\mathrm{Po}}{\mathrm{P}}\right)-1\right)}=\frac{1}{\mathrm{WmC}}+\frac{\mathrm{C}-1}{\mathrm{WmC}}\left(\frac{\mathrm{P}}{\mathrm{Po}}\right) \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (4.1)$$

Where W = weight of gas adsorbed, P/P0 = relative pressure, Wm = weight of adsorbate as monolayer C, C = BET Constant

BET equation requires a linear plot of 1/ [W (P/P0)-1] against P/Po

Slope (s) $S = \frac{C-1}{WmC}$ , Intercept (i) $i = \frac{1}{WmC}$ , Wm (weight of monolayer) $Wm = \frac{1}{s+i}$

Relative error between single and multipoint BET, (typically measured at P/Po of 0.3) C=(s/i) +1

Total Surface area (St) can then be derived

$$S = \frac{Wm\ N\ Acs}{M} \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots . (4.2)$$

Where N = Avogadro's number ($6.023 \times 10^{23}$), M = Molecular weight of Adsorbate, Acs = Adsorbate cross sectional area ($16.2 Å^2$ for Nitrogen)

Table 7: BET Data

| Relative Pressure P/Po | Volume @ STP cc/g | 1 / [W ((Po/P) - 1)] |
|---|---|---|
| 5.31330e-02 | 8.8450 | 5.0761e+00 |
| 1.12975e-01 | 18.8455 | 5.4074e+00 |
| 1.73235e-01 | 28.8090 | 5.8194e+00 |
| 2.34635e-01 | 38.8813 | 6.3086e+00 |
| 2.97506e-01 | 48.9813 | 6.9179e+00 |

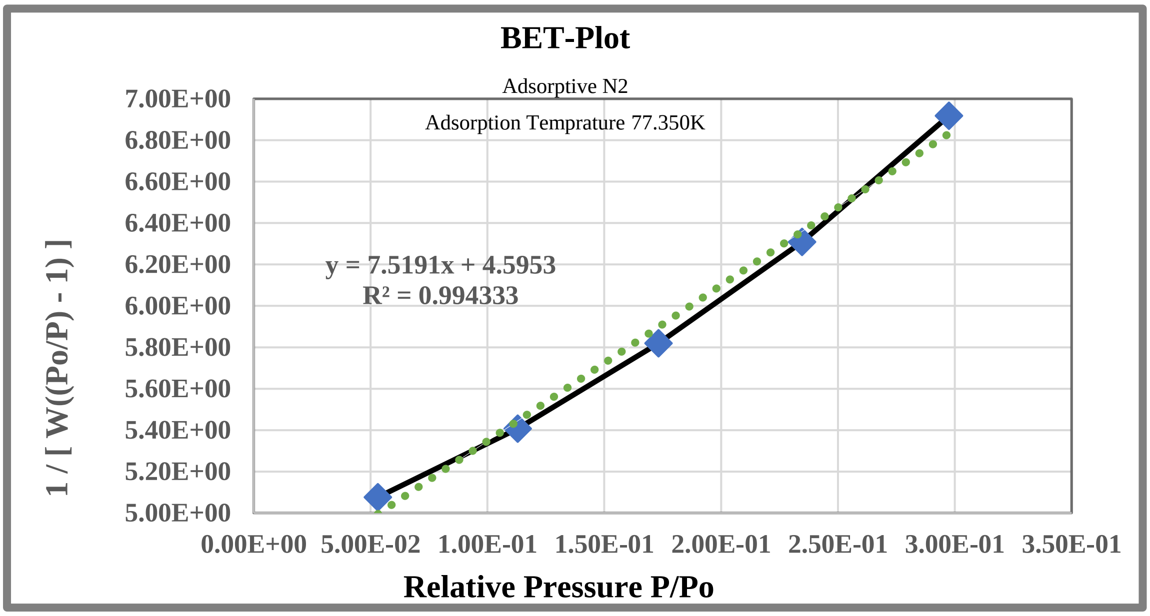



Figure 3: Multi point BET Plot

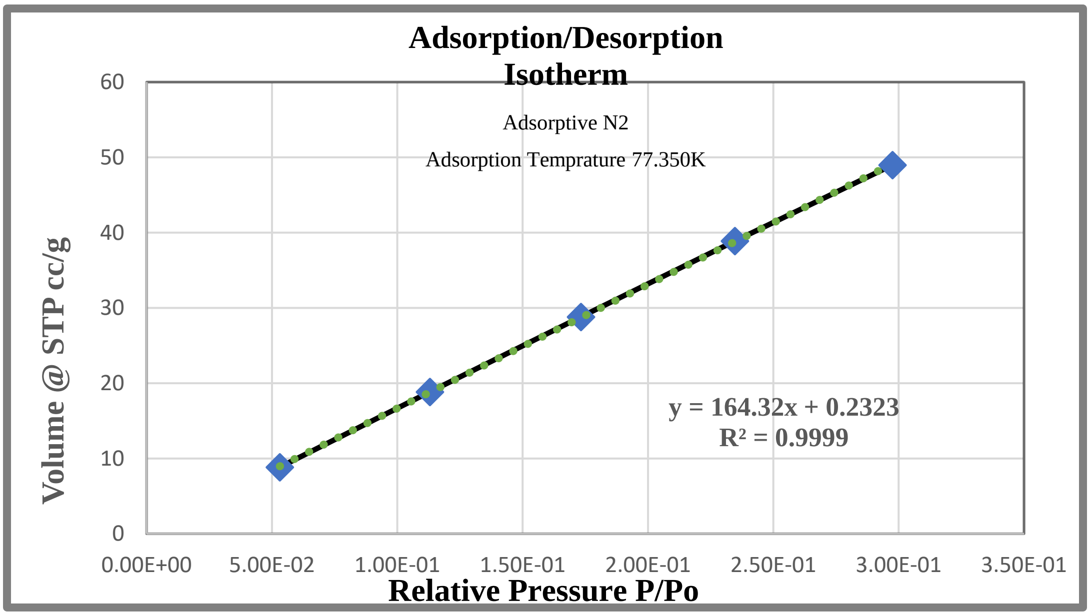



Figure 4: Adsorption/Desorption Isotherm graph

***Scanning Electron Microscope (SEM)***

Scanning Electron Microscope used to be employed to decide the surface characteristics of organized adsorbent earlier than and after ashing. The surface of adsorbent MASA can be described each exterior and indoors relying on their depth and width ratio. As considered in the SEM micrographs Figure (5), earlier than and after ashing suggests the SEM picture of the microstructures of the untreated and treated with adsorbent surface structures of each precursors had been hard and uneven. The surface of the untreated adsorbent earlier than ashing is indicates difficult mesoporous particles which turns into seen as many surface particles whilst the SEM photograph after ashing (treated) suggests that have a number of pores due to the modification. A substantial pore shape exists with a collection of hard cavities disbursed over the surface of MASA. This used to be due to the breakdown of the lingo cellulosic materials at excessive temperature accompanied by way of the evaporation of volatile compounds leaving samples with well-developed pores. During the treatment process, the adsorbent reaction rate used to be increased, therefore ensuing in carbon ‘burn off’, thereby creating excellent pores on the sample. Physical remedy produce vast exterior surface with irregular cavities and pores due to evaporation of volatile compounds, carbon in the structure of CO and CO2 throughout drying leaving empty areas (pores) for adsorption of material unto them (Bello, Adegoke, and Akinyunni 2017). The change in surface texture and pore development of adsorbents are needless to say distinct. The SEM pictures of organized adsorbent MASA seems rough and porous. The well-developed porous shape was once due to the fast volatilization of organic components in the biomass and this shape used to be advisable to the attachment of metal ions.

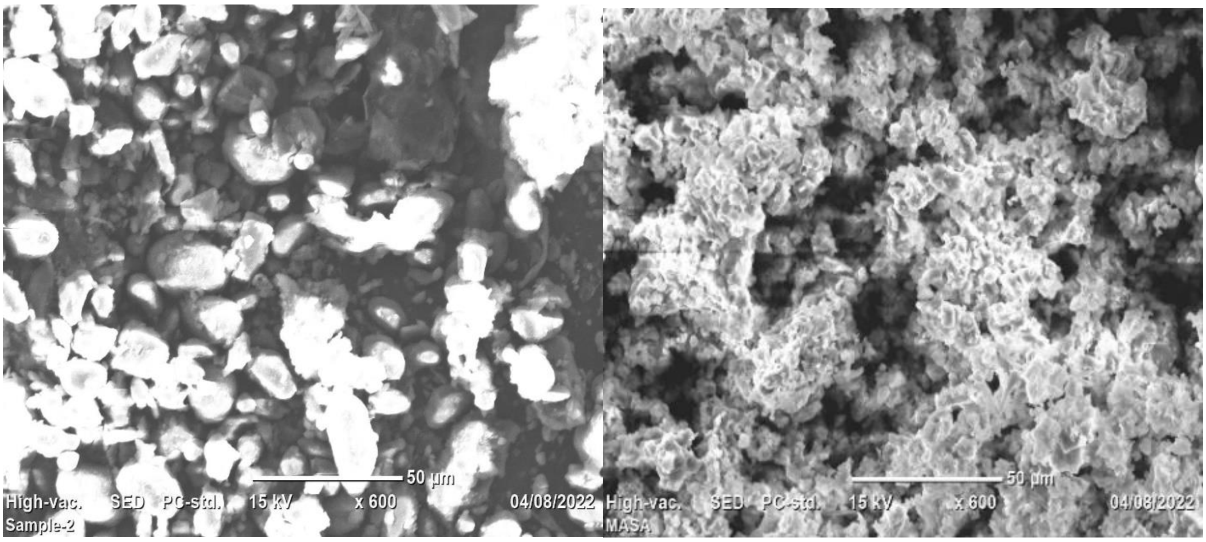



Figure 5: SEM images of MASA magnified to (600x) before and after Ashing.

***Fourier Transform Infrared Spectroscopy (FTIR)***

FTIR analysis used to be carried out for prepared adsorbents in order to decide the impact of the surface functional groups. The spectra of MASA bought from FTIR spectroscopy are introduced in Figure (6). The peaks contained single bond location (2500-4000 cm-1) no wide absorption band in the range of between 3650 and 3250 cm-1, indicating there is no hydrogen bond in the material. Peaks at between 3000 and 3200 cm-1, replying the aromatic ring. No aldehyde peak was once detected at between 2700 and 2800 cm-1. Regarding the triple bond region (2000- 2500 cm-1), no peak was once detected, informing no C≡C bonding. In the double bond region (1500-2000 cm-1), two peaks had been detected: at 1523.88 and 1660.70 cm-1, informing active carbonyl groups, in which this need to be from ring-carbonyl carbons. This informs some carbonyl double bond, which can be from ketones, aldehydes, esters, or carboxyl. Since there is no specific peak for aldehyde at between 2700 and 2800 cm-1 (as described in the preceding description), the prospective peak for carbonyl have to be from ketone. In the fingerprint region (600-1500 cm-1), strong signal used to be observed at about 1376.16 cm-1 (informing aromatic ring). Vinyl- associated compound used to be additionally determined at about 1042.64 cm-1. Based on the above analysis, the evaluation confirmed that the material has aromatic ring, and easy purposeful bonding (methyl) (Nandiyanto, Oktiani, and Ragadhita 2019). Namely C-H bending vibration with the intensity of medium absorption to strong which every so often has single or multiple of absorption bands found in the location between 850 and 670 cm-1. The top at 1042.64 cm−1 can be assigned to stretching vibration of C-OH of alcoholic groups and carboxylic acids and aliphatic acid group, vibration at 1230cm−1 to deformation vibration of C-O and stretching formation of –OH of carboxylic acids and phenols. The peaks at 1376.16cm−1 might also be assigned to symmetric stretching of –COO− of pectin whilst uneven and symmetric stretching vibrations of ionic carboxylic groups (–COO−), respectively, seemed at 1464.79, and 1660.70cm−1 (Nandiyanto, Oktiani, and Ragadhita 2019). It is in reality recognized the presence of carboxyl and hydroxyl group. Regarding the quantity of peaks, there are extra than 5 peaks, informing that the analyzed chemical. The spectrum displays ten express bands in the wave range vary of 4,000–500 cm-1 for the complete vary of observation. From these results, it can be concluded that these adsorbents, commonly incorporate presence of hydroxyl groups. According to the fundamental of acidic and basic character of adsorbent surface, the acidic conduct is related with oxygen-containing purposeful companies like hydroxyl and phenols (Boontham and Babel 2018). Based on above interpretation, quite a few conclusions can be obtained, together with the analyzed material has no hydrate component. This material has ketones-related component, no triple bond in the material. Since the peaks have been only about 10 peaks, the material have to be a small organic compound (Nandiyanto, Oktiani, and Ragadhita 2019). Oxygen surface groups are generally considered to be accountable for the adsorption of heavy metal ions. Therefore, some bands that corresponding to phenols consists of proteins and the inhibition of the bands related to the amino and hydroxyl corporations predicted to help the effectivity of $Pb^{2+}$adsorption.

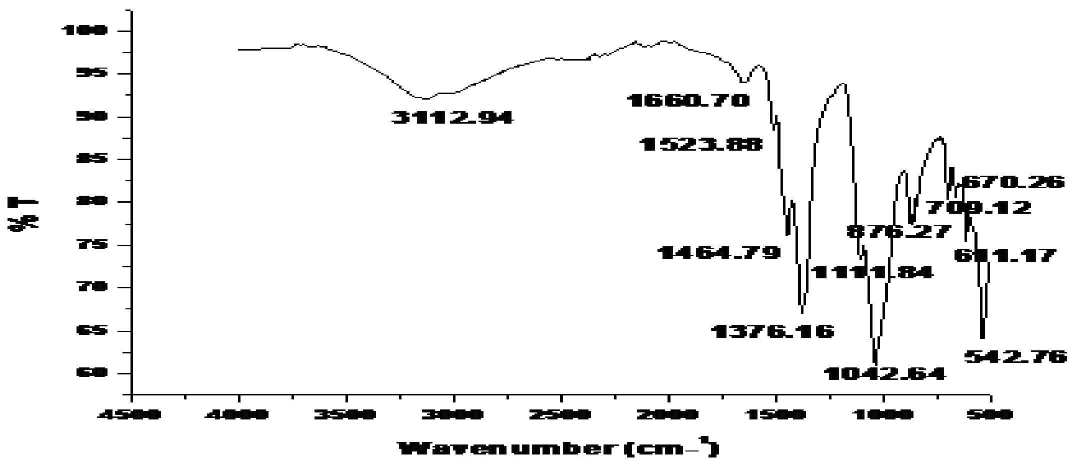



Figure 6: FT-IR spectra of MASA

### 4.2 Characterization of untreated and treated Nefas Silk paint industry wastewater based on wastewater parameter.

#### 4.2.1 Physicochemical Characteristic of Nefas Silk paint industry Wastewater

Discussion on paint waste water analyzed for lead ion. The evaluation made on samples taken from the equalization tank which is Latex (water-based paint) wastewater shows, in Table (9). The presence of lead ion, Total suspended solids, BOD, COD, Turbidity and pH earlier than and after treatment by using adsorbent MASA. Attention is given to heavy metal lead which seems to be in higher concentration in samples (1-3). In addition to exceeding the permissible restriction of heavy metal for wastewater sated with the aid of Ethiopian Environmental Standard, these heavy metal additionally show off unfavorable environmental and health hazards. As can be viewed from Table (9) a lead content varying from 0.0422 mg/L to 0.0639 mg/L used to be observed from three samples taken on the site. It may additionally reason outcomes on environment, human and animal existence via ecological meals chain. It has carcinogenic and mutagenic property which may additionally purpose to cancer, decreased intellectual and central anxious function. Lead is a poisonous metal that motives unfavorable results on each human health and the environment. While lead publicity is additionally detrimental to adults, lead publicity harms teenagers at lots decrease levels, and the health consequences are usually irreversible and can have a lifelong have an effect on (WHO, 2015). The youthful the child, the greater unsafe lead can be, and kids with dietary deficiencies take in ingested lead at an elevated rate. The human fetus is the most vulnerable, and a pregnant lady can switch lead that has amassed in her physique to her creating child. Lead is additionally transferred thru breast milk when lead is existing in a nursing mom (WHO, 2010). The different parameters such as BOD5, COD, TSS and turbidity had been above the restrict for effluent discharge, and these can also reason outcomes on aquatic existence due to limits mild penetration, Covers aquatic animals and plant and brings insoluble toxins into water bodies (Al-Rekabi, Qiang, and Qiang 2007). Treated Physicochemical evaluation of Nefas Silk paint manufacturing factory wastewater is the highest quality treatment value.

Table 8: Physicochemical Analysis of Nefas Silk paint factory wastewater before and after treated by adsorbent MASA.

| S. No. | Parameters | Unit | Untreated wastewater (S1) | Untreated wastewater (S2) | Untreated wastewater (S3) | Treated wastewater by MASA (S2) | WHO Standard (mg/L) |
|---|---|---|---|---|---|---|---|
| 1 | pH | _ | 7.74 | 6.95 | 6.12 | 6.0 | 6.0-8.5 |
| 2 | Temperature | $^0$C | 20.00 | 20.00 | 20.00 | 20.00 | _ |
| 3 | Turbidity | NTU | 3012.87 | 4520.41 | 645.67 | 1.12 | 5 |
| 4 | Lead (pb) | µg/L | 42.8 | 63.9 | 42.2 | 0.30 | 0.04 |
| 5 | Total Suspended Solids | mg/L | 1512.00 | 1262.00 | 568.00 | 40 | 30 |
| 6 | $BOD_5$ | mg/L | 13.00 | 51.00 | 570.00 | 36 | 15 |
| 7 | COD | mg/L | 5500.00 | 4394.72 | 920.00 | 147.60 | 40 |

#### 4.2.1.1 Instrument Calibration

Calibration curve Pb was obtained by using suitable standard solution prepared from stock solution. The quality of end result received for heavy metal evaluation the use of Graphite Furnace Atomic Absorption spectrometer (Model: Analytikjena novAA400P) at wavelength 283.3nm is seriously affected by the calibration and standard solution preparation procedures. Calibration standards for the element analyzed were prepared in concentration range expected for the analyses in the sample analyzed. In addition, the calibration requirements have been organized through taking into consideration the optimum working ranges of the element. The correlation coefficient ($R^2$) values that are nearer to the absolute value of one point out that there is a strong relationship between the variables being correlated whereas values nearer to zero point out that there is no linear relationship (Takele 2018). Can be considered in Figure (7) the correlation coefficient of metal was once determined to be 0.9992 which point out strong relationship. The correlation coefficient of the factor was once decided the usage of prepared standards versus their corresponding absorbance. The prepared standard concentration and the corresponding correlation coefficient of the calibration curve for the metal in the wastewater are proven in Figure (7). Also the concentration of the working concentration and the absorbance are introduced in Table (10) below.

Table 9: Calibration Points for each Standards of Pb

| | **Conc. Pb (µg/l )** | **Absorbance** |
|---|---|---|
| Blank | 0 | 0.00090 |
| Standard 1 | 10 | 0.03138 |
| Standard 2 | 30 | 0.11843 |
| Standard 3 | 50 | 0.20428 |
| Standard 4 | 100 | 0.42025 |

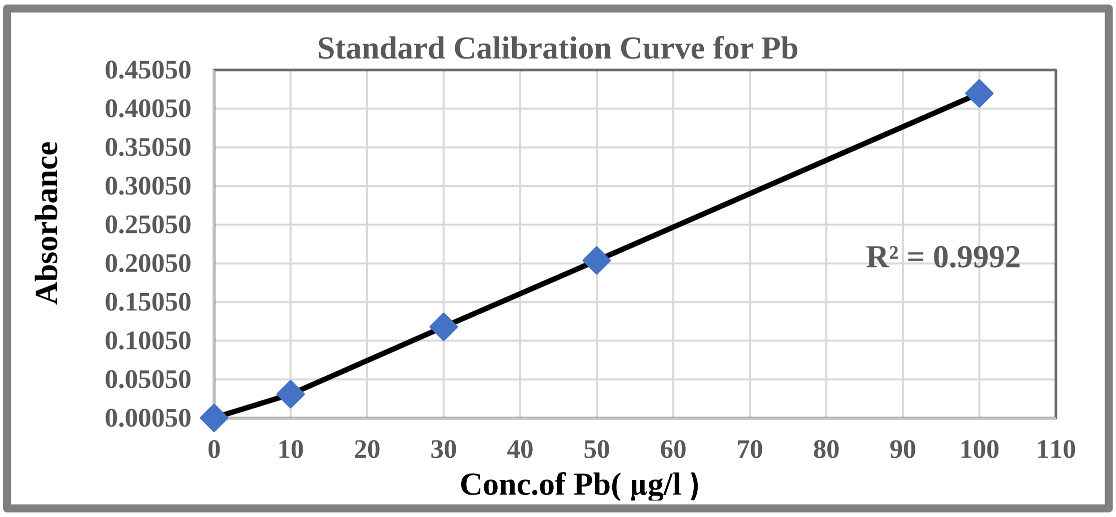



Figure 7: Standard Calibration Curve of Pb (II)

**4.3 Evaluation of efficiency and performance of adsorbent for removal of lead metal ion from Nefas Silk paint industry wastewater.**

**4.3.1 Batch Adsorption and Effect of Various Factors on the Adsorption of $Pb^{2+}$**

The idea of the optimum operating conditions would assist and indicate better design and modelling adsorption processes. Therefore, the results from batch studies to find optimum adsorbent dose, pH and contact time are described concisely under the following sections. The Pb removal efficiencies of MASA adsorbent used to be investigated based on the following equations. The percentage of lead (II) removal was obtained using Equation (3.10) while the adsorbent capacity q was calculated with Equation (3.11) cited in methodology section.

Table 10: Lead removal efficiency and removal capacity of the adsorbent MASA at different Factors and Levels after adsorption.

| Std | Run | Space Type | Factor 1 A: MASA Dose (gm) | Factor 2 B: Contact time (min) | Factor 3 C: pH | Response 1 Lead removal efficiency (%) | Lead removal Capacity of Adsorbent (mg/g), q |
|---|---|---|---|---|---|---|---|
| 1 | 13 | Factorial | 0.5 | 30 | 2 | 67.626 | 0.086 |
| 2 | 1 | Factorial | 2 | 30 | 2 | 74.664 | 0.024 |
| 3 | 8 | Factorial | 0.5 | 120 | 2 | 65.593 | 0.084 |
| 4 | 11 | Factorial | 2 | 120 | 2 | 75.759 | 0.024 |
| 5 | 4 | Factorial | 0.5 | 30 | 9 | 62.778 | 0.080 |
| 6 | 19 | Factorial | 2 | 30 | 9 | 64.967 | 0.021 |
| 7 | 7 | Factorial | 0.5 | 120 | 9 | 62.621 | 0.080 |
| 8 | 17 | Factorial | 2 | 120 | 9 | 70.128 | 0.022 |
| 9 | 14 | Axial | 0.5 | 75 | 5.5 | 82.640 | 0.106 |
| 10 | 16 | Axial | 2 | 75 | 5.5 | 98.613 | 0.032 |
| 11 | 3 | Axial | 1.25 | 30 | 5.5 | 97.498 | 0.050 |
| 12 | 10 | Axial | 1.25 | 120 | 5.5 | 99.531 | 0.051 |
| 13 | 5 | Axial | 1.25 | 75 | 2 | 84.204 | 0.050 |
| 14 | 15 | Axial | 1.25 | 75 | 9 | 75.446 | 0.039 |
| 15 | 18 | Center | 1.25 | 75 | 5.5 | 98.420 | 0.050 |
| 16 | 20 | Center | 1.25 | 75 | 5.5 | 98.431 | 0.050 |
| 17 | 6 | Center | 1.25 | 75 | 5.5 | 98.436 | 0.050 |
| 18 | 12 | Center | 1.25 | 75 | 5.5 | 98.439 | 0.050 |
| 19 | 2 | Center | 1.25 | 75 | 5.5 | 98.452 | 0.050 |
| 20 | 9 | Center | 1.25 | 75 | 5.5 | 98.438 | 0.050 |

#### 4.3.1.1 Effect of Contact Time on Adsorption Efficiency of Pb (II)

Contact time is an essential factor in the adsorption of Pb (II). The quantity of metal ion adsorbed at the contact time is a reflection of the most adsorption capability performed by way of the adsorbent under the working conditions (Ugwu et al. 2020). As illustrated in Table (12), the effect of contact time varied from 30 to 120min. Adsorption effectivity of MASA adsorbent used to be carried out below consistent experimental conditions along with pH (pH = 5.5), adsorbent dose (1.25 g/L), agitation speed (150 rpm) and initial concentration of adsorbate (0.064 mg/L).

Table 11: Effect of contact time on Pb2+ removal efficiency

| Contact time (min) | pH | Adsorbent dose (g/L) | Pb Adsorption % | q mg/g |
|---|---|---|---|---|
| 30 | 5.5 | 1.25 | 97.498 | 0.050 |
| 75 | 5.5 | 1.25 | 98.452 | 0.050 |
| 120 | 5.5 | 1.25 | 99.531 | 0.051 |

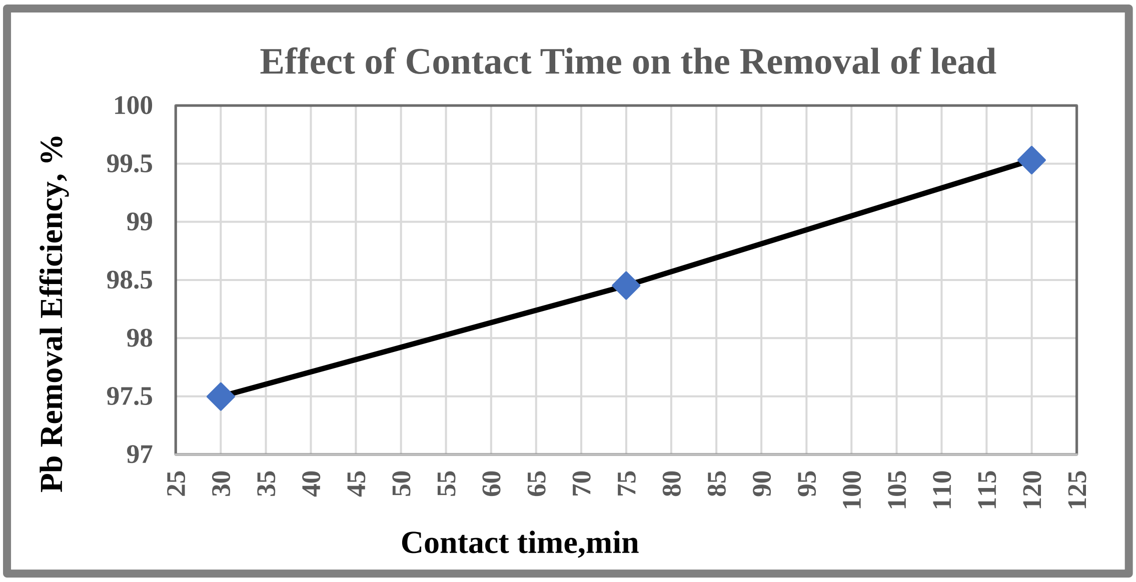



Figure 8: Effects of Contact time on the removal efficiency of Pb (II)

According to the effects in Table (12) & Figure (8), the adsorption percentage of Pb (II) elevated with expanded contact up to 120min. A comparable vogue used to be perceived with Pb2+ uptake in mg/g, which accelerated with contact time up to 120min. The majority (97.498%) of lead adsorption occurred within the first 30min, and was once attributed to the presence of lots of active sites on the adsorbent surface at the starting (Birhanu and Leta 2021). The optimum contact time for most adsorption of Pb (II) was once 120 min. Subsequently, there was once an insignificant lowering trend. As proven in Table (12) & Figure (8), the very best adsorption proportion and lead uptake in mg/g at 120 min was once 99.531% and 0.051mg/g, respectively.

#### 4.3.1.2 Effect of pH on Adsorption Efficiency of Pb (II)

The pH of the solution is a necessary controlling parameter in the adsorption of Pb2+. The adsorption capacity of Pb2+ was strongly affected by the variation of pH of the solution (Birhanu and Leta 2021). In this study, the impact of pH on Pb (II) adsorption efficiency was studied by varying pH levels from 2 to 9 with a one-unit interval. At pH values higher than 6, precipitation is dominant, or metal hydroxide formation turns into a significant mechanism in the metal removal system. This situation is not desirable as the metal precipitation may want to a misunderstanding of the adsorbent’s adsorption capacity. Because metal hydroxides are typically now not stabilized forms of heavy metal, precipitation can sometimes decompose upon the effluent’s neutralization from the wastewater treatment plant. As a result, the solubility of the metals will increase recontamination by metal ions (Birhanu and Leta 2021).

In this study, the impact of pH on Pb (II) adsorption efficiency was undertaken with a 75 min contact time, 1.25g/L of adsorbent dose, 0.064 mg/L of adsorbate concentration, and 150 rpm agitation speed. As observed in Table (13) & Figure (9), the adsorption percentage of Pb (II) with the aid of MASA adsorbent increased while the pH of the solution increased from 2 to 5.5. This incremental trend of adsorption capacity of Pb2+ with growing solution pH was used to be validated via preceding research. Therefore, in this experimental setup, pH 5.5 was the optimum solution pH that exhibited the most adsorption percentage of Pb2+. As revealed in Table (13) & Figure (9), at the optimum pH condition, the highest adsorption percentage and comparable uptake in mg/g of Pb2+ by MASA adsorbent was 98.452% and 0.050 mg/g, respectively. The lowest adsorption percentage and adsorbent uptake in mg/g had been bought at pH 9, which have been 75.446%, and 0.039 mg/g, respectively, and might also be due to the competitive influence of H+ ions. H+ ions compete with the metal ions for the active sites on the adsorbent, causing the reduction of adsorption of Pb (II) ions (Ugwu et al. 2020).

Table 12: Effect of pH on $Pb^{2+}$ removal efficiency

| pH | Contact time (min) | Adsorbent dose (g/L) | Pb Adsorption % | q mg/g |
|---|---|---|---|---|
| 2 | 75 | 1.25 | 84.204 | 0.050 |
| 5.5 | 75 | 1.25 | 98.452 | 0.050 |
| 9 | 75 | 1.25 | 75.446 | 0.039 |

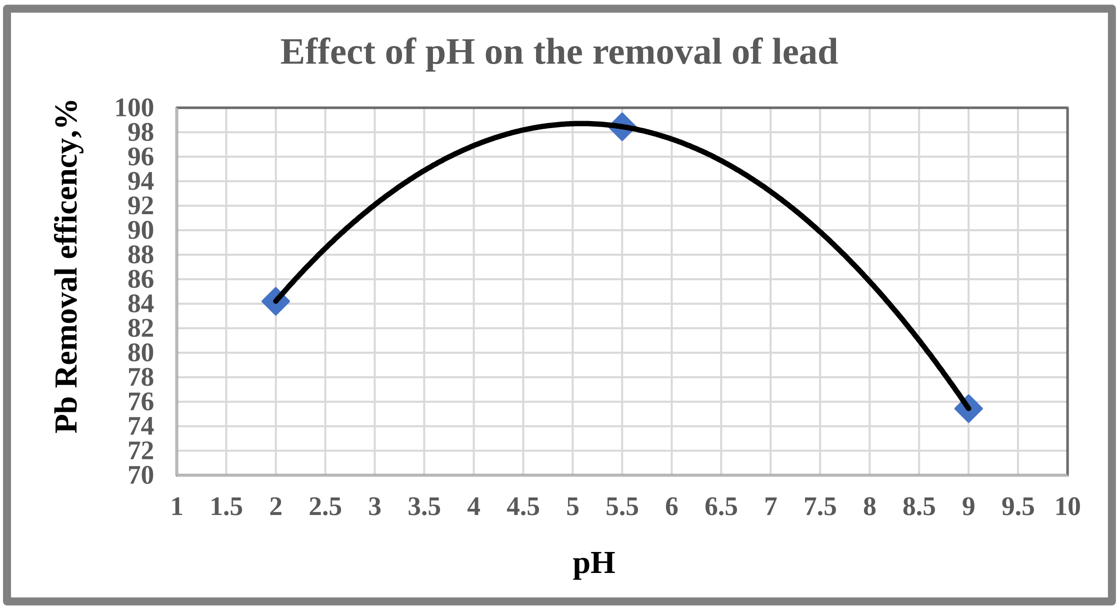



Figure 9: Effects of pH on the removal efficiency of Pb (II)

#### 4.3.1.3 Effect of Adsorbent Dose on Adsorption Efficiency of Pb (II)

Experiments with the use of different dosages of MASA adsorbent at 0.5, 1.25, and 2g/L had been carried out to consider the impact of adsorbent dosage on adsorption of Pb2+ ions optimum experimental conditions of 120 min contact time, 150 rpm agitation speed, 0.064 mg/L initial concentration of adsorbate and solution pH of 5.5. The impact of the adsorbent dose was determined by varying its weight from 0.5 to 2 g/L. As proven in Table (14) & Figure (10), the adsorption percentage of Pb2+ ions have been determined to make bigger with the increase of MASA adsorbent per liter of wastewater solution. The adsorption proportion of Pb2+ ions was once improved from 82.640% to 98.613 %, with an increase in the adsorbent dose from 0.5 to 2g/L. Because of the intensification of active sites of the adsorbent, increased availability of the exchangeable sites, and surface area, the adsorption percentage of lead ions elevated with an increase of adsorbent dosage (Ugwu et al. 2020). Therefore, 2g/L of the adsorbent dose used to be viewed the most useful dose underneath the experimental prerequisites indicated in Table (14) & Figure (10), and the uptake result, suggests the communicate affiliation between adsorbent dose and uptake of Pb2+ ions in mg/g. As the adsorbent dose expanded from 0.5 to 2g/L, the uptake of lead ion decreased. According to Table (14) & Figure (10), the minimal uptake used to be mentioned at 2g/L of adsorbent dose, which was once 0.032mg/g. The most uptake (0.106 mg/g) used to be recorded at pH 5.5 with 0.5g/L of adsorbent dose. The lowering style of uptake of lead ions in mg/g whilst growing adsorbent dose used to be additionally discovered by means of different researchers (Ugwu et al. 2020).

Table 13: Effect of adsorbent dose on $Pb^{2+}$ removal efficiency

| Adsorbent dose (g/L) | pH | Contact time (min) | Pb Adsorption % | q mg/g |
|---|---|---|---|---|
| 0.5 | 5.5 | 75 | 82.640 | 0.106 |
| 1.25 | 5.5 | 75 | 98.452 | 0.050 |
| 2 | 5.5 | 75 | 98.613 | 0.032 |

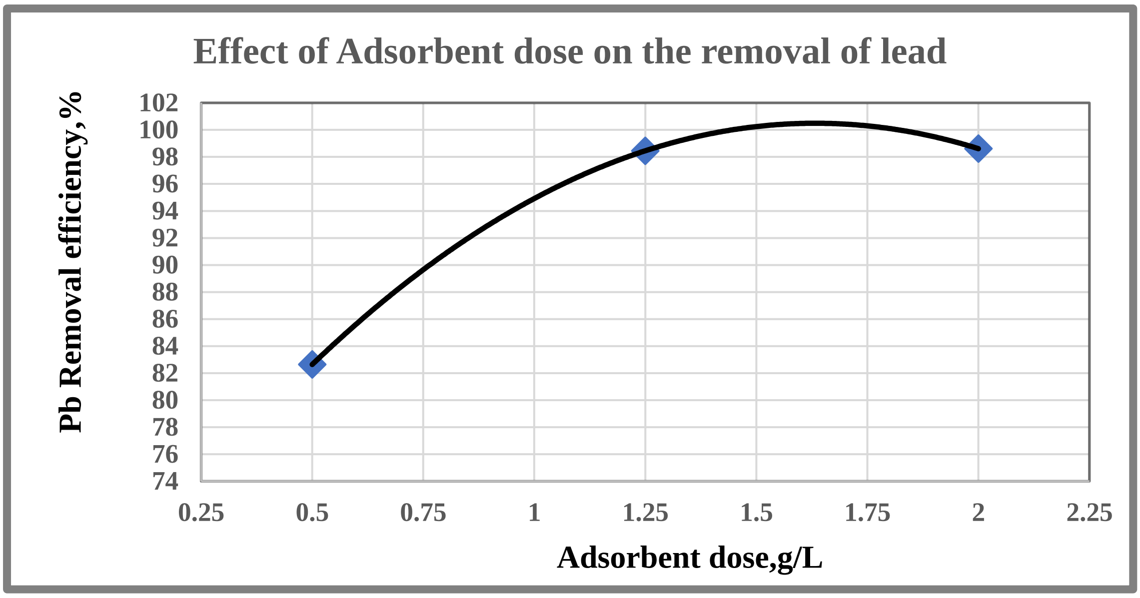



Figure 10: Effects of Adsorbent dose on the removal efficiency of Pb (II)

## 4.4 Optimization of removal efficiency, pH, Contact time and adsorbent dosage for the removal of Pb (II) from Nefas Silk paint industry wastewater by Mango and Avocado Seed adsorbent.

### 4.4.1 Response Surface Method (RSM) of $Pb^{2+}$ Adsorption

RSM was once used to consider the influence of three essential absorption parameters, namely, adsorbent dosage, contact time, and pH, on the adsorption of Pb (II). The experiments designed via CCD of RSM are listed in Table (11) above. Based on the adsorption efficiencies decided from the designed experiments, a quadratic equation in coded factors Equation (4.3) beneath will bought to specific the relationship between the response and independent variables. In the equations and A, B, C are adsorbent dosage (g/l), Contact time (min.), and pH, respectively. The coded equation is beneficial for figuring out the relative effect of the factors through evaluating their coefficients. Thus, the effect of the three factors on the adsorption efficiency used to be in a descending order of pH > Contact time > adsorbent dosage, in accordance to Equation (4.3). Also, the interaction between adsorbent dosage and Contact time used to be greater significant. Specifically, the impact on the pH on adsorption efficiency grew to be incredibly full-size at greater Contact time, as proven in Figure (11). Likewise, contact time performed an extra and extra essential role as the adsorbent dosage expanded Figure (12). Figure (13) shows that adsorbent dosage solely exerted apparent have an effect on adsorption efficiency at low pH (e.g., 2-5.5).

Final Equation in Terms of Coded Factors

$$Lead\ Removal\ Efficiency = +0.0100 - 0.0008A - 0.0001B + 0.0006C + 0.0002AB + 0.0001AC - 0.0002BC + 0.0014A^2 + 0.0004B^2 + 0.0029C^2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots 4.3)$$

The equation in terms of coded factors can be used to make predictions about the response for given degrees of every factor. By default, the high levels of the factors are coded as +1 and the low levels are coded as -1. The coded equation is beneficial for figuring out the relative influence of the factors by means of evaluating the factor coefficients.

As illustrated under in Figures (11–13), the 2D contour and 3D response surface plots display the independent variables' interaction effects on the response. According to the factors' impact indicated in Table (11), Figures (12), and Equation (4.3), adsorbent dose and contact time had more significant positive effects on lead adsorption.

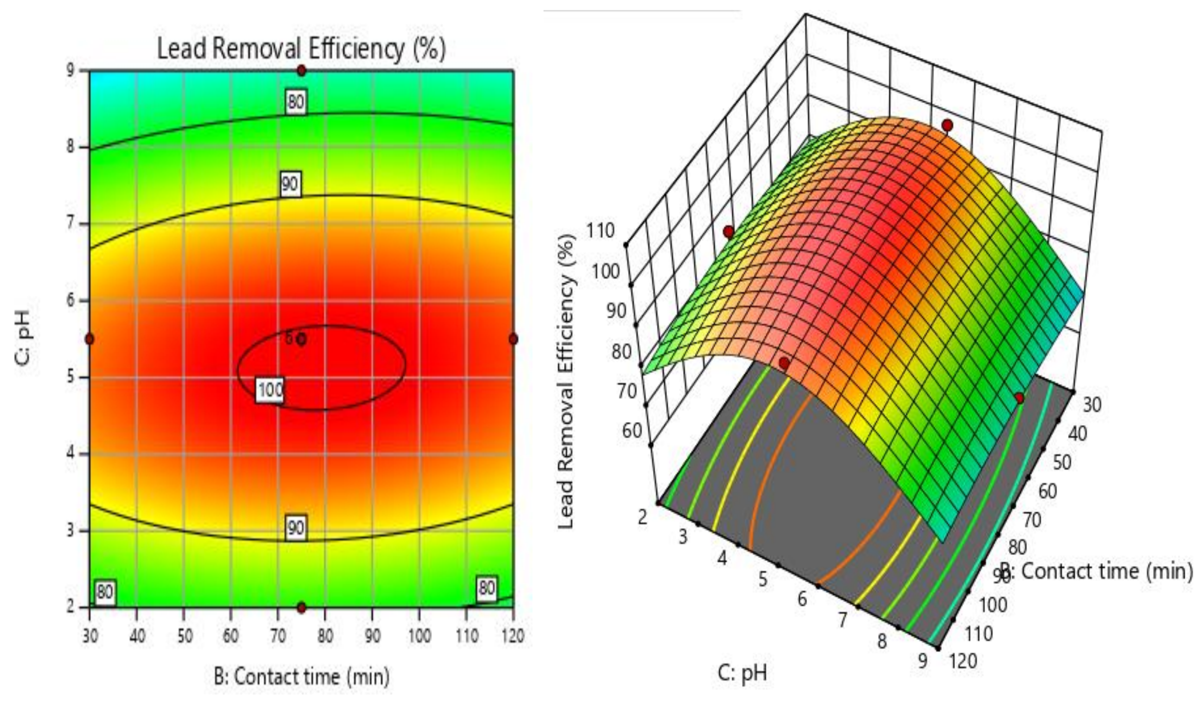



Figure 11: Two-dimensional contour and three-dimensional surface plots on the relation between contributed factors (contact time and pH) and $Pb^{2+}$ removal.

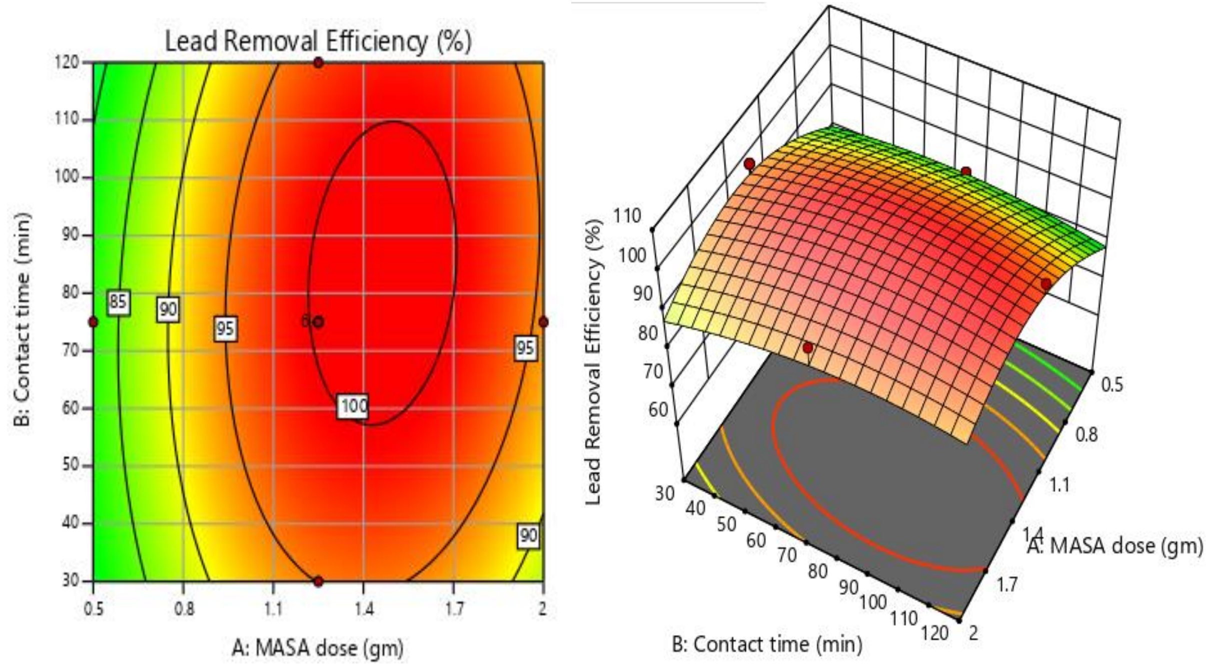



Figure 12: Two-dimensional contour and three-dimensional surface plots on the relation between contributed factors (contact time and MASA dose) and $Pb^{2+}$ removal.

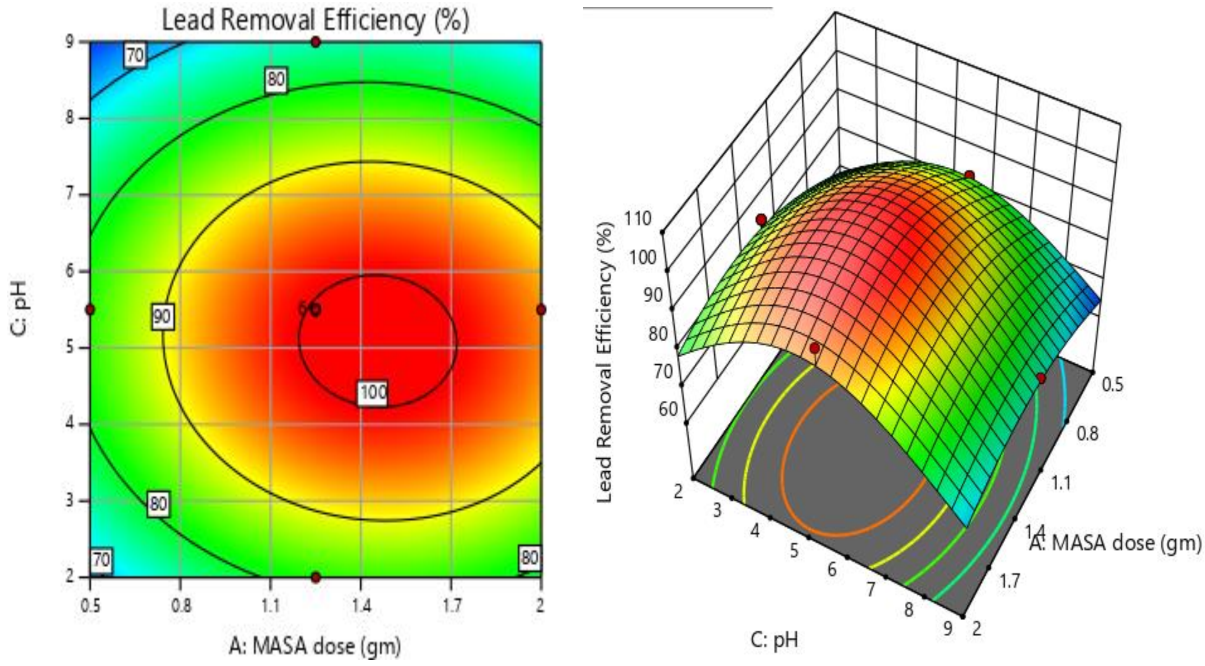



Figure 13: Two-dimensional contour and three-dimensional surface plots on the relation between contributed factors (pH and MASA dose) and $Pb^{2+}$ removal

#### 4.4.1.1 Second-Order Polynomial Modeling

The experimental information was checked for model adequacy to see if the fitted model would produce in correct or misleading results. The experimental statistics have been fitted up the usage of four-degree polynomial models, consisting of linear, interactive (2FI), cubic, and quadratic models (Birhanu and Leta 2021). In this study, two distinct tests, the sequential model sum of squares and the model summary statistics, have been run to investigate the suitability of the various models for representing the responses. The adequate model summary output confirmed that the quadratic model was statistically highly significant due to the fact of its larger R2 and lower p value ($p<0.0001$), in contrast to the different models Table (15). As a result, the quadratic model was once chosen in this learn about to study how method variables have an effect on a response (Lead removal efficiency from wastewater).

Table 14: Fit Summary

| Source | Sequential p-value | Lack of Fit p-value | Adjusted $R^2$ | Predicted $R^2$ | |
|---|---|---|---|---|---|
| Linear | 0.6295 | < 0.0001 | -0.0689 | -0.6430 | |
| 2FI | 0.9887 | < 0.0001 | -0.3035 | -5.7956 | |
| **Quadratic** | **< 0.0001** | **< 0.0001** | **0.9839** | **0.9536** | **Suggested** |
| Cubic | 0.8370 | < 0.0001 | 0.9782 | -7.4529 | **Aliased** |

#### 4.4.1.2 Quadratic Model Experimental Design Analysis

To measure the relationship between the response variable (Pb2+ removal) and the independent variables such as contact time, pH, and adsorbent dose, response surface methodology was employed. A central composite design (CCD) model indicated a quadratic model represented the correlation between the response variable and all factors. On the other hand, In Table (16) a summary of fit statistics data validated that adjusted and predicted R2 have been close to each other the difference the distinction being much less than 0.2. The coefficient of determination (R2) approached 1, and the precision that measures the signal to noise ratio suggests an accurate sign seeing that it used to be greater than 4. As proven in Equation (3.12) on methodology section, the anticipated response was once calculated in phrases of a second-order polynomial equation with single, interaction, and quadratic phrases representing the last quadratic model for the adsorption percentage of lead metal ion. The RSM model can be viewed reproducible when the coefficient of variance (CV) value is less than 10% (Birhanu and Leta 2021). In this regard, From Table (16) the value of the coefficient of variance of this learn about was once 2.35, which infers the model’s reproducibility.

Table 15: Fit Statistics

| | | | |
|---|---|---|---|
| Std. Dev. | 0.0003 | $R^2$ | 0.9915 |
| Mean | 0.0123 | **Adjusted $R^2$** | 0.9839 |
| C.V. % | 2.35 | **Predicted $R^2$** | 0.9536 |
| | | **Adeq Precision** | 29.3202 |

The **Predicted $R^2$** of 0.9536 is in life like settlement with the **Adjusted $R^2$** of 0.9839; i.e. the distinction is much less than 0.2.**Adeq Precision** measures the signal to noise ratio. A ratio higher than 4 is desirable. Your ratio of 29.320 shows an enough signal. This model can be used to navigate the design space. Furthermore; in this experiment, the **$R^2$** value was 0.991 which, in some other check, implied the model to be significant.

### 4.4.1.3 Central Composite Design (CCD) Statistical Analysis

The ANOVA evaluation proven in the lower section of Table (17) proves the effects mentioned above at a confidence level of 95%. In the ANOVA, the mean squares have been acquired by way of dividing the sum of the squares of every of the variant sources the mode and the error variance, through the respective degrees of freedom. The fishers' variance ratio, F-value is the ratio of the mean square owing to regression to the mean square owing to error. The greater the F-value, the greater is the significance of the corresponding variable to cause effect. In addition if Prob.>F much less than 0.05, the model phrases are viewed as significant. In the mathematical model, A, B, and C are independent singular factors, whereas AB, AC, and BC are interactional factors, and the quadratic phrases consist $A^2$, $B^2$ and $C^2$. According to assessment outcomes of of the evaluation of variance confirmed in Table (17), the p-values for the individual parameters, interaction factors, and the quadratic terms such as A, C, $A^2$, $B^2$ and $C^2$, and AB have been significant. However, the p-values of other interaction factors and quadratic terms such as B, AC and BC had been higher than 0.05.

Table 16: ANOVA results of the quadratic model for adsorption of $Pb^{2+}$ by MASA.

| **Source** | **Sum of Squares** | **df** | **Mean Square** | **F-value** | **p-value** | **Remarks** |
|---|---|---|---|---|---|---|
| Model | 0.0001 | 9 | 0.0000 | 129.99 | < 0.0001 | significant |
| A-MASA dose | 5.846E-06 | 1 | 5.846E-06 | 69.38 | < 0.0001 | significant |
| B-Contact time | 1.077E-07 | 1 | 1.077E-07 | 1.28 | 0.2846 | Not significant |
| C-pH | 3.973E-06 | 1 | 3.973E-06 | 47.15 | < 0.0001 | significant |
| AB | 4.161E-07 | 1 | 4.161E-07 | 4.94 | 0.04505 | significant |
| AC | 1.780E-07 | 1 | 1.780E-07 | 2.11 | 0.1768 | Not significant |
| BC | 2.305E-07 | 1 | 2.305E-07 | 2.74 | 0.1292 | Not significant |
| $A^2$ | 5.522E-06 | 1 | 5.522E-06 | 65.54 | < 0.0001 | significant |

| | | | | | | |
|---|---|---|---|---|---|---|
| $B^2$ | 5.526E-07 | 1 | 5.526E-07 | 6.56 | 0.0283 | significant |
| $C^2$ | 0.0000 | 1 | 0.0000 | 267.26 | < 0.0001 | significant |
| Residual | 8.426E-07 | 10 | 8.426E-08 | | | |
| Lack of Fit | 8.426E-07 | 5 | 1.685E-07 | 1.511E+05 | <0.0.1428 | insignificant |
| Pure Error | 5.575E-12 | 5 | 1.115E-12 | | | |
| Cor Total | 0.0001 | 19 | | | | |

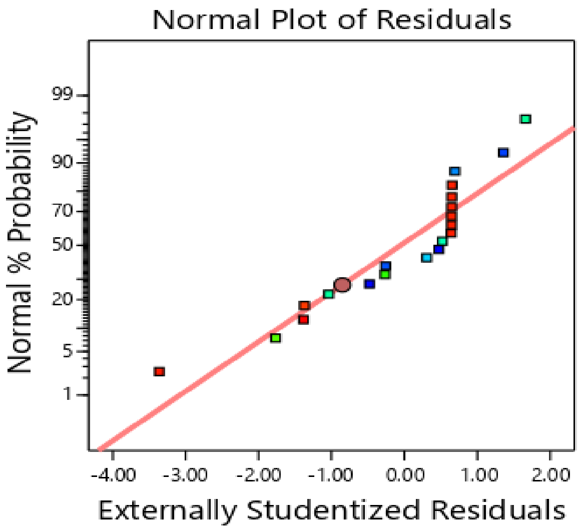
The Model F-value of 129.99 implies the model is significant. There is only a 0.01% chance that an F-value this large ought to happen due to noise. P-values less than 0.0500 indicate model terms are significant. In this case A, C, $A^2$, $B^2$, $C^2$ and AB are significant model terms. Values larger than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting these required to aid hierarchy), model reduction may additionally enhance your model. The Lack of Fit F-value of 151133.92 implies the Lack of Fit is insignificant.

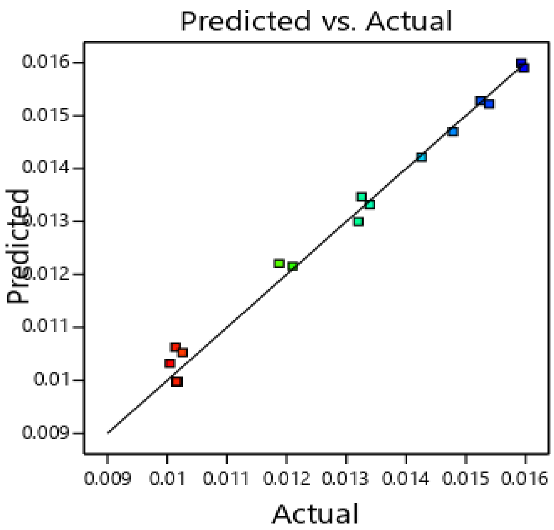
#### 4.4.1.4 Model Validation

As validated under in Figure (14a), the RSM model's adequacy is additionally evaluated through residual diagnostic plots, which are the difference between the observed and predicted responses (Birhanu and Leta 2021). Accordingly, the experimental statistics had been fitted in the RSM model to set up the relationship between the observed and estimated values. As illustrated in Figure (14a), all the data points are distributed near the straight line, indicating the quadratic model should be a beneficial model to predict the response. As indicated in Figure (14b), the predicted and actual value plots had been close to each other, indorsing the suitability of the model.

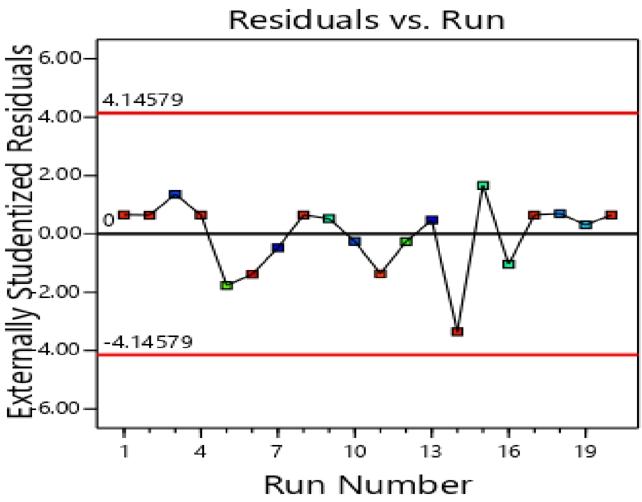
The expected values for the removal of lead had been compared to the experimental values. The proposed model was once proven to be reliable and valid due to the fact there used to be a sturdy correlation between experimental outcomes and expected values Figure (14b) below. The normal probability plot of the residuals given in Figure (14a) proven that there are minimal departures from normality. Majority of records are inside straight line i.e. facts plotted well-known shows ordinary conduct shows the residuals are typically alongside a straight line, and this implies the residuals have a normal distribution in the given probability range. The residuals are the distinction between the actual and predicted values of experimental runs by the design expert. Thus, one can generalize that there is now not a trouble with the normality in the data. Hence, there are no extreme outliers to be found. The factors in the plots for this experimental information fit in to the straight line in the figure, demonstrating that the quadratic polynomial model satisfies the evaluation of variance (ANOVA) assumptions that the error distribution is estimated normally. As proven in Figure (14b), the expected vs. actual figure determine represents that all factors are close to the straight line, hence the regression is best fit to the model. On the other hand, the residual vs. run additionally indicates that there are no outliers of statistics which verify the system's stability and the factors scattered are dispersed internal the red restricted lines Figure (14c).

The estimated output power by Design Expert (simulation result) versus the realistic experimental result implies that the expected values of output energy got from the model from RSM/ CCD and the actual experimental records (DoE) are in an appropriate agreement. Their consistency and accuracy of telling both results from simulation and experiment are encouraging and promising. In contrast, the Normal Plot of Residuals graph implies that the data is typically distributed. Generally, the normal probability plot is a graphical technique to identify any departures from normality which consists of any outliers, skewness, a need for transformations and combinations (K. Y. Yap, H.S. Chua, M. J. K. Bashir, F.Y.C. Albert 2019).




**(a)** **(b)**




**(c)**

Figure 14: Diagnostic plots for the adequacy of proposed model for removal of Pb (II) (a) Normal Plot of Residuals graph (b) Predicted versus actual graph (c) Residual versus actual graph.

**4.4.2 Optimization of Adsorption Process**

For response, the second-order polynomial developed models in this learn about have been utilized in order to gain the favored optimum values. Numerical optimization by the design expert was once used to decide the nice prerequisites for lead removal to produce maximum removal efficiency. One of the primary targets of this find out about used to be to discover the optimum process parameters which MASA produced ought to have an excessive lead ($Pb^{2+}$) removal efficiency and adsorption amount. However, it is difficult to optimize both responses under the same condition because the interest region of factors is different. When removal efficiency increases, adsorption potential of MASA will decrease and vice versa. Therefore, the characteristic of desirability used to be utilized the use of Design Expert® software version 13.0.5.0 (Stat –Ease, Inc.), in order to compromise between these two responses. In the optimization analysis, the goal criteria was set as maximum values for the two responses of lead removal efficiency and MASA adsorption amount while the values of the three variables had been set in the levels being studied. The experimental prerequisites with the very best desirability had been chosen to be verified. The predicted and experimental results of lead removal efficiency and MASA adsorption capacity obtained at optimum conditions are listed in Table (18).

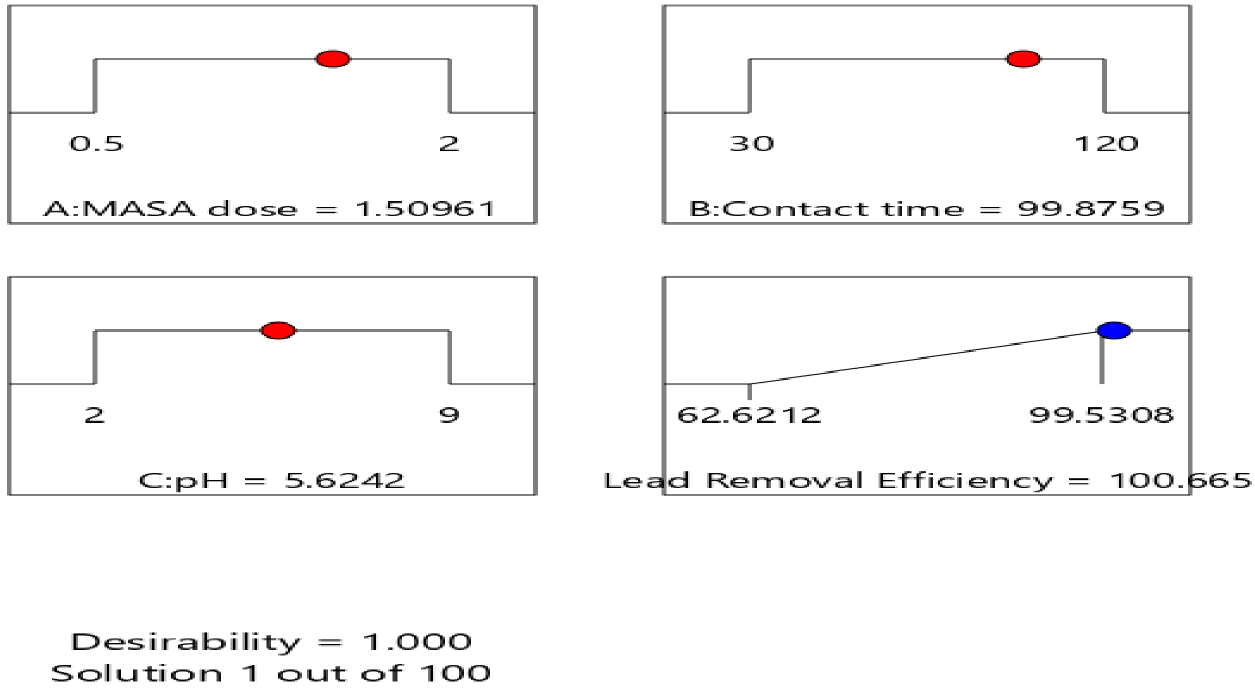



Figure 15: Desirability ramp for numerical optimization of four selected variables

Table 17: Predicted and Experimental Optimum Conditions for Selected Parameters by Design of Experiment

| **Predicted Optimum Conditions** | | **Experimental Optimum Conditions** | |
|---|---|---|---|
| **Variables** | **Optimum value** | **Variables** | **Optimum value** |
| Adsorbent dosage | 1.50961g | Adsorbent dosage | 1.25g |
| Contact time | 99.8759min | Contact time | 120min |
| pH | 5.6242 | pH | 5.5 |
| Lead removal efficiency | 100.665% | Lead removal efficiency | 99.53% |
| Adsorption amount | 0.004 mg/g | Adsorption amount | 0.005 mg/g |

The optimum lead removal efficiency of 99.53% by Mango and Avocado Seed Adsorbent had been got by means of the use of contact time, pH and adsorbent dosage; 120min, 5.5 and 1.25g respectively. The most fulfilling adsorption quantity showed 0.005 mg/g by Mango and Avocado Seed Adsorbent got via the use of contact time, pH and adsorbent dosage; 120min, 5.5 and 1.25g respectively. The outcomes above have proven that the lead removal process variables and the interaction among the variables in order to achieve the perfect percentage removal of lead the use of the model regression developed. Therefore, in order to gain the most maximum percentage removal of lead, the estimated combination of parameters was as follows: adsorbent dosage of 1.50961g, pH of 5.6242 and Contact time of 99.8759 minutes. Under this conditions, the model predicted lead removal of 100.665% with a desirability value of 1.

### 4.5 Determination of adsorption models of the adsorbent by different isotherm and kinetic models.

#### 4.5.1 Adsorption Isotherms Models

The effects received on the adsorption of $Pb^{2+}$ ions with different adsorbent dose and fixed initial concentrations and pH were analyzed by using the models given by Langmuir and Freundlich which correspond to homogenous and heterogeneous adsorbent surfaces, respectively. The batch equilibrium experimental facts of chosen adsorbents had been fitted and analyzed by means of the most two in many instances used models in the literature in the following sub-sections. The batch equilibrium facts analyzed by Langmuir and Freundlich isotherms used to be bought the use of the preliminary lead concentrations; 0.064 mg/l.

Table 18: Langmuir and Freundlich Adsorption Isotherm parameters for Adsorption of $Pb^{2+}$ ions

| Adsorbent dose (g) | Time (min) | pH | Initial $Pb^{+2}$ conc. $C_i$ (mg/l) | $C_e$ (mg/l) | $Q_e$ (mg/g) | $Ce/Q_e$ (g/l) | Log $C_e$ | Log $Q_e$ |
|---|---|---|---|---|---|---|---|---|
| 1.25 | 75 | 5.5 | 0.064 | 0.001 | 0.050 | 0.020 | -3.001 | -1.298 |
| 1.25 | 120 | 5.5 | 0.064 | 0.0003 | 0.051 | 0.006 | -3.523 | -1.293 |
| 1.25 | 30 | 5.5 | 0.064 | 0.002 | 0.050 | 0.032 | -2.796 | -1.302 |
| 0.5 | 120 | 2 | 0.064 | 0.022 | 0.084 | 0.262 | -1.658 | -1.076 |
| 0.5 | 120 | 9 | 0.064 | 0.024 | 0.080 | 0.298 | -1.622 | -1.096 |
| 0.5 | 30 | 2 | 0.064 | 0.021 | 0.086 | 0.239 | -1.684 | -1.063 |
| 2 | 75 | 5.5 | 0.064 | 0.001 | 0.032 | 0.028 | -3.052 | -1.501 |

##### 4.5.1.1 Langmuir Isotherm Model

Langmuir‘s isotherm calculated by the use of Equation (3.14) mentioned in methodology part and the end result is tabulated in Table (20) below. Langmuir isotherm model assumes monolayer sorption with the aid of physical forces. The information from adsorption experiments was once examined via linear regression of Langmuir isotherm equation and the graphs are plotted as proven in Figure (16).

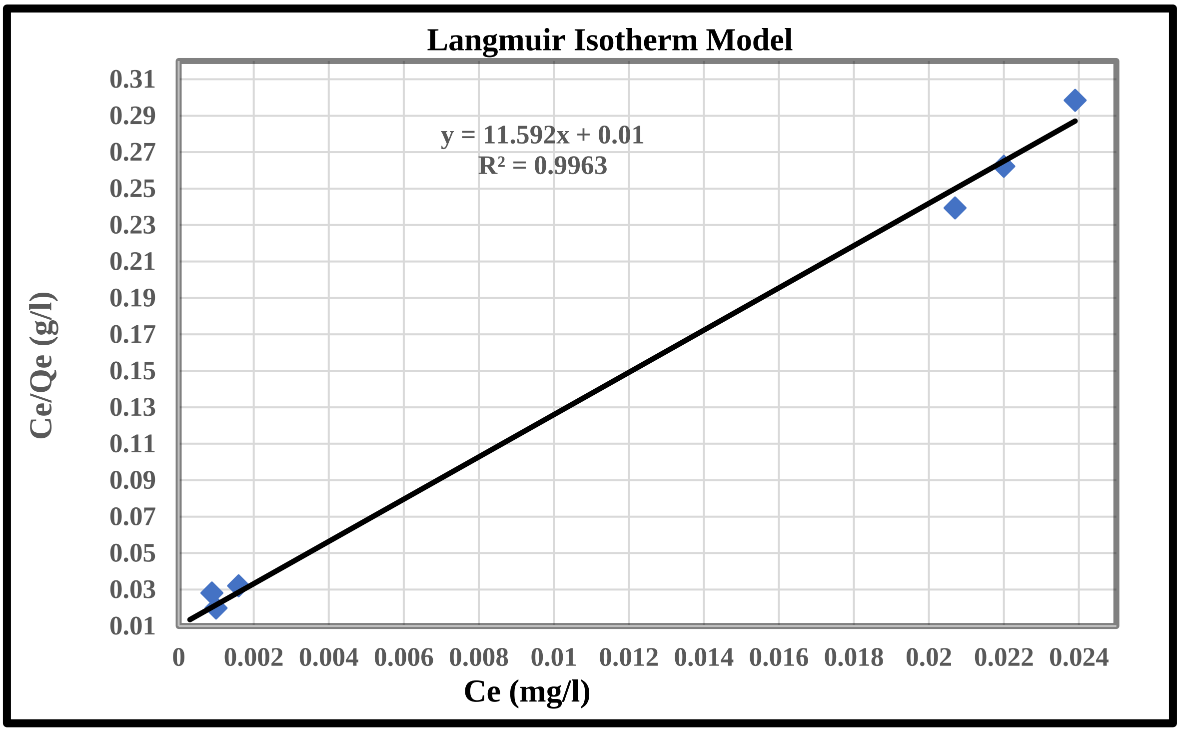



Figure 16: Langmuir adsorption isotherm for adsorption of $Pb^{2+}$

According to Figure (16), the graph of Ce/Qe opposition Ce create a linear line, which accepted applicability of Langmuir isotherm. The Langmuir constants, qm and $K_L$ are computed from intercept and slope of got plots, and is listed in Table (20).

Table 19: Results of Langmuir isotherm model for the adsorption of Pb (II) ions

| Adsor bent | Equations | Correlation Coefficient ($R^2$) | Surface energy (qm) | Monolayer adsorption capacity ($K_L$) |
|---|---|---|---|---|
| MASA | y=11.592x+0.01 | 0.9963 | 100.000 | 8.627 |

As proven in Figure (16), the batch equilibrium information of MASA has perfectly fitted in the Langmuir model, with a correlation coefficient ($R^2$) of 0.9963. This phenomenon demonstrates that there is a monolayer adsorption takes place on particular homogeneous sites. To affirm the favorability of the adsorption process, the separation factor (RL) was calculated and introduced in Table (21) below. Additional evaluation of Langmuir isotherm used to be made the use of a dimensionless parameter (RL) shown in Equation (3.15) in methodology section. Equation (3.15) was used to predict whether the adsorption manner is favorable ($0 < RL < 1$) or unfavorable ($RL > 1$). The lower the value of RL, the greater the affinity of the adsorbent to the adsorbate (Birhanu and Leta 2021). As published in Table (21), the end result attained in this find out about suggests the Langmuir isotherm model's favorability.

Table 20: Separation Factor (RL) for MASA adsorbents

| Initial lead concentration (mg/l) | RL |
|---|---|
| | MASA |
| 0.064 | 0.6443 |

As viewed from Table (21), the RL value for adsorbent used to be 0.6443 observed for 0.064mg/l initial lead concentrations. This confirms that the lead adsorption adsorbents was once favorable for uptake of lead by way of adsorption process.

### 4.5.1.2 Freundlich Isotherm Model

The fundamental assumption of Freundlich model is the heterogeneous surface energy of adsorption. The relationship the quantity of lead adsorbed per unit mass of the adsorbents (qe) and equilibrium lead concentration (Ce) was once bought from the Freundlich isotherm models as represented in Figure (17).

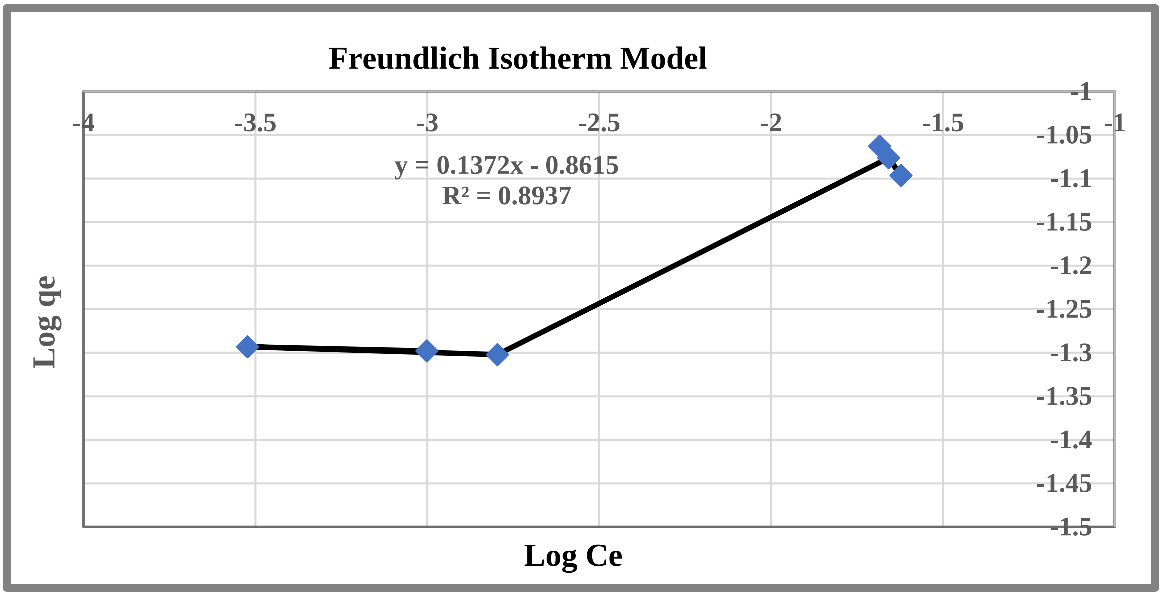



Figure 17: Freundlich adsorption isotherm for adsorption of $Pb^{2+}$ ion

As considered from Figure (17), the relationship from graph of log qe vs. log Ce gave straight line with $R^2$=0.8937. The constants in Freundlich isotherm can be calculated from the plot of log qe versus log Ce listed in Table (22). The $R^2$ value obtained from Freundlich model of MASA are not well fitted in this isotherm as in contrast to Langmuir isotherm.

Table 21: Results of Freundlich isotherm model for the adsorption of Pb (II) ions

| Adsorbent | Equations | Correlation coefficient ($R^2$) | $K_f$ | 1/n | n |
|---|---|---|---|---|---|
| MASA | y =0.1372x – 0.8615 | 0.8937 | 0.4225 | 0.1372 | 7.2886 |

If 1/n is < 1, it designates ordinary adsorption, and if it is > 1, it implies cooperative adsorption. The value of slope (1/n) values lied between 0 – 1 for adsorbent and this confirms the make bigger in bond energies with enlarge in planar density. The 1/n value less than one suggests favorable and chemisorption of the adsorption procedure (Tsegaye 2011). (Tsegaye 2011). If 1/n is < 1, it designates ordinary adsorption, and if it is > 1, it implies cooperative adsorption. The value of slope (1/n) values lied between 0 – 1 for adsorbent and this confirms the make bigger in bond energies with enlarge in planar density. The 1/n value less than one suggests favorable and chemisorption of the adsorption procedure (Birhanu and Leta 2021). As introduced in Table (22), the value of 1/n received from this find out about used to be 0.1372, which suggests that the molecules accountable for the adsorption of $Pb^{2+}$ onto MASA adsorbent favor adsorption, which shows a chemisorption adsorption process. In another way, the value of the correlation coefficient result acquired from the plot validates the appropriateness of the Freundlich isotherm model to provide an explanation of the adsorption process.

### 4.5.2 Adsorption Kinetics Model

Studies Adsorption kinetics explains the lead removal rate as a function of equilibrium contact time. The batch kinetic data analyzed through pseudo first and second order kinetic models.

Table 22: pseudo first and second order kinetic models parameters for Adsorption of $Pb^{2+}$ ions

| **Time (min)** | **Adsorbent dosage (g)** | **pH** | **Initial $Pb^{+2}$ conc. $C_i$ (mg/l)** | **$C_e$ (mg/l)** | **qe (mg/g)** | **qt (mg/g)** | **qe-qt (mg/g)** | **Log qe** | **Log (qe-qt)** | **t/qt** |
|---|---|---|---|---|---|---|---|---|---|---|
| 120 | 2 | 2 | 0.064 | 0.016 | 0.051 | 0.024 | 0.027 | -1.293 | -1.574 | 4954.583 |
| 120 | 2 | 9 | 0.064 | 0.019 | 0.051 | 0.022 | 0.028 | -1.293 | -1.545 | 5352.364 |
| 75 | 1.25 | 5.5 | 0.064 | 0.001 | 0.051 | 0.050 | 0.001 | -1.293 | -3.246 | 1489.751 |
| 75 | 1.25 | 5.5 | 0.064 | 0.001 | 0.051 | 0.050 | 0.001 | -1.293 | -3.253 | 1489.466 |
| 30 | 1.25 | 5.5 | 0.064 | 0.002 | 0.051 | 0.050 | 0.001 | -1.293 | -2.983 | 601.540 |

#### 4.5.2.1 Pseudo First Order Kinetic Model

In methodology section Equation (3.18) qe represents the quantity of $Pb^{2+}$ ions adsorbed per unit weight of the adsorbents at equilibrium, qt (mg $g^{-1}$) represents the quantity of $Pb^{2+}$ ions adsorbed per unit weight of the adsorbents at time t (min), and the rate constant of the pseudo-first-order kinetic model is represented by $k_1$. In order to elucidate the adsorption kinetic process, the data in Table (23) above was once utilized for the two most broadly used models (i.e. pseudo- first order rate and pseudo-second order rate models).

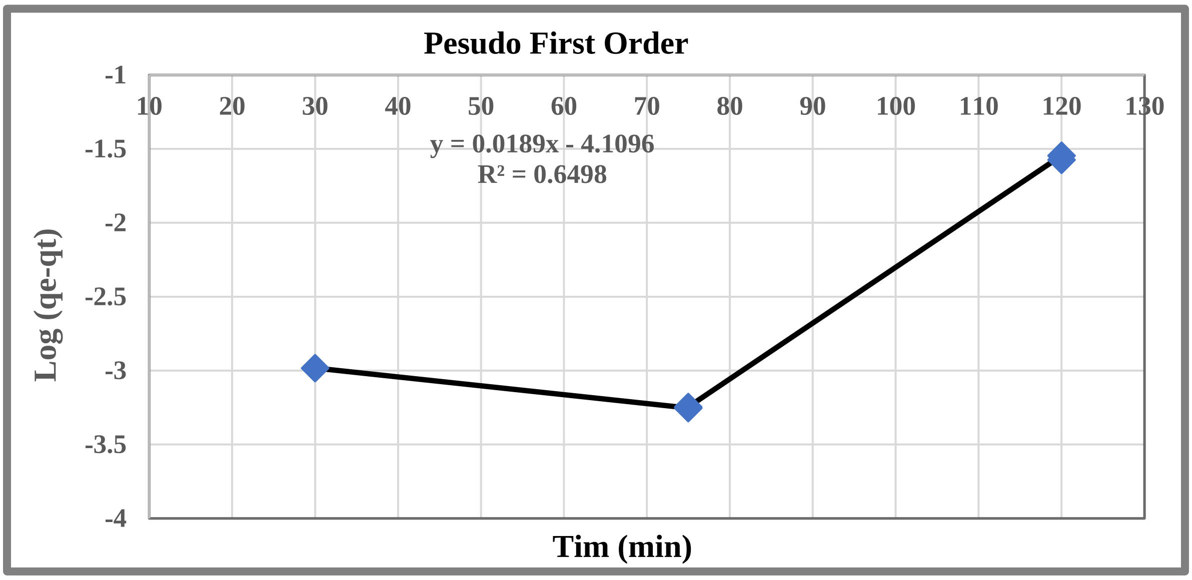



Figure 18: Pseudo-first-order kinetics plots for the adsorption of $Pb^{2+}$ ions

The plot in Figure (18) suggests that lead (II) adsorption with different contact times consisted of two-stages; a fast preliminary stage where the adsorption was quickly and a slower second stage where the adsorption equilibrium was achieved. If the plot of log (qe − qt) towards time (t) suggests a linear relationship, the pseudo-first-order is appropriate, the rate constant ($k_1$), qe (cal) and the correlation coefficient ($R^2$) being decided from the straight-line plot of the log (qe − qt) versus t. The values of $k_1$ and qe (cal) in mg/g of $Pb^{2+}$ predicted from the plot proven in Figure (18) and listed in Table (24) below are -0.00011 and 0.0164 mg/g, respectively

#### 4.5.2.2 Pseudo Second Order Kinetic Model

In methodology section from Equation (3.19) the rate constant ($K_2$) and calculated equilibrium adsorption potential (qe (cal)) can be measured from the slope and intercept of the plot t/qt versus t, which is shown in Figure (19). The adsorption kinetics of lead ions listed in Table (24) supported through the pseudo-second-order model. Therefore, this learn about endorses that the rate-limiting feature in the adsorption of lead (II) by MASA adsorbent is chemisorption involving the exchange of $Pb^{2+}$ ions with functional groups in the adsorbent.

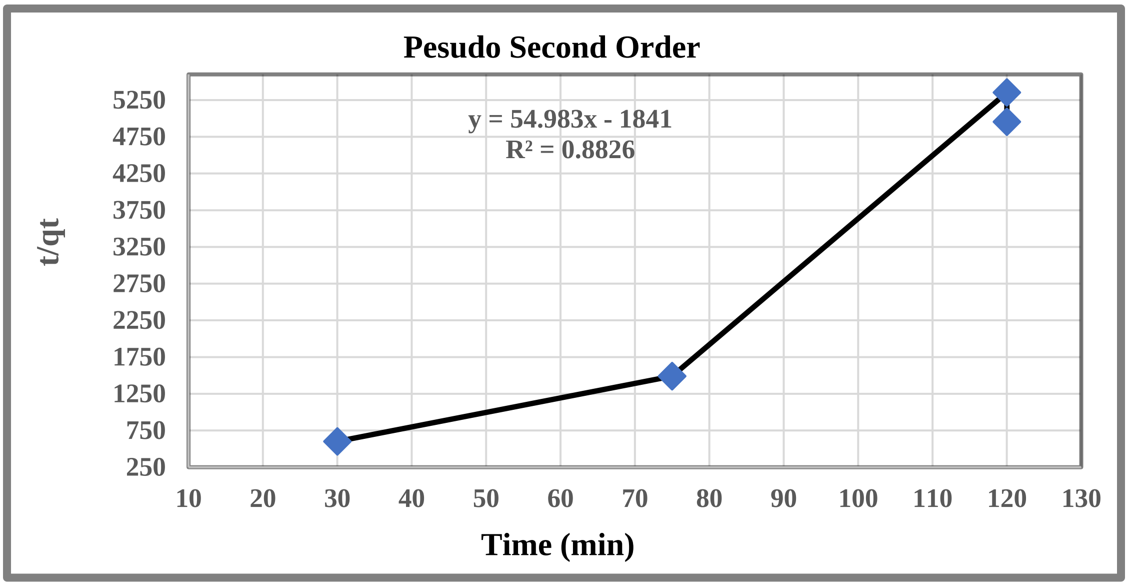



Figure 19: Pseudo-second-order kinetics plots for the adsorption of $Pb^{2+}$ ions

Table 23: Line fit model of Pseudo first and second-order kinetics for $Pb^{2+}$

| Adsorbent | Order | Equations | $R^2$ | qe | K-value |
|---|---|---|---|---|---|
| MASA | First order kinetics | Y = -0.0189x-4.1096 | 0.6498 | 0.0164 | $K_1$= -0.00011 |
| | Second order kinetics | Y =54.983x-1841 | 0.8826 | 0.0182 | $K_2$= -16421.13 |

## 4.6 Comparison of Adsorption Capacity of MASA with Other Low-Cost Adsorbents for Removal of Pb (II)

The adsorption capacity of Pb (II) onto MASA was compared with other Conventional adsorbents reported in the literature and were appeared in Table (25). It can be observed that the adsorbent created from MASA compares well with the Routine adsorbents from most of the crude materials recorded and the MASA can be considered to be a doable adsorbent for the removal of Pb (II) from paint industry waste water. The value for lead sorption observed in this work is in great understanding to compare with values found by other analysts. Contrasts of metal uptake are due to the properties of each adsorbent such as structure, functional groups and surface area (Singh et al. 2008).

Table 24: Removal Efficiency (%) of adsorbent and Pb (II) adsorption capacity (mg/g) of previously reported Conventional adsorbents

| Adsorbent | Modification | Maximum Adsorption Capacity (mg/g) or (mmol/Kg) | Lead Removal Efficiency (%) | Ref. |
|---|---|---|---|---|
| Bottom Ash | _ | 0.315 | _ | (Gorme et al. 2010) |
| Granular activated carbon: | $Na_2S$ | 2.89 | _ | (Kouakou et al. 2014) |
| Marine green algae activated carbon: | $NaSO_4$ | 24.15 | 97.34 | (Chandrasekaran and Pseudo-first-order 2014) |
| Activated alumina | ferrite permanent magnets | _ | 95.36 | (Szatyłowicz and Skoczko 2018) |
| Natural zeolite and chamotte clay | _ | 14 & 11 | _ | (Rakhym, Seilkhanova, and Kurmanbayeva 2020) |
| Zeolite Nanoparticles | _ | 43.91 | _ | (Joshi 2016) |
| Silica gel | 3 mmol of L-proline solution | 11.4 | 92.4 | (Kushwaha, Gupta, and Chattopadhyaya 2017) |
| Cow bone activated carbon | $HNO_3$ | 42.3 | _ | (Cechinel, Ulson De Souza, and Ulson De Souza 2014) |
| MASA | _ | 0.051 | 99.5 | This Study |

# CHAPTER FIVE

# 5. CONCLUSION AND RECOMENDATION

## 5.1. Conclusions

Based on the findings of this study, it can be concluded that the adsorbent prepared from Mango and Avocado Seed is effective in removing heavy metal $Pb^{2+}$ ions from paint industry wastewater. The optimal pH for lead removal was decided to be 5.6242, and the percentage of lead uptake was influenced by the adsorbent dose and contact time. Higher sorbate concentrations resulted in lowered percentage removal due to limited available adsorption sites. The adsorption capacity decreased with increasing adsorbent dose, however the efficiency increased. Additionally, the efficiency of the adsorbent lowered with higher pH values. The MASA adsorbent tested fast lead removal in much less than 2hrs. Statistical evaluation validated the value of these findings. The regression models exhibited good agreement between experimental and estimated values, with the Langmuir isotherm model supplying the best correlation ($R^2$) of 0.9841. The adsorption kinetics accompanied a pseudo-second-order model, similarly supporting the effectiveness of the adsorbent. Overall, this find out about establishes that cheaper and easily accessible fruit waste can serve as an effective adsorbent for wastewater treatment processes, providing doable potential cost savings and practicality.

## 5.2. Recommendation

Based on the information and insights received from this study, countless pointers can be made for future lookup in the manufacturing and utility of adsorbents from Mango and Avocado Seed waste for heavy metal removal from wastewater:

- Conduct batch kinetic research at more than a few temperatures and agitation speeds to decide the thermodynamic parameters for lead adsorption on Mango and Avocado Seed adsorbents. This will provide a higher perception of the adsorption technique under different conditions and help optimize the efficiency of the adsorbent.
- Additional research by means of various initial metal ion concentration and the adsorbent size, indicated that the simultaneous enchantment of the adsorption ability of MASA adsorbent and the corresponding percentage removal for $Pb^{2+}$ metal ion.
- Consider pilot research and column research to check out the effectiveness of Mango and Avocado Seed waste adsorbents in the removal of other heavy metals. This will supply

perception into the adsorbents achievable for the simultaneous removal of multiple heavy metals and its potential to deal with competitive adsorption. As lead is not the only metal present in paint industry wastewater, it is encouraged to learn about the adsorption efficiency of Mango and Avocado Seed waste adsorbents for other different metals regularly observed in comparable wastewater streams. This will provide a comprehensive understanding of the adsorbent's capabilities and enlarge its applicability past lead removal.

- Explore the practicable of Mango and Avocado Seed waste for other wastewater purification applications. Investigate their effectiveness in putting off dissolved solids, free chlorine, and Kjeldahl Nitrogen (TKN). This will increase the scope of their purposes and discover their versatile use in wastewater treatment processes.
- Regeneration and reusability research of the surface characterization of Mango and Avocado Seed waste adsorbents on the adsorption technique after experimental process have to be similarly studied at one of a kind technique variables such as; concentration, volume and contact time.

By pursuing these future lookup directions, we can in addition enhance the utilization of Mango and Avocado Seed waste as an environment friendly and sustainable adsorbent for heavy metal removal from a variety wastewater sources.

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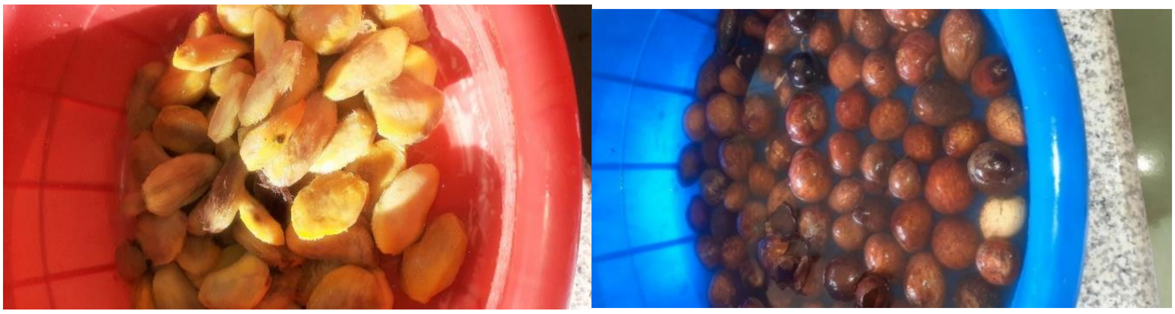
## ANNEXES

Table A1: Advantage and Disadvantage of Technologies Used to Remove Heavy Metals from Wastewater

| **Technologies** | **Advantage** | **Disadvantage** | **Ref** |
|---|---|---|---|
| Chemical Precipitation | Easy to use<br>Inexpensive nature<br>Apply for wide kind of metals | Requirement of an excess amount of chemical reagents<br>Production of sludge to a large quantity<br>High cost for disposal of sludge | (Chakraborty et al. 2020) |
| Membrane Technology | Can filter particle lower than 0.001µm<br>Less solid waste produced<br>Less chemical consumption<br>High efficiency (>95% for single metal)<br>Small space requirement<br>Low pressure requirement | High initial and running cost<br>Low flow rates<br>Removal (%) decreases with the presence of other metals<br>Complex process<br>Generation of sludge | (Agarwal and Chaudhry 2015) |
| Ione Exchange | High treatment capacity<br>High removal efficiency<br>Fast kinetics<br>High metal recovery, fewer sludge volume and limited pH tolerance. | Not all ion exchange resin is suitable for metal removal<br>The process needs high capital cost and high on maintenance | (Chakraborty et al. 2020). |
| Solvent Extraction | Higher concentrations to obtain high pure solutions | Large amount of solvent of the extracted phase should be refreshed in a costly stripping step<br>Need to remove heavy metals whose concentration is very high<br>Recovery cost will be very high | (Rao et al. 2010). |
| Coagulation and Flocculation | Sludge settling<br>Dewatering<br>Quick process, inexpensive, straightforward process and coagulating agents are easily accessible. | Low efficiency removal and required extra process such as sedimentation and filtration<br>Production of sludge, transfer of toxic compounds into solid phase | (Tang et al. 2016)<br>(Raouf MS and Raheim ARM 2016). |

| | | | |
|---|---|---|---|
| Electro dialysis | To generate a highly concentrated stream for recovery<br>The denying of unpleasing dirt from water | Disposal of hazardous waste<br>Redeem and salvage metals from the sludge | (Boontham and Babel 2018). |
| Adsorption | Process is of low operating cost for low-cost adsorbent<br>It is metal selective process<br>High removal capacity, most metals can be removed, High efficiency (>99%)<br>Regenerative for low-cost adsorbent<br>No generation of toxic sludge in this treatment for low-cost adsorbent<br>A wide range of adsorbent, excellent adsorption capacity, simple and low cost. | Performance depends upon adsorbent<br>Different adsorption capacity for different type of adsorbent.<br>High cost in case of activated carbon | (Shafiq, Alazba, and Amin 2018)(Kaur and Sharma 2017) (Devanna, Begum, and Chari 2019). |

## Annex A: MAS and MASA Adsorbent preparation Processes



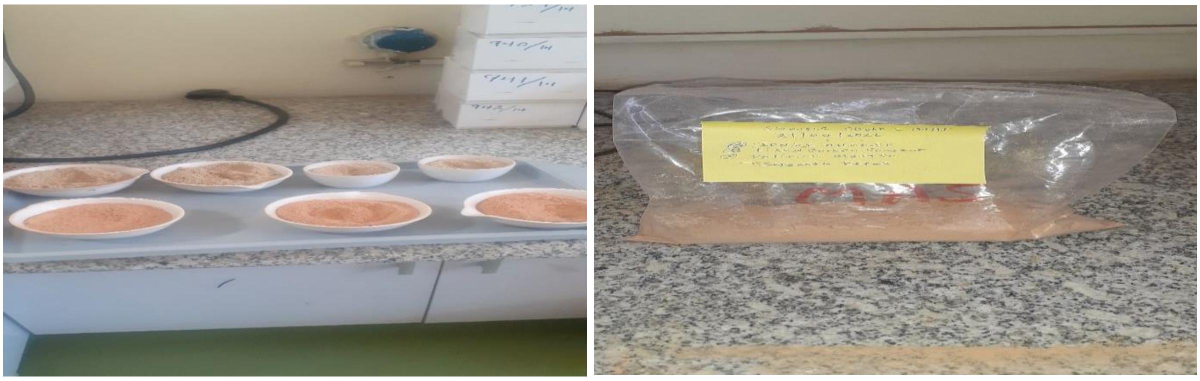
(a) (b)

(a) Mango and (b) Avocado Seed waste washed by tap water to remove impurity

Mango and Avocado Seed Cut into small pieces and sun-dried for one day to remove excess moisture

Mango and Avocado Seed dried in an oven at 110$^0$C for 12 hours

Mango and Avocado dried seeds were crushed and passed through a 250-µm sieve to obtain a fine powder




To ensure homogeneity, the mango and avocado seed powders were mixed thoroughly. The resulting mixture, referred to as Mango and Avocado Seeds (MAS) powder, was stored in airtight plastic bags for further experimental analysis.


The pretreated MAS powder will be carefully placed in open crucibles and subjected to a furnace at 600°C for a duration of four hours to produce MASA adsorbent.

**Annex B: Sample collection and characterization of Nefasesilk paint factory wastewater**

AAiT

School of Chemical & Bioengineering

Date. April 15, 2022

Ref.No. SCBE- 523/2014

To: Nifasilk Paint Factory

**Subject:- Requesting for Cooperation**

The School of Chemical and Bio Engineering in Addis Ababa institute of Technology, AAU is rendering Postgraduate programs in different MSc and PhD streams to its Students. Thus, our MSc student has requested the School to write Cooperation letter for organizations to enable her to attain the necessary information /data pertaining to the research work she is engaged.

Therefore, this is to kindly request you to Cooperation our student, *Ms.Tseganesh Kegne* to make research visit in your organization tenable her to collect the required information /west water Samples associated with the research work She is occupied..

Thank you very much for your cooperation in advance.

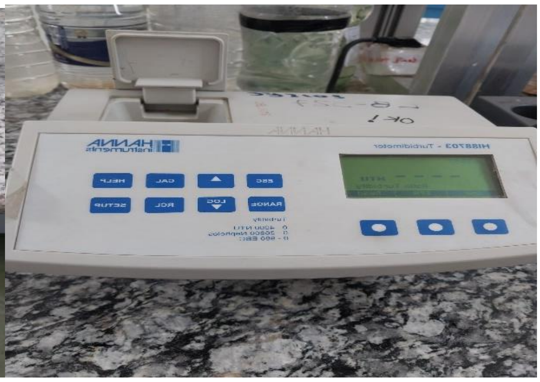
Postgraduate Programs Coordinator

School of Chemical and Bio Engineering, AAiT,AAU

Addis Ababa Institute of Technology | King George VI Street | Addis Ababa | Ethiopia | P.O. Box 385

Fax. 011 - 12 39 480 | info@aait.edu.et | www.aait.edu.et

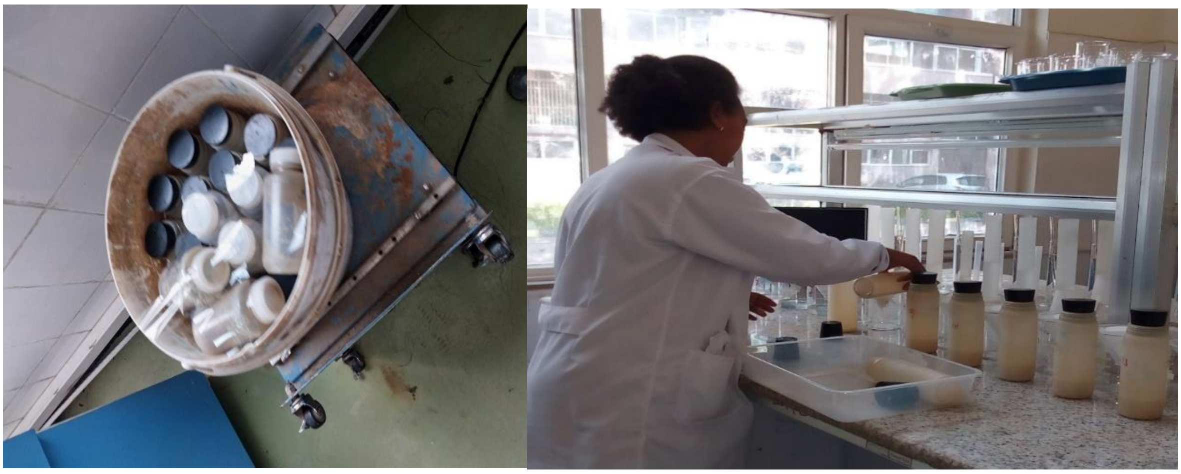
Letter for Collection of Nifassilk Paint Industry Wastewater & Nifassilk Paint Industry equalization tank of Wastewater



pH & Turbidity meter used for test pH of wastewater and turbidity of wastewater respectively.

BOD Incubator & COD analysis of wastewater respectively

**Annex C; Experimental processes for treatment of Nefasesilk paint factory wastewater by MASA adsorbent**

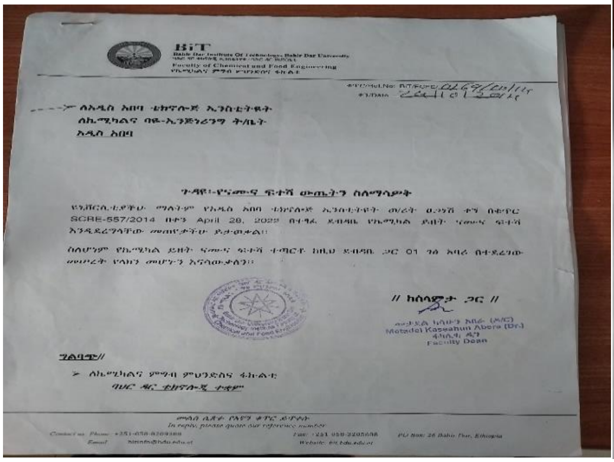


Shaking and filtering treated wastewater samples by MASA adsorbent

MASA adsorbent after treating wastewater sample

Graphite Furnace Atomic Absorption Spectroscopy for reading of Lead metal ion for untreated wastewater sample & wastewater treated by MASA adsorbent

## Annex D; List of Laboratory analysis Results



BiT

Bahir Dar Institute of Technology, Bahir Dar University

Faculty of Chemical and Food Engineering

Metadel Kassahun Abera (Dr.)

Faculty Dean

In reply, please quote our reference number

BiT

Bahir Dar Institute of Technology - Bahir Dar University

Faculty of Chemical and Food Engineering

No:

Date: 2/09/2014

**Term of agreement between the faculty of Chemical and Food Engineering and Tseganesh Qagne**

The faculty has entered to a contract to perform the duties indicated in the table as per the price given below. The following table is the summery yuiof the service to be provided by the faculty with the probable costs for each item. The faculty will commence the work as soon as the payment is due through Bahir Dar University, Engineering faculty A/C 1000013094563.

| S/N | Type of experiment to be conducted | Total required lab hour | Fee per hour | Professional Fee | Utility cost (5%) | Admin cost (15%) | University Fee (10%) | TOTAL |
|---|---|---|---|---|---|---|---|---|
| 1 | BET | 14.00 | 45.00 | 630.00 | 31.5 | 99.225 | 66.15 | 827.00 |
| Grand Total –827.00 | | | | | | | | |

**Prepared by**

Name: Neima Ahmed

Signature

**Approved by**

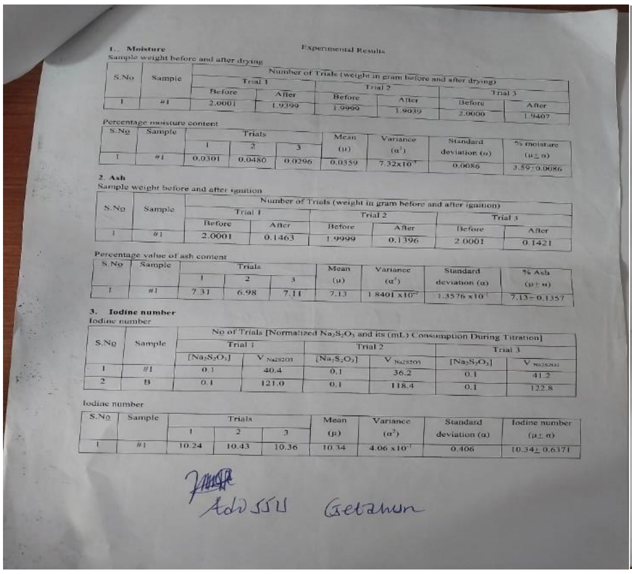
Name Metadel Kassahun ... Dean

Signature

In Reply, Please Quote Our Reference Number

Contact Us: Tel: +251-582-209212 Fax: +251-582-264471 PoB:26 Web: www.bit.bdu.edu.et

Bahir Dar Ethiopia



Experimental Results

**1. Moisture**

Sample weight before and after drying

| S.No | Sample | Number of Trials (weight in gram before and after drying) | | | | | |
|---|---|---|---|---|---|---|---|
| | | Trial 1 | | Trial 2 | | Trial 3 | |
| | | Before | After | Before | After | Before | After |
| 1 | #1 | 2.0001 | 1.9399 | 1.9999 | 1.9039 | 2.0000 | 1.9407 |

Percentage moisture content

| S.No | Sample | Trials | | | Mean (μ) | Variance ($\alpha^2$) | Standard deviation (α) | % moisture (μ ± α) |
|---|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | | | | |
| 1 | #1 | 0.0301 | 0.0480 | 0.0296 | 0.0359 | 7.32x10⁻⁵ | 0.0086 | 3.59±0.0086 |

**2. Ash**

Sample weight before and after ignition

| S.No | Sample | Number of Trials (weight in gram before and after ignition) | | | | | |
|---|---|---|---|---|---|---|---|
| | | Trial 1 | | Trial 2 | | Trial 3 | |
| | | Before | After | Before | After | Before | After |
| 1 | #1 | 2.0001 | 0.1463 | 1.9999 | 0.1396 | 2.0001 | 0.1421 |

Percentage value of ash content

| S.No | Sample | Trials | | | Mean (μ) | Variance ($\alpha^2$) | Standard deviation (α) | % Ash (μ ± α) |
|---|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | | | | |
| 1 | #1 | 7.31 | 6.98 | 7.11 | 7.13 | 1.8401 x10⁻² | 1.3576 x10⁻¹ | 7.13±0.1357 |

**3. Iodine number**

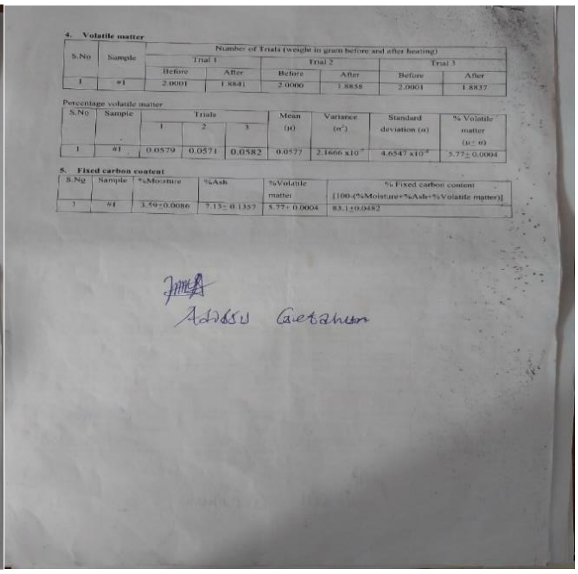
Iodine number

| S.No | Sample | No of Trials [Normalized $Na_2S_2O_3$ and its (mL) Consumption During Titration] | | | | | |
|---|---|---|---|---|---|---|---|
| | | Trial 1 | | Trial 2 | | Trial 3 | |
| | | [$Na_2S_2O_3$] | $V_{Na2S2O3}$ | [$Na_2S_2O_3$] | $V_{Na2S2O3}$ | [$Na_2S_2O_3$] | $V_{Na2S2O3}$ |
| 1 | #1 | 0.1 | 40.4 | 0.1 | 36.2 | 0.1 | 41.2 |
| 2 | B | 0.1 | 121.0 | 0.1 | 118.4 | 0.1 | 122.8 |

Iodine number

| S.No | Sample | Trials | | | Mean (μ) | Variance ($\alpha^2$) | Standard deviation (α) | Iodine number (μ ± α) |
|---|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | | | | |
| 1 | #1 | 10.24 | 10.43 | 10.36 | 10.34 | 4.06 x10⁻¹ | 0.406 | 10.34± 0.6371 |

Addisu Getahun



**4. Volatile matter**

| S.No | Sample | Number of Trials (weight in gram before and after heating) | | | | | |
|---|---|---|---|---|---|---|---|
| | | Trial 1 | | Trial 2 | | Trial 3 | |
| | | Before | After | Before | After | Before | After |
| 1 | #1 | 2.0001 | 1.8841 | 2.0000 | 1.8858 | 2.0001 | 1.8837 |

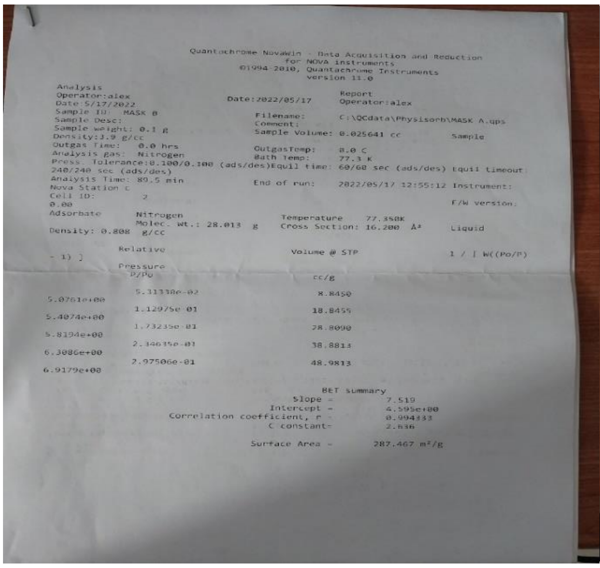
Percentage volatile matter

| S.No | Sample | Trials | | | Mean (μ) | Variance ($\sigma^2$) | Standard deviation (σ) | % Volatile matter (μ ± σ) |
|---|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | | | | |
| 1 | #1 | 0.0579 | 0.0571 | 0.0582 | 0.0577 | 2.1666 x10⁻⁷ | 4.6547 x10⁻⁴ | 5.77± 0.0004 |

**5. Fixed carbon content**

| S.No | Sample | %Moisture | %Ash | %Volatile matter | % Fixed carbon content [100-(%Moisture+%Ash+%Volatile matter)] |
|---|---|---|---|---|---|
| 1 | #1 | 3.59±0.0086 | 7.13± 0.1357 | 5.77± 0.0004 | 83.1±0.0482 |

Addisu Getahun



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Quantachrome NovaWin - Data Acquisition and Reduction
for NOVA instruments
©1994-2010, Quantachrome Instruments
version 11.0

Analysis                                         Report
Operator:alex              Date:2022/05/17       Operator:alex
Date:5/17/2022
Sample ID:  MASK B         Filename:    C:\QCdata\Physisorb\MASK A.qps
Sample Desc:               Comment:
Sample weight: 0.1 g       Sample Volume: 0.025641 cc       Sample
Density:3.9 g/cc
Outgas Time:   0.0 hrs     OutgasTemp:   0.0 C
Analysis gas:  Nitrogen    Bath Temp:    77.3 K
Press. Tolerance:0.100/0.100 (ads/des)Equil time: 60/60 sec (ads/des) Equil timeout:
240/240 sec (ads/des)
Analysis Time: 89.5 min    End of run:   2022/05/17 12:55:12 Instrument:
Nova Station c
Cell ID:       2
0.00                                                         F/W version:
Adsorbate      Nitrogen              Temperature   77.350K
               Molec. Wt.: 28.013 g  Cross Section: 16.200 Å²   Liquid
Density: 0.808 g/cc

              Relative               Volume @ STP            1 / [ W((Po/P)
- 1) ]
              Pressure
                P/Po                   cc/g
              5.31338e-02              8.8450
5.0761e+00
              1.12975e-01              18.8455
5.4074e+00
              1.73235e-01              28.8090
5.8194e+00
              2.34635e-01              38.8813
6.3086e+00
              2.97506e-01              48.9813
6.9179e+00

                        BET summary
                     Slope =            7.519
                 Intercept =            4.595e+00
  Correlation coefficient, r =          0.994333
                C constant=             2.636

              Surface Area =          287.467 m²/g
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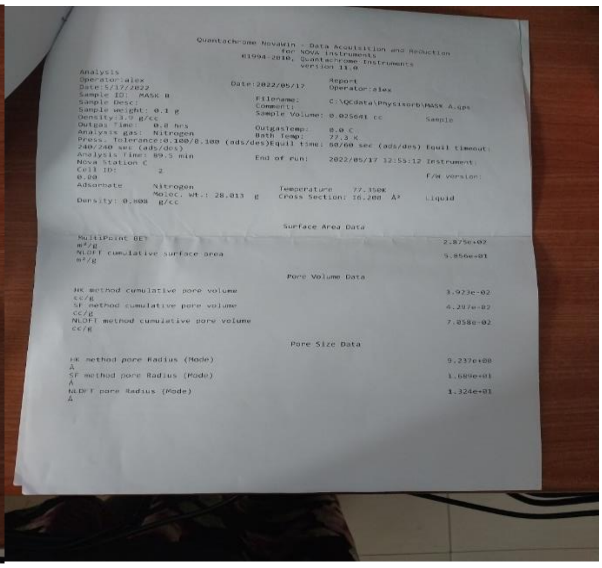

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Quantachrome NovaWin - Data Acquisition and Reduction
for NOVA instruments
©1994-2010, Quantachrome Instruments
version 11.0

Analysis                                         Report
Operator:alex              Date:2022/05/17       Operator:alex
Date:5/17/2022
Sample ID:  MASK B         Filename:    C:\QCdata\Physisorb\MASK A.qps
Sample Desc:               Comment:
Sample weight: 0.1 g       Sample Volume: 0.025641 cc       Sample
Density:3.9 g/cc
Outgas Time:   0.0 hrs     OutgasTemp:   0.0 C
Analysis gas:  Nitrogen    Bath Temp:    77.3 K
Press. Tolerance:0.100/0.100 (ads/des)Equil time: 60/60 sec (ads/des) Equil timeout:
240/240 sec (ads/des)
Analysis Time: 89.5 min    End of run:   2022/05/17 12:55:12 Instrument:
Nova Station C
Cell ID:       2
0.00                                                         F/W version:
Adsorbate      Nitrogen              Temperature   77.350K
               Molec. Wt.: 28.013 g  Cross Section: 16.200 Å²   Liquid
Density: 0.808 g/cc

                        Surface Area Data
MultiPoint BET                                               2.875e+02
m²/g
NLDFT cumulative surface area                                5.856e+01
m²/g

                        Pore Volume Data
HK method cumulative pore volume                             3.973e-02
cc/g
SF method cumulative pore volume                             4.297e-02
cc/g
NLDFT method cumulative pore volume                          7.858e-02
cc/g

                        Pore Size Data
HK method pore Radius (Mode)                                 9.237e+00
A
SF method pore Radius (Mode)                                 1.609e+01
A
NLDFT pore Radius (Mode)                                     1.324e+01
A
```

KIND SOLUTION & CONSULTANCY PLC

Ref. No...... Kind/102/2/2022

Date.............. Sept/20/2022

To: Tseganesh Kegne

Subject: Giving FTIR Analysis Result

Dear Tseganesh,

This is to inform you that our company has performed FTIR analysis for your samples. Attached herewith please find the FTIR analysis result of one of your samples with sample code sample-1 (MASA), as well as the raw data on excel sheet too.



Kind Regards,

Tesfaye Gabriel (PhD)
General Manager

In replying Please Quote Our Reference No & Date
Phone: +251-974-01-22-01; +251-974-01-33-01; +251-118-63-98-81; +251-118-68-30-31
Email: kindsolution2022@gmail.com; Website: www.kindsolutionandconsultancy.com; Office: AA, Yeka Subcity, Megenagna Metebaber Edget Building Office Number 609-B; P.O.Box: 20642

አዳማ ሳይንስና ቴክኖሎጂ ዩኒቨርሲቲ
Adama Science and Technology University

1888 Phone+251-222-11-01-20 Fax: +251-221-100038 Email: kerojemal@gmail.com

Adama, Ethiopia

Date 31 AUG 2023

To Addis Abeba Institute of Technology

Addis Abeba University

Dean, School of applied Natural Science

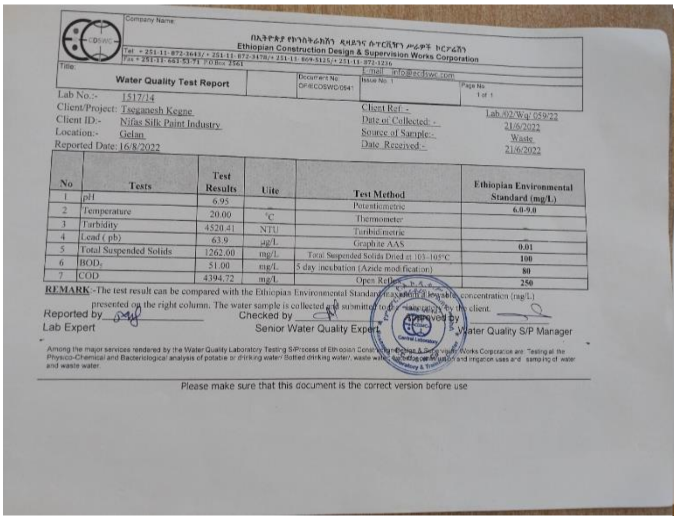
Kero Jemal Adem( Ph.D)

Subject Attestation of Payment

Teganesh Kegna, a staff AAiT, Addis Abeba University, has requested the Department of Applied Biology to provide her of an attestation letter for the payment paid for SEM service here at the department of Applied Biology, ASTU. The Department witnesses that the service was provided for three samples (as per the attached receipt), which was 1800 birr in total.

Regards

Kero Jemal Adem (PhD)
Dean,School of Applied Natural Science



Ethiopian Construction Design & Supervision Works Corporation

Tel +251-11-872-3643/+251-11-872-3478/+251-11-869-5125/+251-11-872-1236
Fax +251-11-661-53-71 P.O.Box 2561
E-mail info@ecdswc.com

Water Quality Test Report — Document No: OF/ECOSWC/0941 — Issue No. 1 — Page No 1 of 1

Lab No.:- 1517/14
Client/Project: Tseganesh Kegne
Client ID:- Nifas Silk Paint Industry
Location:- Gelan
Reported Date: 16/8/2022

Client Ref:- Lab/02/Wq/059/22
Date of Collected:- 21/6/2022
Source of Sample:- Waste
Date Received:- 21/6/2022

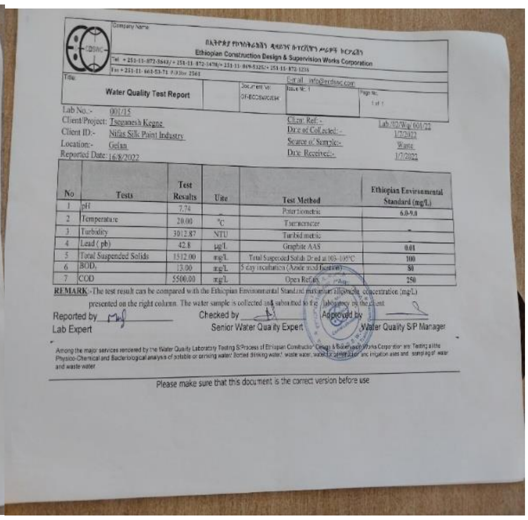
| No | Tests | Test Results | Uite | Test Method | Ethiopian Environmental Standard (mg/L) |
|---|---|---|---|---|---|
| 1 | pH | 6.95 | - | Potentiometric | 6.0-9.0 |
| 2 | Temperature | 20.00 | °C | Thermometer | |
| 3 | Turbidity | 4520.41 | NTU | Turibidimetric | - |
| 4 | Lead ( pb) | 63.9 | µg/L | Graphite AAS | - |
| 5 | Total Suspended Solids | 1262.00 | mg/L | Total Suspended Solids Dried at 103-105°C | 0.01 |
| 6 | $BOD_5$ | 51.00 | mg/L | 5 day incubation (Azide modification) | 100 |
| 7 | COD | 4394.72 | mg/L | Open Reflux | 80 |
| | | | | | 250 |

REMARK:-The test result can be compared with the Ethiopian Environmental Standard maximum allowable concentration (mg/L) presented on the right column. The water sample is collected and submitted to the laboratory by the client.

Reported by Lab Expert — Checked by Senior Water Quality Expert — Approved by Water Quality S/P Manager

Among the major services rendered by the Water Quality Laboratory Testing S/Process of Ethiopian Construction Design & Supervision Works Corporation are: Testing all the Physico-Chemical and Bacteriological analysis of potable or drinking water/ Bottled drinking water/, waste water, water for construction and irrigation uses and sampling of water and waste water.

Please make sure that this document is the correct version before use



Ethiopian Construction Design & Supervision Works Corporation

Water Quality Test Report

Lab No.:- 001/15
Client/Project: Tseganesh Kegne
Client ID:- Nifas Silk Paint Industry
Location:- Gelan
Reported Date: 16/8/2022

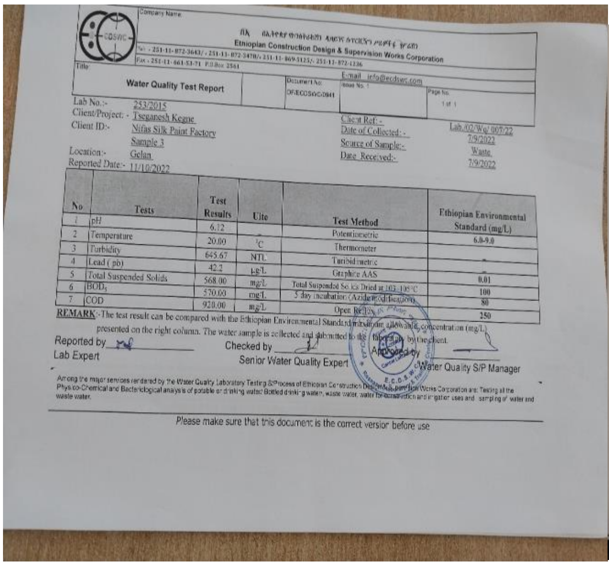
Client Ref:- Lab/02/Wq/001/22
Date of Collected:- 1/7/2022
Source of Sample:- Waste
Date Received:- 1/7/2022

| No | Tests | Test Results | Uite | Test Method | Ethiopian Environmental Standard (mg/L) |
|---|---|---|---|---|---|
| 1 | pH | 7.74 | - | Potentiometric | 6.0-9.0 |
| 2 | Temperature | 20.00 | °C | Thermometer | - |
| 3 | Turbidity | 3012.87 | NTU | Turbidimetric | - |
| 4 | Lead ( pb) | 42.8 | µg/L | Graphite AAS | 0.01 |
| 5 | Total Suspended Solids | 1512.00 | mg/L | Total Suspended Solids Dried at 103-105°C | 100 |
| 6 | $BOD_5$ | 13.00 | mg/L | 5 day incubation (Azide modification) | 80 |
| 7 | COD | 5500.00 | mg/L | Open Reflux | 250 |

REMARK:-The test result can be compared with the Ethiopian Environmental Standard maximum allowable concentration (mg/L) presented on the right column. The water sample is collected and submitted to the laboratory by the client.

Reported by Lab Expert — Checked by Senior Water Quality Expert — Approved by Water Quality S/P Manager

Please make sure that this document is the correct version before use



Ethiopian Construction Design & Supervision Works Corporation

Water Quality Test Report

Lab No.:- 253/2015
Client/Project: - Tseganesh Kegne
Client ID:- Nifas Silk Paint Factory Sample 3
Location:- Gelan
Reported Date:- 11/10/2022

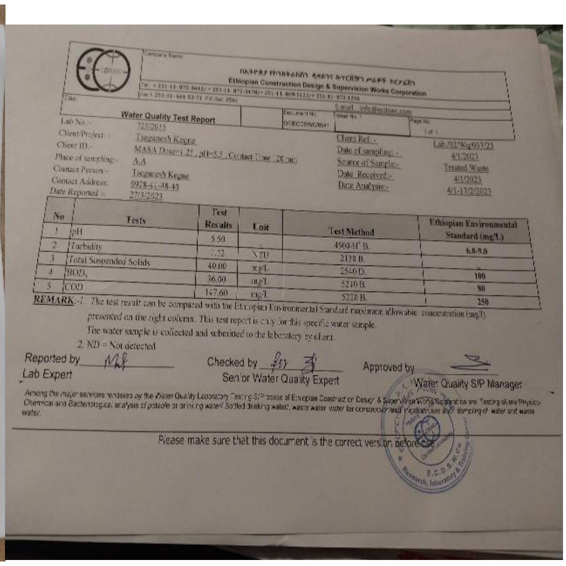
Client Ref:- Lab/02/Wq/007/22
Date of Collected:- 7/9/2022
Source of Sample:- Waste
Date Received:- 7/9/2022

| No | Tests | Test Results | Uite | Test Method | Ethiopian Environmental Standard (mg/L) |
|---|---|---|---|---|---|
| 1 | pH | 6.12 | - | Potentiometric | 6.0-9.0 |
| 2 | Temperature | 20.00 | °C | Thermometer | - |
| 3 | Turbidity | 645.67 | NTU | Turibidimetric | - |
| 4 | Lead ( pb) | 42.2 | µg/L | Graphite AAS | 0.01 |
| 5 | Total Suspended Solids | 568.00 | mg/L | Total Suspended Solids Dried at 103-105°C | 100 |
| 6 | $BOD_5$ | 570.00 | mg/L | 5 day incubation (Azide modification) | 80 |
| 7 | COD | 920.00 | mg/L | Open Reflux | 250 |

REMARK:-The test result can be compared with the Ethiopian Environmental Standard maximum allowable concentration (mg/L) presented on the right column. The water sample is collected and submitted to the laboratory by the client.

Reported by Lab Expert — Checked by Senior Water Quality Expert — Approved by Water Quality S/P Manager

Please make sure that this document is the correct version before use



Ethiopian Construction Design & Supervision Works Corporation

Water Quality Test Report

Lab No.:- 723/2015
Client/Project:- Tseganesh Kegne
Client ID.- MASA Dose=1.25, pH=5.5, Contact Time (20 min)
Place of sampling:- A.A
Contact Person:- Tseganesh Kegne
Contact Address: 0928-41-48-43
Date Reported:- 27/3/2023

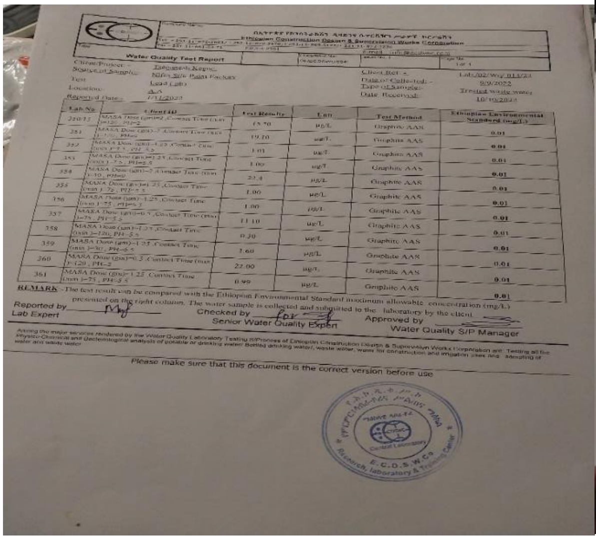
Client Ref:- Lab/02/Wq/037/23
Date of sampling:- 4/1/2023
Source of Sample:- Treated Waste
Date Received:- 4/1/2023
Date Analysis:- 4/1-17/2/2023

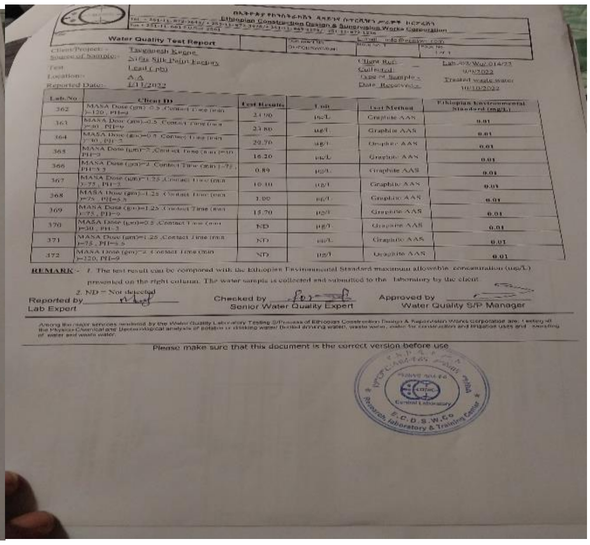
| No | Tests | Test Results | Unit | Test Method | Ethiopian Environmental Standard (mg/L) |
|---|---|---|---|---|---|
| 1 | pH | 5.50 | - | 4500-H⁺ B. | 6.0-9.0 |
| 2 | Turbidity | 7.12 | NTU | 2130 B. | - |
| 3 | Total Suspended Solids | 40.00 | mg/L | 2540 D. | 100 |
| 4 | $BOD_5$ | 36.00 | mg/L | 5210 B. | 80 |
| 5 | COD | 147.60 | mg/L | 5220 B. | 250 |

REMARK:-1. The test result can be compared with the Ethiopian Environmental Standard maximum allowable concentration (mg/l) presented on the right column. This test report is only for this specific water sample. The water sample is collected and submitted to the laboratory by client.
2. ND = Not detected

Reported by Lab Expert — Checked by Senior Water Quality Expert — Approved by Water Quality S/P Manager

Please make sure that this document is the correct version before use





**Annex E; Pictures that are taken from the design expert analysis (Centeral Composite Design under Response methodology)**

The effects of main effects on the response