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PHYSICO-CHEMICAL CHARACTERIZATION OF RWANDAN LIMESTONE AND ASSESSMENT OF ITS ADSORPTION CAPACITY AS ALTERNATIVE SOLUTION FOR WASTEWATER TREATMENT.

A dissertation submitted to the Department of Chemistry, School of Science, College of Science and Technology, University of Rwanda, in partial fulfillment of the requirements for the Degree of Masters of Science in Environmental Chemistry.

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Kigali, September 2024

DECLARATION AND COPYRIGHT

I, **UMUTONI Ange,** hereby declare that, this master dissertation entitled ***"physico-chemical characterization of Rwandan limestone and assessment of its adsorption capacity as alternative solution for wastewater treatment."*** is my own original work. It is submitted at the University of Rwanda for partial fulfilment for the award of the Degree of Masters in Environmental Chemistry of the University of Rwanda. This dissertation has never been submitted and will not be submitted elsewhere for any other award of a degree or academic certificate.

Student:

UMUTONI Ange Date: / /2024 Signature:

Supervisor(s):

We supervisors of this master dissertation, confirm for its originality and that it has been submitted for examination with our approval.

Dr. Jean Nepo HAKIZIMANA Date: / / 2024 Signature:

DEDICATION

I dedicate this work to

My husband MUBERANGABO Martin

My elder sister UMUMARARUNGU Anitha

My brother HAKIZAYEZU Gerard

My younger sister UWACU Emma

My Mother who died early without seeing this great achievement

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ABSTRACT

The adsorption of heavy metals using materials that are readily available at a low cost is the core of this research. Different studies raveled high quality limestone as an excellent adsorbent for heavy metals in wastewater. Limestone taken from two sites in Rwanda (Gishyita and Mpenge limestone deposits) was characterized by determining its physical and chemical composition; thereafter, it was used to remove the selected heavy metals (Pb, Cd, Zn, and Cu) from synthetic wastewater. To determine the impact of adsorbent particle size and dosage, contact time, varying heavy metal concentrations, pH, and temperature, batch adsorption studies were conducted. This research included the study of adsorption isotherms, kinetics, and thermodynamics.

The elemental characterization of the adsorbent was done by XRF. Following the adsorption procedures, the content of these chosen heavy metals in wastewater was assessed using MP-AES. The adsorption studies revealed that Pb, Cd, Cu and Zn were removed to an extent greater than 78.3%, 75%, 65% and 57% respectively, with a dose of 3.5 g while the particle size ranged between 0.1 and 3.5 mm. The optimum contact time was 15 minutes for Pb, 120 minutes for Cd and Cu and greater than 180 minutes for Zn. Moreover, the optimum pH for adsorption was 5, while that for Cd, Cu and Zn was 6. The outcome from isotherm experiments demonstrated that the Pb adsorption was highly suitable for Freundlich, Cd was fitted with the Langmuir adsorption model, and the adsorption of Zn showed no significant difference between the models for Freundlich and Langmuir isotherms. According to the adsorption kinetic results, the pseudo-first-order model greatly promoted the adsorption of Pb, Cd, Cu and Zn. In the thermodynamic study, the standard enthalpy change ($-\Delta H^o$) was negative, impressing the exothermic reaction, while the negative standard free energy ($-\Delta G^o$) indicated a favorable and spontaneous process. According to the results, the Gishyita and Mpenge limestone might be utilized as alternatives for removing Pb,Cd, Cu and Z from wastewater.

Key words: Natural limestone, Rwanda, Heavy metal, Adsorption capacity, adsorption isotherm, adsorption kinetics, thermodynamic study.

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LIST OF ABBREVIATIONS

Ce: equilibrium concentration

Co: initial concentration

$GA_{1:}$ Cleaned Gishita limestone

GA_2: Uncleaned Gishyita limetone

LSS: Limestone sample

MA_1: Cleaned Mpenge limestone

MA_2: Uncleaned Mpenge limestone

m: mass

M: Molarity ml: milliliter

MP-AES: Microwave Plasma- Atomic Emission Spectrophotometer

pH: Hydrogen Potential ppm: parts per million

qe: amount of metal ion adsorbed by adsorbent

rpm: rotation per minute

v: volume

WHO: World Health Organization

XRF: X-ray fluorescence

CHAPTER 1: INTRODUCTION

1.1. Background

There are several methods for water and wastewater treatment to remove different pollutants; these include electrochemical treatment, coagulation-flocculation, adsorption, ion exchange processes, reverse osmosis, bioremediation, solvent extraction, chemical precipitation, and membrane processes. Adsorbent cost, use of industrial, biological, and household waste as adsorbents, ease of availability, low operational costs, ease of operation compared to other processes, ability to reuse adsorbents after regeneration, capacity to remove heavy metal ions over a wide pH range, ability to remove complex forms of metals that are typically not possible by other methods, and environmental benefits are just a few of the advantages the adsorption process has over other technologies. [1, 2, 3].

There are several types of adsorbents that have being utilized for contaminants accumulation, such as activated carbon, silica gel, and activated alumina, Tannins and Moringa as well as phosphate minerals, volcanic rocks and different types of clays but their application is constrained due to their high costs [4]. Even though it is evident from the literature that significant efforts have been put into identifying acceptable heavy metal adsorbents, more work has to be focused on locating affordable and effective adsorbents that can be employed in developing nations. Limestone rocks may meet these specifications [5]. Limestone rocks are mostly available in the Western (Karongi and Rusizi districts) and Northern (Musanze district) parts of Rwanda and with smaller quantities being present in the Gakenke and Rulindo districts [6, 7, 8].

Due to their favourable characteristics, availability in various Rwandan location, high specific surface area, law cost and greater capacity and affinity for different heavy metals sorption from water and wastewater than other commercial adsorbents, limestone rocks have attracted a lot of attention in the past for the removal of heavy metals [9].

By using limestone rocks as adsorbents, lead, cadmium, copper and zinc were removed from synthetic wastewater in this study.

This study's objective was to characterize the Gishyita and Mpenge limestone and look into limestone's ability to remove contaminants from wastewater. To ascertain the effects of pH, adsorbent particle size and dosage, various heavy metal concentrations, contact time, pH, and temperature, several experimental settings were used. Moreover, to analyse the experimental data and to explain the adsorption process, adsorption isotherms, kinetic, and thermodynamic parameters were used.

1.2. Problem statement

Safe plentiful water for drinking or potable uses is an important need for public health. The availability of water globally is questionable in different countries. Similar to other nations in the region, Rwanda suffers from deficiency and limitations of safe freshwater resources needed to meet society's needs. The majority of untreated, contaminated water is likely to be characterized by heavy metals including Lead (Pb), Cadmium (Cd), Copper (Cu), and Zin as well as high pH.

This is mostly caused by different manufacturing industries, the car garage activities as well as the house hold and agricultural activities that release wastewater containing paints and oil as well fertilizers and pesticides in the nearby livers, drainages and swamps. So that surface and groundwater used for many household activities, including cooking, drinking, swimming, fishing, and irrigation, would become contaminated as a result [10, 11].

Other investigations revealed that metal ions contained in water and waste bio-accumulate in fish and plant tissues before being transferred to people and other animals. Some of them like Pb and Cd are teratogens as well as carcinogens to humans, having harmful effects on the kidneys, liver, lungs, and reproductive organs. They may result in renal failure and possibly mortality depending on the exposure period and dose. Most of the national organizations are making efforts to develop cost-effective, efficient, and technologically sound methods for producing sustainable, safe, and clean potable water and for environmental protection at the same time by using different treatment substances like hydrated lime treatment technology, which is an expensive technology. The cost of lime treatment is maximized by the preparation of lime from natural limestone [12, 13].

In Rwanda, we have limestone as a natural resource available in different areas, including the Gishyita deposit in Karongi district, Mpenge limestone in Musanze and Mashyuza deposit in Rusizi District. But, there is no knowledge about the capacity of limestone for water treatment. Therefore, this has been the benchmark for thinking on this research to express that limestone may be an alternative solution to economic and technologically sound wastewater treatment methods for better human health and a sustainable environment [14]. The target was to show that the use of limestone is highly effective according to its efficiency and favourable cost as well as it require less technology for wastewater treatment [15].

1.3. Objectives of the research

1.3.1. Main objective

In order to significantly enhance water quality, this study attempted to characterize and ascertain the ability of Gishyita and Mpenge limestone on wastewater treatment under various experimental settings.

1.3.2. Overarching objectives

1. To characterize the Gishyita and Mpenge limestone by determining their cation exchange capacity, particle density, bulk density, porosity and chemical composition.

2. To determine the effectiveness level of limestone on acidity neutralization and its capacity for the adsorption of selected heavy metals (Pb, Cd, Cu and Zn) from synthetic wastewater.

3. To ascertain the limestone's adsorption isotherm models and capacity for Pb, Cd, Cu, and Zn.

1.4. Research questions

The following research questions were used to lead our study:

- What are the physical characteristics such as the cation exchange capacity, particle density, bulk density, and porosity and chemical composition (in concentrations) of Mpenge and Gishyita limestone?
- To what extent is limestone able to reduce the acidity and remove heavy metals in wastewater?
- What is the adsorption capacity and adsorption isotherm models of the Gishyita and Mpenge limestone?

1.4. Significance of the study

This study has a lot of benefits and outcomes. Firstly, it show that limestone could be an alternative solution for sustainable, safe, and clean drinking water as well as wastewater treatment for reuse and be ready for disposal [16]. Limestone water treatment technology is a cost-effective and less complex method, so it will be a solution for sustainable potable water in rural areas and agglomerations. It will be a solution for diseases such as diarrhea, cholera, intestinal parasites and malnutrition in children caused by a lack of adequate safe water supply, especially in Rwandan rural and agglomeration areas [17].

Again, it will be a solution for effluents from manufacturing industries, the car garage activities as well as the house hold and agricultural activities that are likely to contaminate the nearby livers, drainages and swamps resulting in the toxification of water for cooking, drinking, swimming, fishing, and irrigation as well as their product [10, 18].

Additionally, this research demonstrates how the use of limestone, a naturally occurring mineral found in Rwanda, for water and wastewater treatment may be a strategic means of advancing Rwanda's Vision 2050 goals for sustainable, clean and safe water as well as implementation of the National Strategy for transformation (2018-2024).

Finally, it will be an expertise for developing new case studies to be included in the interdisciplinary research field, providing benefit to academic scholars interested in creative ways to publish in strong journals.

1.5. Scope and delimitation

In this research, the physical-chemical characteristics of Rwandan natural limestone was assessed. The chemical composition, cation exchange capacity, back density, porosity, and particle density was all considered.

Then after, limestone capacity on water and wastewater was examined by applying it on acidity neutralization, selected heavy metals removal and nutrient regularization. This was accomplished by concentrating on (i) Adsorption capacity assessment, (ii) Effect of pH on adsorption, (iii) Effect of adsorbent on pH, (iv) Effect of contact time, (v) Effect of temperature, (vi) adsorption kinetics, isotherms and adsorption kinetics.

Its capacity was recorded and expressed in parentage. This dissertation was conducted at the UR-CST chemistry laboratory based at Nyarugenge campus. It was based on synthetic samples, and the library essentially provides written information about the sample description, handling, and analysis.

It is subdivided into five chapters: chapters: Chapter one is devoted to introduction, and the second chapter is to a literature review, Chapter three is devoted to research methodology and then the fourth Chapter entail the results and discussion while the fifth is devoted to conclusion and recommendations.

CHAPTER 2: LITERATURE REVIEW

2.1. Characterization of water

Depending on the intended use of water, different individuals have varied ideas of what water quality means. An angler views the high quality water as an ideal home for fish and other aquatic life. A farmer, on the other hand, may prefer water with moderate levels of nutrients, such as nitrogen and phosphorus, but may prefer water with minimal sodium or other dissolved salts that could degrade the soil or be hazardous to crops. Therefore, a comprehensive understanding of high quality water takes into account the suitability of its specific purposes.

Pure water is naturally transparent. As the concentration of polluting agents like ions, dyes, etc. increases, water becomes more turbid and polluted

The assessment and adjustment of quality of water by chemical analyses use the parameters like temperature, pH, total hardness, biological oxygen demand, chemical oxygen demand, total dissolved solids, total suspended solids, turbidity, color, alkalinity, chlorides, sulfates, carbonates, bicarbonates, magnesium, calcium, sodium, potassium, nitrate, nitrite, phosphate, oil and grease, conductivity, as well as dissolved oxygen [19].

Table 2.1. Physico-chemical requirements for potable water [20, 21]

Parameter	**Untreated portable water (max limit)**	**Treated portable water(max limit)**
Color (UTCU)	15	50
Turbidity (NTU)	5	25
Ph	6.5-8.5	5.5-9.5
Conductivity	1500	2500
Total dissolved solids (mg/l)	1000	1500
Total suspended matter (mg/l)	No detectable	No detectable
Total heavy metals	≤ 10	≤ 10
Total hardness	300	600

Table 2.2. Dischargeable standards for industrial into water bodies (maximum permissible limits)[22, 21].

Parameter	Permissible limits
Total suspended solids	**50**
Total dissolved solids	**2000**
Oil and grease	**10**
Ph	**5-9**
BOD_5	**50**
COD	**250**
Total heavy metals (mg/g)	**$\leq$ 10**

2.2. Characterization of limestone

The sedimentary rock called limestone, also known as calcium carbonate ($CaCO_3$) is the primary source of the substance lim. It has a density of 2.6 to 2.8 g/cm^3. The sedimentary rock known as limestone, also known as calcium carbonate (CaCO3), is the primary source of the substance lime. Its density ranges from 2.6 to 2.8 g/cm3.

There exist two kinds of limestone such as high calcite/ calcium limestone which is almost entirely calcium and dolomitic limestone which contains a large amount magnesium along with calcium carbonate at about 59.03 wt. % $CaCO_3$ and 40.69 wt. % $MgCO_3$. Its capacity on water and wastewater treatment increase as the amount of calcium content increases [23, 24].

The researchers showed that he deposits of limestone in Rwanda is more concentrated in the Northern and Western provinces but mostly in Northern province region for the average above 40% [6].

2.3. Heavy metals impact on the environments

A "heavy metal" is any metallic element that has a relatively large density and is poisonous or hazardous even in small amounts. Several of them are non-biodegradable inorganic metals which can be teratogenic and carcinogenic at any concentration.

Most of them, like Pb (II) and Cd (II),are frequently found in wastewaters from mining, battery, auto repair, and paint industries. These metals are dangerous pollutants because they tend to spread widely through the environment via their uses. Since they are harmful contaminants, careful treatment is necessary before wastewater discharge into the environment [25].

2.4. Heavy metals occurrence and toxicity

Every aspect of the environment, naturally contains heavy metals. In contrast to other heavy metals that are introduced to natural waters by domestic and industrial waste streams and by agricultural runoff, particularly in areas where phosphate fertilizer has been applied, they participate in bio-geochemical reactions and can be transported between environmental compartments by natural processes, primarily by anthropogenic activities

Metals can also be transferred as a direct result of human activity or as a byproduct, such as through erosive or dissolving natural weathering processes. Metals, for instance, are removed from rocks and soils by acid mine drainage. Additionally, Pb is released through automobile exhaust pipes while Cd and Zn oxides are vaporized and released into the environment during the smelting process. Through atmospheric washing, metals enter water systems. As heavy metals enter natural aquatic systems, they can go through a number of changes that lead to the speciation of dissolved metals, including precipitation and oxidation/reduction, which can significantly change the mobility of the metals [25].

The toxicity of heavy metals enters all every trophic level through the food web. Cadmium (Cd) as one of extremely toxic metals, can enter the soil or the air from the burning of fossil fuels or municipal trash, which pollutes the environment and harms the ecosystem.

In the case of oral intoxication or inhalation in humans may result in issues with the kidneys and respiratory system.

A significant amount of cadmium (Cd) can case acute poisoning, damage to the liver and kidneys, and even alter gene expression. A higher concentration of lead ions in the blood causes memory loss, a rise in blood pressure, fertility issues, nerve diseases, muscle and joint discomfort, and an increase in irritability in addition to Cadmium [26].

2.5. Heavy metals removal technologies

Solvent extraction, chemical precipitation, ion exchange, chelation, reverse osmosis, coagulation-precipitation, electrochemical operation, and others are among the physical and chemical procedures used to remove heavy metal ions from contaminated water or the environments. These mentioned techniques each have benefits and drawbacks [27, 28].

Some of them are mentioned as follows:

1. Chemical precipitation

The precipitant substance, such as lime or calcium carbonate, and the metal ions interact chemically to cause this to happen. Sulphide ion precipitation is more frequently utilized to remove harmful heavy metals from industrial waste effluents. Precipitation uses a lot of chemicals and creates a lot of sludge, which creates environmental issues when they are disposed of [25].

2. Ion exchange

The ability to exchange cations between the materials and the wastewater is specifically the foundation of the ion exchange method. Alumina, carbon, and silicates are a few examples of natural materials that may be employed, while other materials are synthetic (zeolites and resins).

Zeolites are the most often utilized among them in the ion exchange process. Cations and anions are exchanged in an aqueous medium using an ion exchanger as part of the ion exchange process.

The ion exchange process used in this approach is non-selective, and it has the drawbacks of being extremely sensitive to the pH of the solution. Moreover, handling concentrated metal solutions presents challenges [29].

3. Adsorption

Adsorption is a surface phenomenon that is characterized by the concentration of adsorbate from its vapor phase or from a solution near the adsorbent. The surface excess occurs when the attractive energy of a substance with the solid surface (adhesive work) is greater than the cohesion energy of the substance itself. Adsorbent is the substance at whose surface adsorption occurs, whereas adsorbate is the substance that concentrates at the surface. Adsorption is an environmentally friendly strategy since it utilizes various wastes that could harm the environment to address other environmental problems [28].

a. Types and characteristics of adsorbents

According to the source [30, 31] , adsorbents can generally be divided into three categories:

i. Natural adsorbents: Such adsorbents can be found in nature in the form of zeolites, clay minerals, charcoal, red mud, silt and soil, ore minerals, etc. They are easy to obtain and are in plentiful quantity. They are easily adaptable, which raises their capacities for absorption.

ii. Synthetic adsorbents: These adsorbents are created using a variety of raw material, including sewage sludge, agricultural waste, household waste, industrial waste, and polymeric adsorbents. They are expensive in comparison to natural adsorbents.

iii. Bio-adsorbents: The majority of agricultural and plant wastes are utilized as bio- adsorbents in the treatment of wastewater. Agricultural waste is promising bio-adsorbents, including potato peels, sawdust, mango peels, citrus peels, almond shells, tea waste, dried parthenium powder, sugarcane bagasse, peanut shells, sunflower stalks, banana peels, rice husks, maize cobs, and black gram husk.

b. Factors affecting the adsorption process [32]

(i) Temperature: At higher temperatures heavy metals removal is typically more effective. Over the range of temperatures that are actually encountered in water and wastewater, temperature impacts on adsorption are typically not significant. As a result, minor temperature change has little impact on the adsorption process.

(ii) pH: Adsorption is affected to a certain extent by the pH of the liquid from which it takes place. Since, hydrogen and hydroxide ions are adsorbed quite strongly, the adsorption of other ions is influenced by the pH of the solution. In addition, the concentration of H3O + ions are high at low pH and they compete with metal ions in the solution for the active sites on the adsorbent material and hence reducing adsorption capacities of the adsorbents.

(iii) Adsorbent surface area: Adsorption grows with increased surface area since it is a surface phenomenon. The adsorption efficiency will therefore rise for each large molecule with large surface area.

(iv) **Adsorbent dose:** It is a way to gauge how much adsorbent is being used to absorb metals. This relies on how many sorption are present on the adsorbent's surface. By producing solutions with set metals concentrations and altering pH adsorbent dosage, the experiment can be carried out. The rate of adsorption increases with increasing adsorbent dosage, and vice versa.

(v) Initial Concentration: The experiment can be performed by preparing solutions with fixed adsorbent dosage and pH with varying heavy metals concentrations. The adsorption depends on the vacant binding sites on the surface of the adsorbent. The rate of adsorption is higher when the metals concentration is low and vice versa.

(vi) Contact time: It gauges how long the adsorbent and adsorbate are in direct contact with one another. You can do the experiment by making a solution with constant adsorbent dosage, adsorbate concentration, and pH while permitting varying adsorbent and adsorbate contact times.

2.6. The basis of limestone treatment

Wastewater is typically treated before being discharged into the environment to reduce the concentration of environmental contaminants, such as heavy metals and other inorganic and organic components, to the level permitted by environmental regulations.

It has been demonstrated that limestone could be one of the economically viable waste water treatment methods [33, 34]. Natural limestone mainly uses the method of binding adsorption on heavy metals removal. Calcite and magnesium make up the majority of limestone chemical and physical composition, although it also contains varying amounts of san, silt and clay impurities. Based on the outcomes of these properties assessments, the best effective option was chosen. One of the most common applications for limestone is the elimination of BOD, COD, and toxic metals from sewage while also modifying acid water to be acceptable for other uses.

Limestone reacts with acidity in water to return it into alkalinity by the following equation:

$$\mathrm{CaCO3} + H^{+} \rightarrow Ca^{2+} + HC0_{3}^{-}$$

Limestone dissolved in wastewater give water with high pH so that the basicity heavy and trace metals is removed [35, 34]. Different systems had achieved that limestone increase the pH and also different metals such as Al, Cu, As, Pb, Fe, Zn, Cu, Ni, Co and Cd precipitate and/or bind, then removed to the level above 80% [36]. In addition, limestone can remove from water Nitrate (NO_3^{2-}) and phosphate ions (PO_4^{3-}) as the agent of eutrophication in water bodies as well as COD and BOD removal as well as the adjusting of the physical parameters including the total Suspended solids , Total Dissolved Solids and Turbidity [37].

2.7. Isotherm determination

Adsorption isotherms are useful for the characterization of how the heavy metal ions concentrations interact with the surface of limestone adsorbent. This can help to improve the sorbent surface for the removable heavy metal ions. They are one of the basic requirements to understand adsorption systems. Additionally, the values of the isotherm constants can be used to forecast the maximum adsorption capacity and to explain the affinity and surface characteristics of the adsorbent [38]. This study was conducted with 3.5 g of adsorbent in 100 ml of solution, a contact time of 120 minutes, and a pH of 6 at room temperature while varying the concentration of heavy metals from 2 to 12 ppm. Although we distinguish between several adsorption isotherms, the major applicable isotherm models are thought to be the Langmuir and Freundlich isotherm models.

a. Langmuir isotherm

The maximum capacity of the adsorbent is calculated from complete monolayer coverage of the adsorbent surface according to the Langmuir adsorption isotherm, which quantitatively explains the creation of monolayer coverage of the adsorbate onto the surface of the adsorbent. The following is the linear equation for the Langmuir isotherm.

$$\frac{1}{Q_e} = \frac{1}{Q_m} + \frac{1}{K_L Q_m C_e}$$

Where Q_e represents the amount adsorbed at equilibrium time (mg/g), $\mathbf{Q_m}$ is maximum adsorption capacity (mg/g), $\mathbf{K_L}$ is Langmuir constant (L/mg), and $\mathbf{C_e}$ is the concentration of heavy metals in solution at equilibrium time (mg/L).

The dimensionless equilibrium parameter (R_L) is expressed as $\mathbf{R_L} = \frac{1}{1+K_L C_0}$ where R_L is the dimensionless equilibrium constant that shows the nature of adsorption and its value lies in the range of 0-1, The Langmuir equilibrium constant was obtained by the plot of $\frac{1}{qe} vs\ 1/Ce$ which can be expressed by a separation factor. depending on the magnitude of R_L , the isotherms are either irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear (R_L,=0) or unfavorable $R_L > 1$ [38].

The adsorption capacity (qm) might be calculated thanks to the Langmuir model's linear plot. The outcomes are shown in the following table 4.9 and figure 4.7.

b. Freundlich isotherm

For single layer adsorption onto heterogeneous surfaces in a non-ideal system, the freundlich isotherm model provided an empirical adsorption relation [38].

The formula is provided as follows,

$\boldsymbol{log\ q_e = \frac{1}{n} log C_e + log\ K_f}$ **,** Where $\boldsymbol{K_f}$ is Freundlich constant (L/g) and $\boldsymbol{n}$ is Freundlich exponent. The values of these constants can be derived using the Freundlich model's linear plot ($\log qe\ vs \log Ce$. where, 1/n represents the slope and $\log K_f$ represents the intercept**.**

2.8. Adsorption kinetics and thermodynamics

Two kinetic models, pseudo-first order and pseudo-second order models were used to determine the adsorption rate and mechanism of adsorption reactions. [39].

The pseudo first-order equation for the kinetic process of liquid-solid phase adsorption will be determined by the general statement expression: $\frac{dq_t}{d_t} = K_1(q_e - q_t)$

The linear form of the equation is written as $\ln(qe - qt) = lnqe - K_1\, t$, where qe and qt are the amounts (mg/g) of adsorbed material at equilibrium and time t, respectively. First order rate constant (min^{-1}) is K_1. The slope and intercept of the linear plots of $\ln qe(qe - qt)$ at various concentrations were used to derive the values of K_1 and qe.

$q_t = 0$ at t=0 , $q_t = q_e$ when $t = t_e$

When toxic metals occur in two steps, the first step being a sharp increase in solute removal during the first contact time between the solution and solid phase and the second step being a slow increase until equilibrium was reached and was described by the pseudo-second order kinetic model.

$\frac{q_t}{d_t} = K_2(Q_e - Q)^2$, Where K_2 is the second-order adsorption rate constant (g/mg.min). The equation in linear form is given by:

$$\frac{1}{Q} = \frac{1}{k_2 Q_e^{\,2} t} + \frac{1}{Q_e}$$

After integrating the aforementioned equation with the boundary conditions t = 0 to t = t and q = 0 to q = q, we obtain:

If the second – order kinetic theory is used, the plot of 1/q versus 1/t to get a linear relationship from which the slop and intercept of the curve can be used to get q_e and k_2.

$$\mathbf{h} = \mathbf{k_2 Q_e^2}$$

CHAPTER 3: RESEARCH METHODOLOGY

3.1. Sampling and sample preparation

a) sampling

The limestone and synthetic wastewater were used. Limestone rocks was taken from two sites, such as the Mpenge limestone deposit in Musanze district and the Gishyita limestone deposit in Karongi district. Wastewater samples was synthesized in the laboratory.

b) Preparation of limestone adsorbent

Both cleaned and uncleaned samples was used. To remove dusts, the limestone rocks was crushed into small particles using a mortar and pestle to obtain roughly 0.1-6.5 mm particle sizes, then the substance was washed in distilled water while being stirred at 200 rpm for 30 minutes. After cleaning within 12 hours the substance material was dried at 105 °C in oven. Thereafter, it was branded as “limestone sample(LSS)". [40, 41] .

c) Wastewater synthesis

By dissolving heavy metals salts in distilled water to a concentration of 1000 ppm of stock solution for the chosen heavy metals such as Lead, Cadmium, Copper and Zinc were made. The required concentrations were obtained through serial dilution.

3.2. Characterization of the adsorbent

Following the preparation of limestone as an adsorbent, its elemental composition was analyzed by X-ray fluorescence (X-RF) spectrophotometer. Also the physical properties such as the cation exchange capacity, particle density, bulk density and porosity as well as the determination of chemical composition and the adsorption isotherms was done by different experiments and mathematical calculations [15].

3.2.1. Cation exchange capacity

The cation exchange capacity was determined by the method of ammonium acetate Ph 7 leaching and expressed in meq/100g[42].

Procedure

5g of sieved limestone sample (LSS) was measured in a 50 mL container and, then 33 mL of 1N Ammonium Acetate added at pH 7 and shaken for 15 min in a reciprocal shaker.

Thereafter, the supernatant was centrifuged and filtered in a clean 100 mL volumetric flask with qualitative fine porous filter paper and the procedure repeated two more times to obtain a total of approximately 100 mL at the end. Then fill up to the 100 mL mark with ammonium acetate and mixed well. The samples in 50 mL centrifuge tubes was subjected to two consecutive washes with 96% ethanol. To displace the adsorbed ammonium ions NH_4^+ and 33 mL of a 10% NaCl Solution was added to the sample then shacked for 15 minutes, centrifuge and filter into a clean 100 mL volumetric flask. The process was repeated two more times and fill up to 100 mL with NaCl and mix well to obtain a total of approximately 100 mL at the end. The ratio of the mass of sample in the centrifuge tube to the concentration of displaced NH_4^+ in the leachate yields the CEC [43].

3.2.2. Bulk density

Bulk density , which is expressed in g/cm^3, represents the mass of solid limestone per unit volume[44]. It was obtained by placing 100ml of distilled water in in a 250 ml measuring cylinder, and the volume recorded. The sample and measuring cylinder weights were also measured and recorded on the weighing scale [45]. Then the bulk density be determined by the equation:

$$Bulk\ density = \frac{mass\ of\ \text{LSS}\ (g)}{total\ volume\ of\ \text{LSS}(cm^3)}\ ;\quad \varrho_b = \frac{D(g)}{A(cm^3)},$$

where: A = volume of LSS obtained by B-C, B = volume of LSS + volume of distilled water, C = volume of water, D = weight of the LSS sample obtained

3.2.3. Particle density

Particle density was determined from the mass of limestone sample (LSS) per unit volume while air has been removed [45]. To obtain appropriate measurement, the mass and volume the solid particles in a LSS was only measured, not the air or water included in the pore spaces between the particles. This was done by putting LSS in a flask with distilled water, LSS and water were boiled together, and then the air was totally removed. Then, water is added to the mixture to a specified volume after it has cooled down over 24 hours. The mixture's mass was then measured. The mass of water was subtracted from that LSS and water mixture. The mass of the solid particles in a given volume was used to determine the particle density [46].

It was determined by the formula:

$$\varrho_p = \frac{mass\ of\ dry\ \text{LSS}}{volume\ of\ \text{LSS}(\ air\ removed)\ \ (cm^3)}$$

3.2.4. Porosity

Porosity was used to determine the amount of void (or open space) occupied by air and water in the sample. Porosity value is expressed as a fraction or percentage. To obtain porosity, half of a 500ml measuring cylinder was filled with water, and the volume recorded. Dry limestone sample was added to second 500 ml measuring cylinder and its volume was again measured[44, 45]. Then, by the following equation, porosity will be obtained:

Porosity, $\frac{A-(C-B)}{A} \times 100 = \frac{A+B-C}{A} \times 100$, where A is the bulk volume of the sample, B is the volume of water, C is the mixture of A and B.

The following equation was also used and then compare the results to make sure that the obtained results are accurate.

$$Porosity\ = 1 - \left(\frac{Bulk\ density}{Particle\ density}\right) \times 100$$

$$p = \frac{\varrho_b}{\varrho_p} \times 100$$

3.2.5. Chemical composition

Chemical composition of Mpenge and Gishyita Limestone was determined using X-ray fluorescence (XRF) spectrophotometer. On BMET-8000 XRF the dry samples was used and the results recorded [42, 47, 48] .

3. 3. Adsorption capacity determination

The adsorption capacity of limestone during water and wastewater treatment was determined by its capacity on acidity neutralization/ pH elevation, heavy metals removal (Cd(II), Cu(II), Ni, Fe, Mn, Pb(II), and Zn(II)) [49]. The analysis on water and wastewater quality and composition was done before, during adsorption process within a determined interval of time and after adsorption process.

3.3.1. Experimental set-up

To work adsorption capacity, in a 250 ml conical flask covered with aluminum foil, one hundred milliliters of polluted water with a given concentration of pollutant was mixed with one gram of the LSS sample (pH 6.00±0.1). The solutions in contact with the adsorbent was maintained at a constant temperature, the mixture being vigorously stirred by means of orbital shaker at 200 rpm for two hours, then filtered on a filter paper.

The concentration of residual metal ions in the solution was measured in triplicate using Microwave Plasma- Atomic Emission Spectrophotometer (MP-AES), and the average result is considered.

Initial solutions containing lead (II), Cadmium (II), Copper (II) and Zinc (II), ions concentrations was prepared one by one by dissolving the required weights of the salts $Cd(NO_3)_2.4H_2O$, $Cu(NO_3)_2.2H_2O$, $Pb(NO_3)_2$, ($FeCl_3$.6H2O) and $Zn(NO_3)_2$.6H2O) in distilled water [50, 42].

The following equation can be used to express the adsorption capacity, qe(mg/g), and percentage removal, A (%) of limestone on heavy metals:

$$q_e = \frac{(C_O - C_e) \times V}{M}$$

$$A(\%) = \frac{(C_O - C_e)}{C_O} \times 100$$

where, C_O is the initial concentration of heavy metals in contact with adsorbents (mmg/L), q_e is the amount of heavy metals adsorbed per unit mass of the adsorbent (mg/g); M is the mass of the adsorbent (g);C_e is the concentration of the heavy metal in the aqueous solution at time t (mg/L); V is the initial volume of the aqueous solution in contact with the adsorbents during the adsorption test (t); and A(%) is the amount heavy metals adsorbed given in percentage.

3.3.2. The varied adsorbent dose effect on adsorption

Different adsorbent doses (2.5, 3, 3.5, 4, 4.5 and 5g) was used in 100mL of wastewater sample with 10ppm as the concentration of heavy metals.to determine the impact of adsorbent. Batch adsorption tests were carried out. The mixtures were shaken at 200rpm on orbital shaker within 120 min while the pH and temperature was maintained at 6 and 25 ^{0}C respectively. The mixture lifted for 30 minutes to settle before being subjected to a MP-AES analysis to determine the content of any leftover heavy metals.

3.3.3. The varied contact time effect

In a series of batch adsorption studies, limestone in the amount of 3.5 was combined with 100 ml of wastewater. This experiment aims to establish the ideal contact period necessary for the greatest elimination of heavy metals. The impact of numerous interaction period of 15, 30, 60, 90, 120, 150 and 180 minutes was examined. Within 120 minutes, the flasks were shaken at 200 rpm on orbital shaker.

Following the shaking procedure, the samples were given 30 minutes to settle before being subjected to a MP-AES analysis. The following equation can be used to express the adsorption capacity, qe (mg/g) and percentage removal, A (%) of limestone on heavy metals:

$$A(\%) = \frac{(C_O - C_e)}{C_O} \times 100$$

$$q_e = \frac{(C_O - C_e) \times V}{M}$$

3.3.4. The pH effect

Experiments for adsorption were conducted at pH 2, 4, 6, 8, 10, and 12 levels while maintaining conditions constants, the temperatures at 25 °C, the initial concentrations of 10 ppm at shaking speed of 200 rpm within 120 min. The pH of the solutions was adjusted by addition of 0.1 M HCl and 0.1 M NaOH dropwise using a pipette. The adsorbent dose was 3.5g in 100ml of wastewater. The resulting mixture was waited for 30 min for settlement, and then the remaining concentrations of heavy metals was analyzed using MP-AES [51] .

3.3.5. The temperature effect

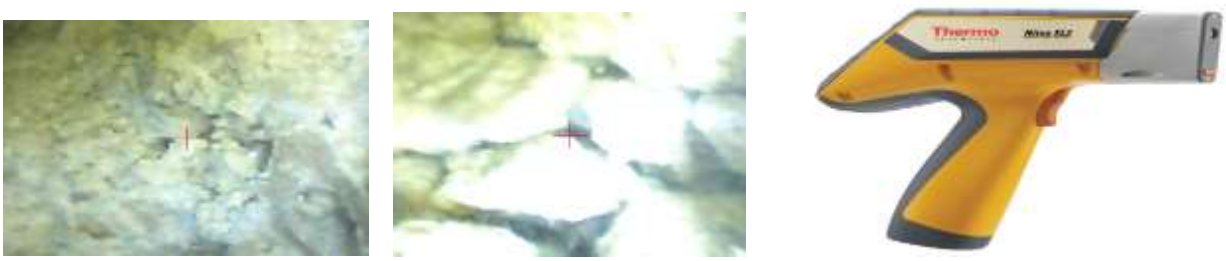
Experiments for adsorption were carried out at different temperature of 25, 30, 35, 40 and 45 ^{0}C in conical flasks using constant dosage of 3.5 g of the adsorbents, contact time of two hours, shaking speed of 200 rpm, pH of 6.0, and initial concentration of 10 ppm for the metal ions. The resulting mixtures were collected, filtered and analyzed for the remaining concentrations of the metals ions using (MP-AES).

CHAPTER 4: RESULTS AND DISCUTION

4.1. Limestone characterization

4.1.1. Chemical composition

The X-Ray Fluorescence Spectrophotometry analysis studied the sample from Gishyita and Mpenge Limestone deposits and revealed Calcium as the dominant element, comprising more than 50 mg/g at both sites for all cleaned and uncleaned samples. However, elements contributing more than 1mg/g in both sample were Mg, Al and Si. The other elements that were present at trace concentrations include P, K, Sr, Sn, and Ba. Results from this study showed that the Gishyita and Mpenge limestone deposit is pure but the Gishyita limestone is highly pure with Calcium concentration ranging between 54.46 and 58.00 than the Mpenge limestone ranging between 44.36 to 50.70 as represented in the table 4.1. their chemical composition was the same as that of the Arhab Area-North Sana with CaO content ranging from 54.70 to 55.50 wt% (expression of the concentration of Ca ions) whereas the other ions are present in a very small concentration including Si (0.20 -0,80 wt%), Al (0.2-0.4 wt%) and K (0.06-1.50wt%).The elemental study revealed that heavy metals (Fe, Mn, Pb, Zn, Cu,V and Cd) are already present in the samples at trace amount [53].



(b) **(b)** **XL2 -800 XRF**

Figure 4.1. XL2-800 XRF images (a) the Mpenge and (b) Gishyita limestone.

Table 4.1. Elemental composition of Gishyita and Mpenge limestone deposits (in mg/g)

Element	Ca	Mg	Al	Si	K	Ba	Fe	Cu	Zn	Mn	Cr	Cd	Ni
Gishyita Uncleaned	58.00 ∓0.04	3.17 ∓0.27	1.00 ∓0.04	1.41 ∓0.03	0.186	0.121 ∓0.01	0.066 ∓0.02	0	<0.005	≤0.5	≤0.5	<0.05	<0.05
Gishyita Cleaned	54.46 ∓0.05	4.17 ∓0.33	1.35 ∓0.05	1.93 ∓0.02	0.27	0.31 ∓0.02	1.11 ∓0.03	0	<0.005	≤0.5	≤0.5	<0.05	<0.05
Mpenge uncleaned	50.70 ∓0.04	3.31 ∓0.25	1.00 ∓0.04	10.20 ∓0.04	0.34	0.073 ∓0.02	21.33 ∓0.07	0	<0.005	≤0.5	≤0.5	<0.05	<0.05
Mpenge Cleaned	44.36 ∓0.02	2.63 ∓0.25	1.00 ∓0.03	4.81 ∓0.02	0.21	0.052 ∓0.01	2.77 ∓0.03	0	<0.005	≤0.5	≤0.5	<0.05	<0.05

4.1.2. The Bulk Density, Particle density and Porosity

The experimental findings demonstrated that the bulk densities of both cleaned is identical and that of uncleaned is identical for samples from both sites. The bulk density for cleaned samples was 2.33g/ml while that of uncleaned samples was 2.00g/ml.

The results on particle density which was determined while the air has been removed from the sample, showed that the particle density of the cleaned sample from Gishyita was 3.60g/ml while that of Mpenge site was 3.84g/ml. The particle density of uncleaned sample from Gishyita site was 3.87g/ml while that of Mpenge was 3.33g/ml.

Porosity which express the amount of void space occupied by air and water was obtained from particle density and bulk density, then expressed in percentage.

The results revealed that the porosity for Gishyita cleaned and uncleaned samples was 35.3% and 48.00% respectively while that of Mpenge cleaned and uncleaned samples was 39.3% and 40.00% respectively.

Table 4.2. The physical characteristics of limestone

Parameters	**Mpenge limestone**		**Gishyita limestone**	
	Cleaned	**Uncleaned**	**Cleaned**	**Uncleaned**
Bulk density (g/ml)	2.33	2.00	2.33	2.00
Particle density (g/ml)	3.87	3.33	3.60	3.84
Porosity (%)	39.3	39.3	35.3	35.3

Effects of limestone on the physical parameters of water (pH, TDS, Conductivity, Salinity and mass change) had also studied. The values for initial physical parameters such as pH, TDS, Conductivity, Salinity and Mass in distilled water had been measured and recorded, then 5g of both cleaned and uncleaned Gishyita and Mpenge limestone was mixed separately with 100ml of distilled water within 30 min on orbital shaker at 200rpm. Thereafter, the mixture was filtered and the limestone residues dried in oven at 105^{o}c overnight. After that, the final physical parameters were recorded. Then the average results have been represented in table 4.2.

Table 4.3. Change in the values of physical parameters

Parameters	**Initial value**	**Final value (average)**
Ph	6.5	7.24-7.37
TDS (mg/l)	0.612	12.44-21.00
Conductivity (μs/cm)	1.41	25.6-43.3
Salinity ($^{0}/_{0}$)	0	0.01-0.02
Mass (g)	5	5

The results showed that limestone affects the physical parameters of water but do not go beyond the acceptable limit as recommended by the WHO (2006). The analytical results show that pH of water varies from 7.2 to 7.4, pH values are within the desirable recommended limits of 6.5 to 8.5. TDS varies from 12.4 to 21.0, which within the recommended range [54]. The results show that there is no change in regarding the solubility of stone in water.

4.2. Calibration results of Cu, Cd, Pb and Zn on MP-AES

After adsorption processes, the samples were analyzed using Microwave Plasma-Atomic Emission Spectrometer (MP-AES). The calibration results obtained are shown in table 4.4 and figure 4.2.

Table 4.4. Calibration results obtained on MP-AES

Concentration	**Intensities**			
	Cu	**Cd**	**Pb**	**Zn**
0.1	0.59063	229.06	80.02	-173.61
0.05	5115.38	1108.02	245.80	545.63
0.1	11118.43	2266.71	465.53	2050.94
0.5	57677.51	11497.02	2059.37	12179.44
1.0	110322.62	22519.28	4000.59	24183.87

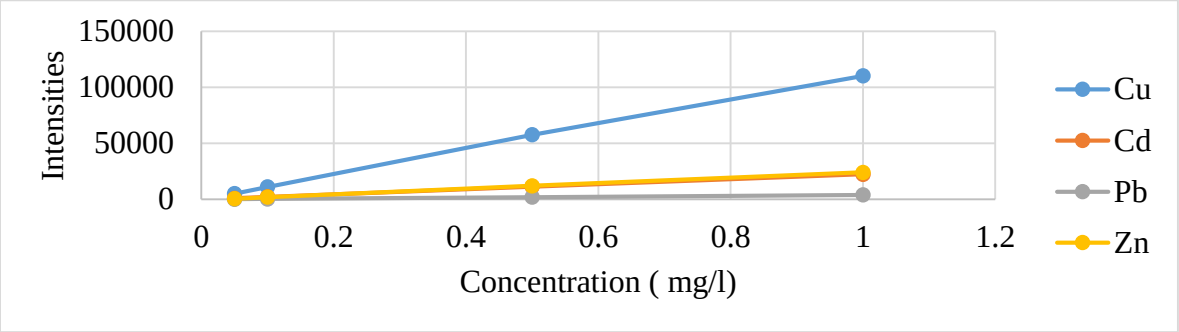


Figure 4.2. Calibration results of Cu, Cd, Pb and Zn

4.3. Adsorption studies

4.3.1. Adsorbent particle size impact on adsorption

The experiment was carried out to study the effects of adsorbent particle size on the adsorption removal of Cu, Cd, Pb and Zn ions by using the limestone samples ranked as GA_1, GA_2, GB_1, GB_2, MA_1, MA_2, MB_1 and MB_2 at 25 °C within 120 min contact time. The adsorbent particle size was ranging between 0.1 and 6.5 mm at pH 6 (table 4.5).

Table 4.5. Sample names and Ranks

Sample name	**Rank**	**Size (mm)**
Gishyita clean sample1	GA_1	0.1 -3.5
Gishyita clean sample 2	GA_2	3.5-6.7
Gishyita unclean sample 1	GB_1	0.1-3.5
Gishyita unclean sample 2	GB_2	3.5-6.7
Mpenge clean sample 1	MA_1	0.1 -3.5
Mpenge clean sample 2	MA_2	3.5-6.7
Mpenge unclean sample 1	MB_1	0.1 -3.5
Mpenge unclean sample 2	MB_2	3.5-6.7

The results demonstrated that when the particle size reduces, the adsorption capacity rises. When we used limestone with particle sizes between (0.1-3.5) mm, the percentage of adsorption was high and it marginally decreased when the size grew to the range between (3.5-6.5) mm. The results strongly supported the hypothesis that as particle size increases, the surface area of interaction between the adsorbent and heavy metals in the solution decreases [41]. So that the adsorbent crystals with smaller size (0.1-3.5mm) was used for the adsorption processes.

4.3.2. The adsorbent dose effect on adsorption

The experiment was carried out to study the effects of limestone adsorbent dose on the adsorption removal of Cu, Cd, Pb and Zn ions by GA_1 and MA_1 at 25°C within 120 min contact time by shaking at speed of 200rpm. The adsorbent dose was increasing from 2.5 g to 5g in 100ml of wastewater at heavy metals concentration of 10ppm for each of Cu, Zn, Pb and Cd at pH of 6.0.
According to the results represented in table 4.3. and figure 4.6, the increase of limestone dosages from 2.5g/100ml to 3.5g/100ml, the heavy metals removal capacity was also highly increased but above that dosage started increase very slowly. The results showed that as adsorbent dosage was raised, the adsorption rate rose as well. This was due to the surface of contact of the adsorbent that increased the availability of active sites. However, heavy metals removal does not increase at higher amount of the adsorbent due to heavy metal concentration shortage in solution [41].
Hamidi Aziz and Mohd Yusof (2008) reported similar findings in their analysis of the removal of Pb, Cd, Zn, Ni, Cu and Cr from water in Malesia by the use of high quality limestone as a post treatment. The ideal adsorbent dose for the adsorption procedure was obtained by rapidly increasing of the adsorption rate in the adsorbent dose ranging from 2.5 to 3.5 g/100ml with just a little increase of the dose above 3.5g/100ml.
The optimum amount of GA_1 and MA_1 adsorbent on adsorption of Pb, Cd, Cu and Zn was 3.5 where the maximum adsorption capacity by GA_1 was 80.9%, 78.1%, 69.2%, 61.9% while for MA_1 adsorbent was 78.3%, 61.5%, 55.0% and 76.7% respectively.

Table 4.6. The adsorbent dose on adsorption

Adsrobent	Dose (g)	Lead adsorption			Cadmium adsorption			Copper adsorption			Zinc adsorption		
		Ce,mg/l	qe, mg/g	% removal	Ce, mg/l	qe, mg/g	% Removal	Ce, mg/l	qe, mg/g	% removal	Ce, mg/l	qe, mg/g	% Removal
GA_1	2.5	6.5	0.13	34.8	4.9	0.20	51.0	4.43	0.22	55.7	8.1	0.07	19.0
	3.0	3.43	0.21	65.7	3.65	0.21	63.5	4.13	0.19	58.7	5.20	0.16	48.0
	3.5	2.17	0.22	78.3	2.5	0.21	75.0	3.56	0.18	65.4	4.30	0.16	57.0
	4.5	1.94	0.18	80.6	2.15	0.14	77.5	3.11	0.15	68.0	3.86	0.13	61.6
	5.0	1.96	0.16	80.9	2.13	0.15	78.1	3.07	0.13	69.2	3.81	0.12	61.9
MA_2	2.5	2.21	0.23	57.9	6.9	0.12	31.0	5.1	0.19	49.0	6.9	0.12	31.0
	3.0	3.46	0.21	65.4	5.7	0.14	43.0	4.61	0.14	53.9	3.8	0.20	62.0
	3.5	2.33	0.22	76.7	4.11	0.17	58.9	4.55	0.15	54.5	2.6	0.21	7.4
	4.5	2.21	0.17	77.9	3.87	0.13	61.3	4.52	0.12	54.8	2.36	0.17	76.1
	5.0	2.17	0.15	78.3	3.85	0.23	61.5	4.50	0.11	55.0	2.33	0.15	76.7
GA_1	2.5	6.52	0.13	34.8	4.9	0.20	51.0	4.43	0.22	55.7	8.1	0.07	19.0
	3.0	3.43	0.21	65.7	3.65	0.21	63.5	4.13	0.19	58.7	5.20	0.16	48.0
	3.5	2.17	0.22	78.3	2.5	0.21	75.0	3.56	0.18	65.4	4.30	0.16	57.0
	4.5	1.94	0.18	80.6	2.15	0.14	77.5	3.11	0.15	68.0	3.86	0.13	61.6
	5.0	1.96	0.16	80.9	2.13	0.15	78.1	3.07	0.13	69.2	3.81	0.12	61.9
MA_2	2.5	4.21	0.23	57.9	6.9	0.12	31.0	5.1	0.19	49.0	6.9	0.12	31.0
	3.0	3.46	0.21	65.4	5.7	0.14	43.0	4.61	0.14	53.9	3.8	0.20	62.0
	3.5	2.33	0.22	76.7	4.11	0.17	58.9	4.55	0.15	54.5	2.6	0.21	7.4
	4.5	2.21	0.17	77.9	3.87	0.13	61.3	4.52	0.12	54.8	2.36	0.17	76.1
	5.0	2.17	0.15	78.3	3.85	0.23	61.5	4.50	0.11	55.0	2.33	0.15	76.7

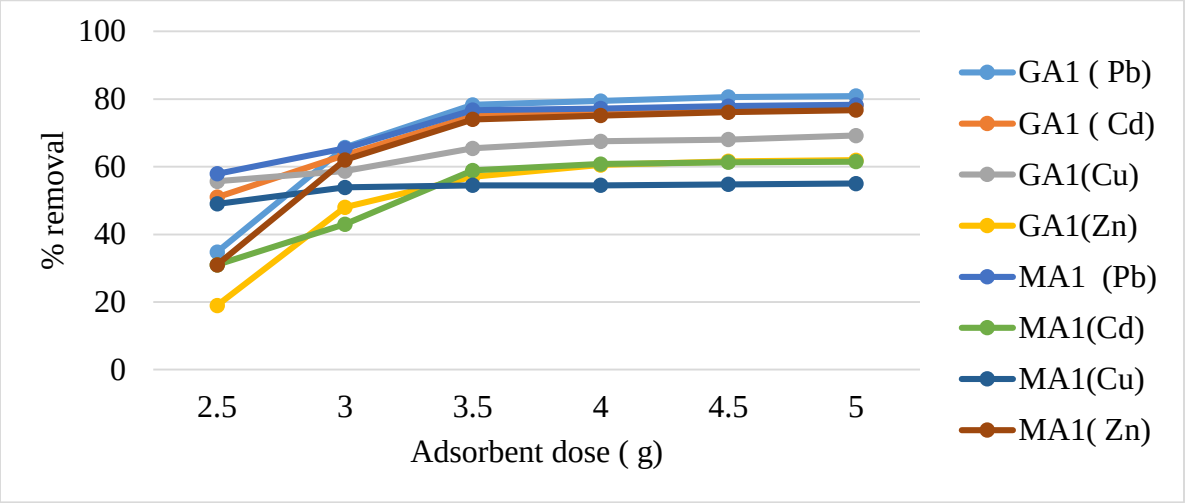


Figure 4.3. Adsorbent effect on adsorption

4.3.3. The effect of interaction period on adsorption

The interaction period was ranging between 0 and 180 minutes to study a solution of 100 ml containing 10 mg/L of heavy metals concentration mixed with 3.5 g of limestone adsorbent. These was done at 6.0 pH and temperature of 25 ^{0}C. The effect of the contact time on the adsorption of Cd, Pb, Cu, and Zn by MA_1 and GA_1 was shown in the table.4. 7. and figure 4.4.

At the beginning adsorption takes place very quickly but slowed down and hen remained constant where there was maximum sorption onto both GA_1 and MA_1 adsorbent. The maximum adsorption of lead was obtained after 15 min, thereafter the adsorption efficiency was not changing, after 120min the adsorption of cadmium and cupper remained constant while the adsorption was continued to increase until at 180 min. Form these observations, the optimum interaction period for the adsorption of lead had obtained at 15 min, 120 min for Cd and Cu, while for Zn was above 180 min. The quick uptake at the shortest time was attributed to available active adsorption sites on the adsorbents surface. However, when the process contact time was increasing, the present active sites were being saturated and resulted in slow uptake till the maximum [55].

The maximum adsorption of Pb, Cd, Cu and Zn by GA_1 adsorbent was 80.5%, 77.3%, 80.6%, 79.4% while the maximum adsorption by MA_1 adsorbent was 77.0%, 72.4%, 70.0 %and 77.8% respectively.

Table 4.7. The effect of interaction period on adsorption

Ads.	T, min	Lead adsorption			Cadmium adsorption			Copper adsorption			Zinc adsorption		
		Ce, mg/l	qe, mg/g	% Removal	Ce, mg/l	qe, mg/g	% removal	Ce, mg/l	qe, mg/g	% removal	Ce, mg/l	qe, mg/g	% Removal
GA1	0	10	0.0	0.00	10	0.0	0.00	10	0.00	0.00	10	0.00	0.00
	15	2.0	0.05	80.0	9.3	0.02	7.0	8.7	0.04	13.0	9.0	0.03	10.0
	30	2.0	0.14	80.0	7.96	0.06	20.5	4.8	0.15	52.0	5.1	0.14	49.0
	60	2.00	0.22	80.0	5.45	0.13	45.5	3.0	0.20	70.0	3.22	0.19	67.8
	90	2.00	0.24	80.0	3.92	0.17	60.8	2.73	0.21	72.7	3.07	0.21	69.3
	120	1.95	0.24	80.5	2.27	0.22	77.3	1.94	0.23	80.6	2.72	0.23	73.0
	150	1.95	0.24	80.5	2.27	0.22	77.3	1.92	0.23	80.1	2.25	0.23	77.5
	180	1.95	0.24	80.5	2.29	0.22	77.1	1.93	0.24	80.7	2.09	0.23	79.4
MA1	0	10	0.0	0.00	10	0.00	0.00	10	0.00	0.00	10	0.00	0.00
	15	2.28	0.05	77.0	9.49	0.05	5.1	9.4	0.02	6.0	9.23	0.02	7.7
	30	2.28	0.13	77.0	6.07	0.11	39.3	6.6	0.10	34.0	6.3	0.10	37.0
	60	2.28	0.22	77.0	5.26	0.13	47.4	4.21	0.16	57.9	5.0	0.14	50.0
	90	1.27	0.23	77.1	4.00	0.17	60.0	3.02	0.20	69.8	3.25	0.19	67.5
	120	2.28	0.24	77.0	2.76	0.20	72.4	2.3	0.22	77.0	2.81	0.21	71.9
	150	2.28	0.24	77.0	2.77	0.21	72.2	2.4	0.23	76.0	2.52	0.22	74.8
	180	2.27	0.23	77.1	2.78	0.21	72.2	2.33	0.23	76.7	2.22	0.23	77.8

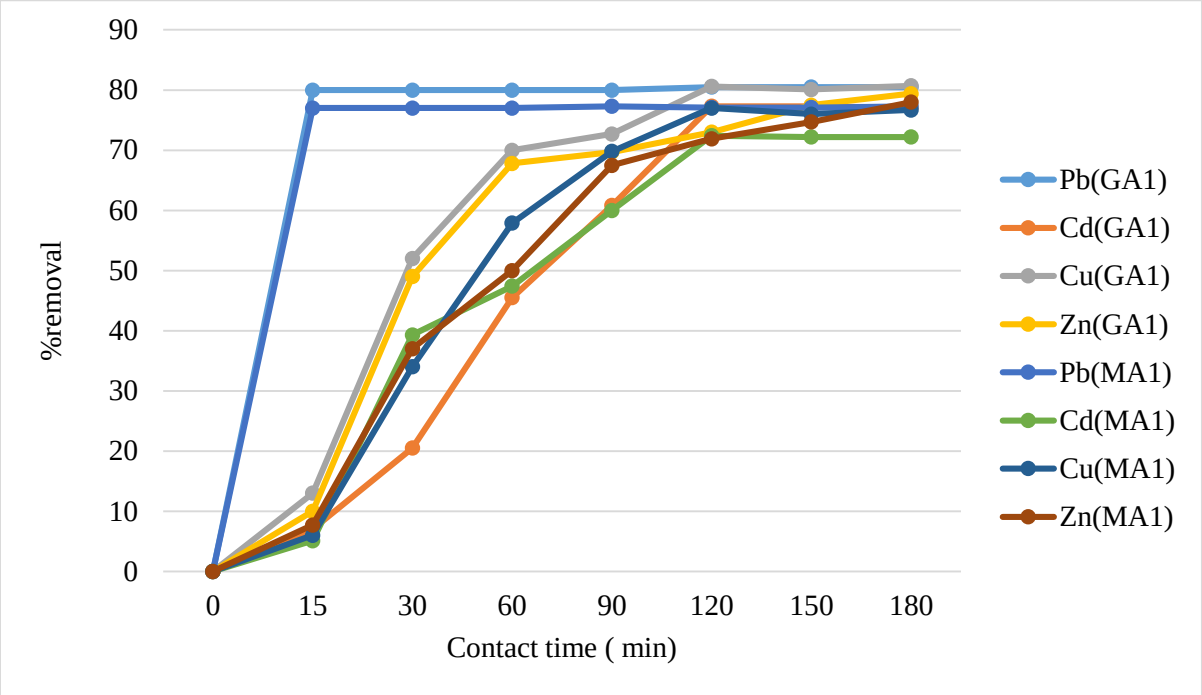


Figure 4.4. The effect of interaction period on adsorption

4.3.4. The effect initial heavy metals concentrations

The initial concentrations of heavy metals (lead, Cadmium, Copper and Zinc) were varied between 2mg/l and 12mg/l in wastewater. The mass of 3.5g of limestone adsorbent were mixed with 100 ml of wastewater and shaken at 200 rpm for within 120 min at pH 6.

As observed and reported in the table.4.8. and figure.4.5. The adsorption efficiency was decreasing with an increasing heavy metal concentration. This results can be associate to the fact that the more heavy metals ions concentration in solution makes adsorbent active site unable to bind all metal ions as the actives sites become saturated leaving most of heavy metals in solution [55]. The maximum adsorption of lead, Cadmium, Copper and Zinc onto GA_1 was 99.0%, 97.0%, 99.0% and 96.0% while the maximum adsorption by MA_1 was 99.5%, 90.0%, 100% and 99.0% respectively. However, the minimum adsorption by GA_1 and MA_1 was 77.5%, 69.1%, 76.6%.4 and 69.5% as well as 67.2%, 62.9%, 68.8%, and 65.3% respectively [54].

Table 4.8. Effect of heavy metals initial concentration

Ads.	Co, mg/l	Lead adsorption			Cadmium adsorption			Copper adsorption			Zinc adsorption		
		Ce, mg/l	qe, mg/g	% removal	Ce, mg/l	qe, mg/g	% Removal	Ce, mg/l	qe, mg/g	% removal	Ce, mg/l	qe, mg/g	% Removal
GA_1	2	0.02	0.05	99.0	0.06	0.05	97.0	0.02	0.05	99.0	0.05	0.06	96.5
	4	0.10	0.11	97.5	0.34	0.10	91.5	0.4	0.10	90.0	0.09	0.09	80.0
	6	0.86	0.14	85.6	0.9	0.15	85.0	0.88	0.14	85.3	1.40	0.16	76.6
	8	1.40	1.88	82.5	1.6	0.19	80.0	1.41	0.21	82.3	2.0	0.17	75.0
	10	2.01	0.22	79.9	2.2	0.22	78.0	1.93	0.23	80.7	2.68	0.20	73.2
	12	2.70	0.26	77.5	3.7	0.23	69.1	2.80	0.26	76.6	3.55	0.33	69.5
MA_1	2	0.01	0.05	99.5	0.02	0.05	99.0	0.00	0.05	100	0.02	0.05	99.0
	4	0.02	0.11	99.5	0.03	0.10	93.2	0.01	0.12	99.7	0.03	0.12	99.2
	6	1.1	0.17	81.6	1.17	0.13	80.5	0.5	0.15	91.6	0.6	0.15	90.0
	8	1.71	0.19	78.6	1.90	0.17	76.2	1.61	0.18	79.8	1.5	0.22	85.0
	10	2.26	0.24	77.4	2.57	0.21	72.9	2.29	0.22	77.1	2.00	0.27	80.0
	12	3.93	0.27	67.2	4.45	0.21	62.9	3.12	0.25	68.8	3.47	0.33	65.3

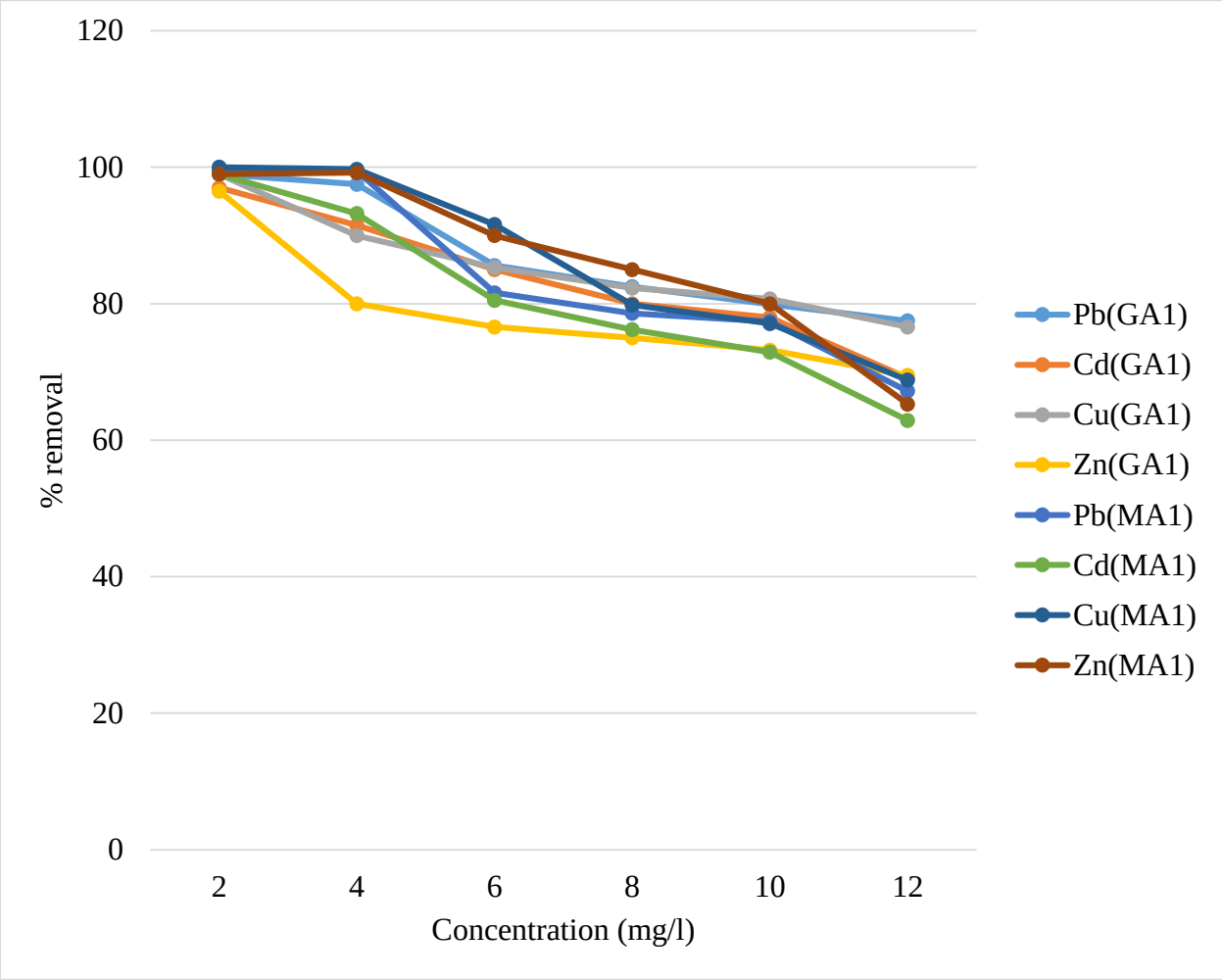


Figure 4.5. Effect of heavy metals initial concentration

4.3.5. The pH effect on adsorption

In 100ml of wastewater with a heavy metal concentration of 10mg/l and 3.5 g of GA_1 and MA_1 adsorbent, the pH changed from 2 to 10 over the duration of 120 minutes of 200 rpm shaking rate. Using a pH meter and 1 M NaOH and 1M HCl solutions, pH of wastewater was adjusted to the desired levels. The pH of the aqueous solution has a significant effect for removal of heavy metal ions by adsorption but it can also affects precipitation [42].

In our study, the analysis was conducted to determine at which pH values adsorption was likely to occur, as reported in the table.4.9. and figure.4.6.

According to the data, Pb adsorption rose at pH levels between 2 and 5, while Cd, Cu and Zn adsorption increased as pH levels increased from 2 to 6, where the adsorption removal start to decrease onto both adsorbents. This could be linked to the fact that in acidic conditions (pH 2− 6) the surface of the adsorbents was protonated by protons (H^+) in the solution which enhanced the electrostatic interaction and there exist less effective completion in week acidic conditions, these result in greater adsorption. However, at the pH of solution near the neutral conditions (pH 6-8) the adsorption capacity started to decrease and then in alkaline solution with pH greater than 8 the adsorbent uptake had been decreased very quickly [56].

This was mainly due to surface of adsorbent which was being deprotonated (OH^+) in the solution that weakened the electrostatic interaction as well as inhibiting the adsorption. At higher pH, lead, cadmium copper and zinc ions form hydroxyl precipitate hence their adsorption decreases while at lower value of pH, hydronium ions and heavy metals ions are competing and their removal efficiency is low. The pH less than 6 was taken as the optimum for adsorption of lead, cadmium, copper and Zinc, a condition that will prevent the possibility of Pb^{2+}, Cd^{2+}, Cu^{2+} and Zn^{2+} precipitation, which could be the source of uncertainty and it is recommended to the other adsorption processes [56].

Table 4.9. The pH effect on adsorption

Ads.	pH	Lead adsorption			Cadmium adsorption			Copper adsorption			Zinc adsorption		
		Ce,mg/l	qe, mg/g	% removal	Ce, mg/l	qe, mg/g	% removal	Ce, mg/l	qe, mg/g	% removal	Ce, mg/l	qe, mg/g	% Removal
GA_1	2	4.0	0.17	60.0	4.6	0.15	54.0	4.3	0.16	57.0	7.00	0.08	30.0
	4	2.63	0.21	73.7	4.1	0.17	59.0	2.66	0.20	73.4	4.68	0.15	53.2
	5	1.93	0.23	80.7	2.9	0.20	71.0	2.33	0.21	76.7	2.99	0.28	70.0
	6	2.60	0.21	74.0	2.2	0.22	78.0	1.92	0.23	80.8	2.71	0.24	72.9
	7	3.24	0.19	67.6	3.4	0.18	64.0	2.76	0.20	72.4	2.94	0.23	70.6
	8	4.0	0.17	60.0	4.1	0.16	59.0	3.3	0.19	67.0	5.28	0.15	47.2
	10	5.8	0.12	42.0	7.2	0.08	28.6	4.41	0.15	55.9	7.92	0.14	20.8
MA_1	2	4.0	0.17	60.0	4.0	0.17	60.0	4.3	0.16	57.0	4.68	0.15	53.2
	4	3.0	0.20	70.0	3.6	0.18	64.0	4.0	0.17	60.0	3.33	0.19	66.7
	5	2.4	0.21	76.0	3.2	0.19	68.0	2.5	0.21	75.0	3.00	0.20	70.0
	6	3.14	0.19	71.0	2.7	0.20	73.0	2.4	0.21	76.0	2.86	0.20	71.4
	7	3.68	0.18	63.2	3.0	0.20	70.0	2.66	0.21	73.4	3.42	0.18	65.0
	8	5.0	0.14	50.0	3.1	0.19	69.0	4.3	0.16	57.0	3.68	0.15	63.2
	10	7.6	0.06	24.0	6.2	0.10	38.6	4.41	0.15	55.9	4.92	0.14	50.8

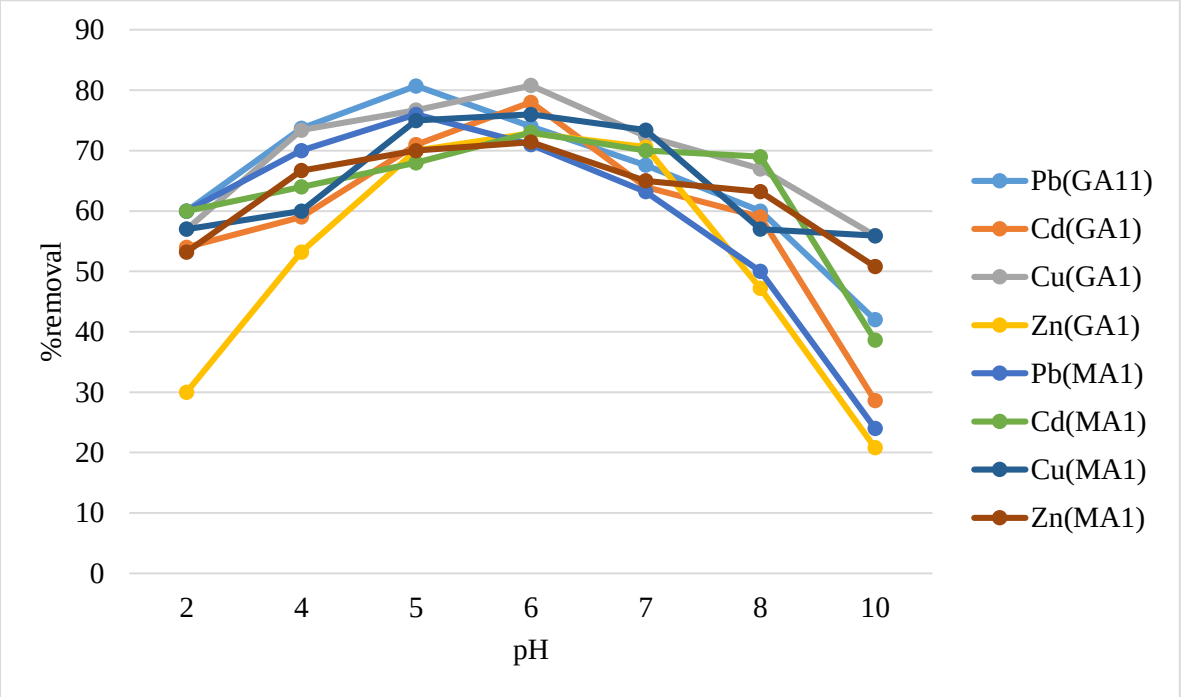


Figure 4.6. The pH effect on adsorption

4.3.6. Temperature effect on adsorption

The temperature variation influences the rate of diffusion, adsorptive forces and mobility of metal ions in solution so that it has significant effect in adsorption process. The considered temperature was varying from 25 to 45^{0}C for studying a solution of 100 ml of the 10 mg/L concentration in heavy metals mixed with 3.5 g of the adsorbent by shaking at 200 rpm within 120 min.

By increasing the diffusion and mobility of heavy metal ions, an increase in temperature was predicted to increase the adsorption capacity [55] . The results shown in table.4.10 and figure.4.7 show that the removal of heavy metal ions from both adsorbents decreased as temperature increased. Thus, when temperature of the system rose, the amount of both metal ions that could be adsorbed decreased, suggesting that the reactions that adsorb Pb, Cd, Cu and Zn were exothermic in nature [54] .

Table 4.10. Effect of temperature

Ads.	T(^{0}C)	Lead adsorption			Cadmium adsorption			Copper adsorption			Zinc adsorption		
		Ce, mg/l	qe, mg/g	% removal	Ce, mg/l	Qe, mg/g	% removal	Ce, mg/l	qe, mg/g	% removal	Ce, mg/l	qe, mg/g	% removal
GA_1	25	1.7	0.23	85.0	2.18	0.22	83.2	1.6	0.24	86.2	1.22	0.25	87.8
	30	1.5	0.24	83.0	1.65	0.24	78.2	1.38	0.25	84.0	1.93	0.23	80.7
	35	3.0	0.20	70.0	3.6	0.18	64.0	3.12	0.19	68.8	3.3	0.19	67.0
	40	3.5	0.18	65.0	3.9	0.17	61.0	3.67	0.18	63.3	3.52	0.18	64.8
	45	5.1	0.16	49.0	5.14	0.14	48.6	4.0	0.17	60.0	4.12	0.17	58.8
MA_1	25	1.94	0.25	86.5	1.9	0.23	82.8	1.70	0.24	85.7	1.8	0.23	87.0
	30	1.35	0.24	80.6	1.72	0.24	81.0	1.43	0.24	83.0	1.3	0.25	82.0
	35	2.9	0.20	71.0	3.36	0.19	66.4	2.6	0.21	74.0	3.44	0.19	65.6
	40	4.00	0.17	60.0	4.11	0.17	58.9	3.3	0.19	67.0	3.5	0.18	65.0
	45	4.74	0.15	52.6	5.9	0.12	41.0	4.5	0.16	55.0	3.75	0.17	62.5

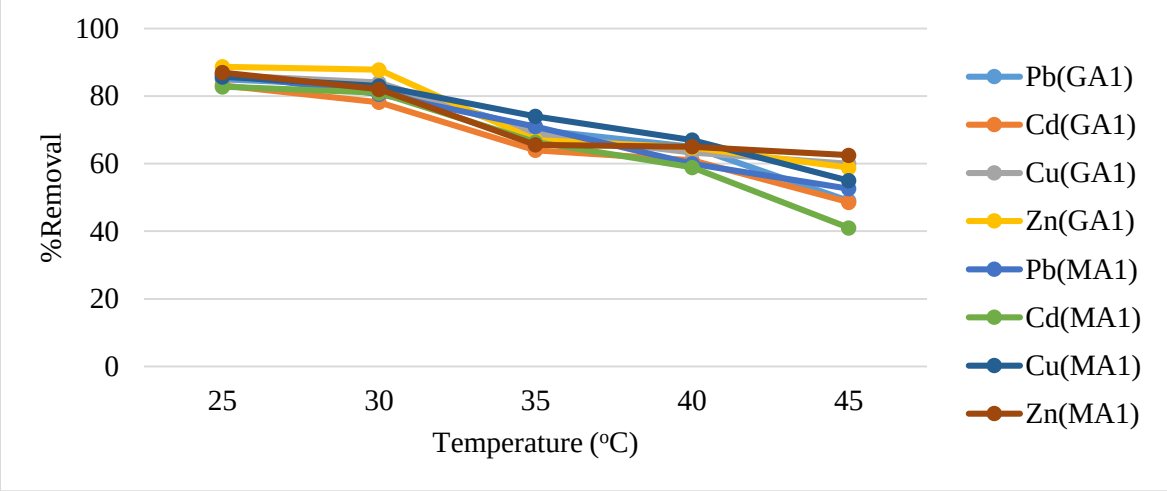


Figure 4.7. Effect of temperature

4.4. Adsorption isotherms study

The purpose of adsorption isotherms is to describe the interactive behavior of adsorbent and adsorbate and it can be applied for optimization of the of adsorbents capacity. The parameters of Langmuir and Freundlich adsorption isotherm models were used to estimate the adsorption interaction, removal process and surface of the adsorbents.

Heavy metals concentration used in this investigation was varied from 2 to 12 ppm, with 3.5 g of adsorbent in 100ml of solution and contact time of 120 min while pH was kept constant at pH 6 at 25^0C.

Langmuir isotherm mathematical expression : $\frac{\mathbf{1}}{\mathbf{q_e}} = \frac{\mathbf{1}}{\mathbf{q_m}} + \frac{\mathbf{1}}{\mathbf{K_L\ q_m\ C_e}}$

Where q_e represents the amount adsorbed at equilibrium time (mg/g), $\mathbf{q_m}$ is maximum adsorption capacity (mg/g), $\mathbf{K_L}$ is Langmuir constant (L/mg), and $\mathbf{C_e}$ is the concentration of heavy metals in solution at equilibrium time (mg/L). The Langmuir equilibrium constant was obtained on the plot of 1/qe Vs 1/ Ce.

Freundlich isotherm: For single layer adsorption onto heterogeneous surfaces, the Frendlich isotherm model provided an empirical adsorption relation for non-ideal system. The formula is provided as follows:

$$log\ q_e = \frac{1}{n} log\ C_e + K_f$$

Where $\boldsymbol{K_f}$ is Freundlich constant (L/g) and $\boldsymbol{n}$ is Freundlich exponent.

The values of these constants was calculated from the linear plot of $\log qe\ vs \log qt$ of the Freundlich model, where $\mathbf{1/n}$ corresponds to the slope and $\mathbf{log}K_f$ gives the value of intercept.

The results for the Langmuir and Freundlich equilibrium models calculated with respect to GA_1 and MA_1 adsorbents are shown in the following table 4.11 and figures 4.8, 4.9, 4.10 and 4.11

Table 4.11. Adsorption isotherm models

Adsorbents		GA1		MA_1	
Lead adsorption		Langmuir 1/qe Vs 1/Ce.	Freundlich $\log qe\ vs \log qt$	Langmuir	Freundlich
	R^2	0.9191	0.9755	0.9308	0.615
	Slope	0.0954	0.1682	0.1426	0.4561
	Intercept	4.4798	-0.6507	4.4997	-0.4143
Cadmium adsorption	R^2	0.9838	0.963	0.8722	0.7882
	Slope	0.9139	0.13731	0.0588	0.2781
	Intercept	5.1954	-0.8152	0.1107	-0.6394
Copper adsorption	R^2	0.8533	0.5034	0.9504	0.8026
	Slope	0.2346	0.1058	0.1554	0.6227
	Intercept	6.3459	-0.9298	0.7414	-0.2068
Zinc adsorption	R^2	0.8148	0.8211	0.819	0.8141
	Slope	0.4854	0.1341	0.2513	0.2402
	Intercept	9.8048	-1.0632	0.819	-0.7377

From the results in table 4.11 and the figure 4.8, it was observed that the adsorption of Lead onto GA_1 fitted with Freundlich adsorption model because it showed the highest correlation coefficient $R^2 = 0.9755$ compared to MA_1 adsorbent as well as the Langmuir model.

As the Freundlich isotherm model gives a correlation coefficient, R^2 higher than that of Langmuir isotherm, this showed that the adsorption of lead on limestone adsorbent did not allow the Langmuir model. So, the Freundlich isotherm is most accurate. Therefore, Lead adsorption to limestone corresponds to multilayer adsorption [57].

The adsorption of Cadmium is most suitable for the GA_1 adsorbent and clearly observed that the adsorption of cadmium onto GA_1 fitted with Langmuir adsorption model (figure 4.8) because it showed $R^2= 0.9869$ as the highest correlation coefficient by comparing to that of Freundlich and MA_1 adsorbents (fig 4.9). Therefore, Cadmium was adsorbed through monolayer and homogeneous mechanism.

The adsorption of Copper is more likely onto MA_1 adsorbent with monolayer adsorption by the langmuir isotherm model as was the one that showed a high correlation coefficient (R^2), fig 4.10. The adsorption of Zinc shows no significant difference onto GA_1 and MA_1 with both the Freundlich and Langmuir isotherm models as their correlation coefficients are too close (fig 4.11).

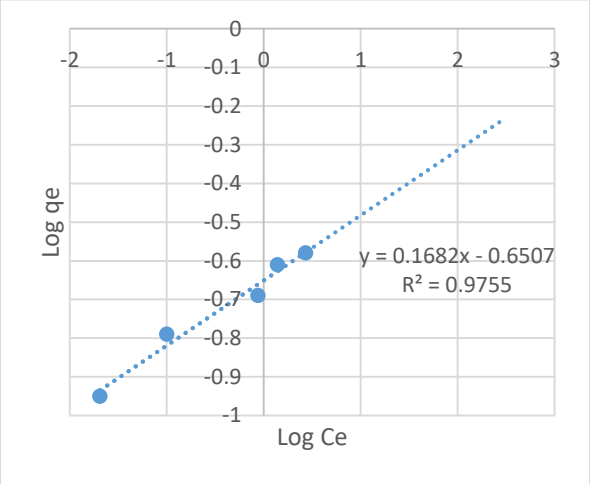


Figure 4.8. Freundlich isotherm for the adsorption of lead onto GA_1

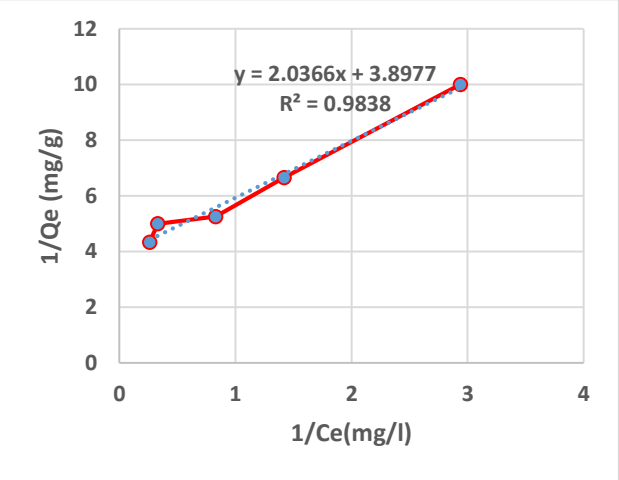


Figure 4.9. Langmuir isotherm adsorption of Cd onto GA_1

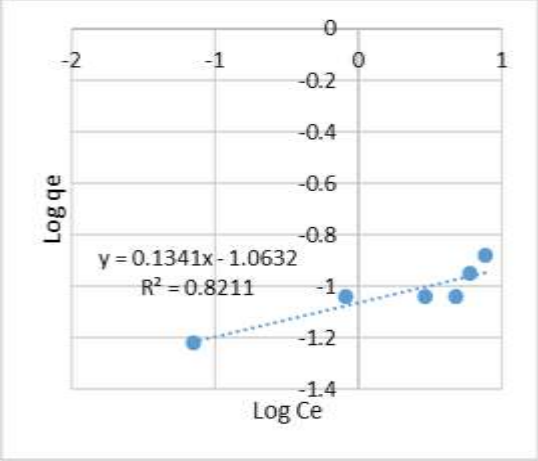


Figure 4.10. Freundlich isotherm for the Adsorption of Zn onto GA_1

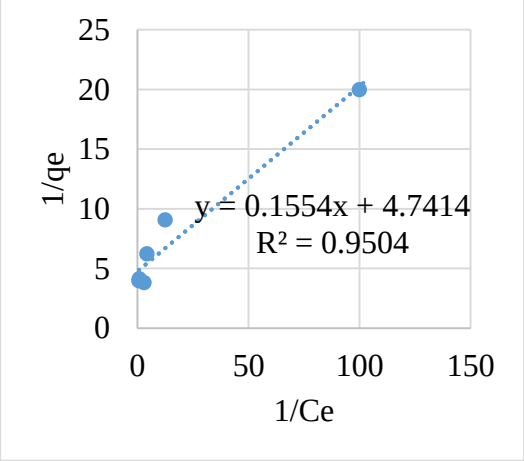


Figure 4.11. Langmuir isotherm for adsorption of Cu onto MA_1

4.5. Adsorption kinetics study

The Pseudo-first order and Pseudo-second order kinetic models were used for kinetic studies to assess the adsorption rate of the selected heavy metals onto MA_1 and MA_1 adsorbents.

Both model equations were written as:

Pseudo-first order: $\log(q_e - q_{t)} = \log q_e - \frac{K_1}{2.303} t$

Pseudo-second order: $\frac{t}{q_t} = \frac{1}{K_2 q_e^2 t} + \frac{t}{q_e}$, qe(mg/g) represent the amount of heavy metals adsorbed at equilibrium while qt is the amount of heavy metals adsorbed at certain time t. K_1 as the adsorption rate constant was determined from the graph of $\log(qe - qt)$versus time by calculating the slop as represented on figure 4.12. The pseudo-second linear regression was determined from the graph of $\frac{t}{qt}$ $vs\ t$ while K_2 which is the second order adsorption rate constant was obtained from the slop of intercept of the graph on figure 4.13.

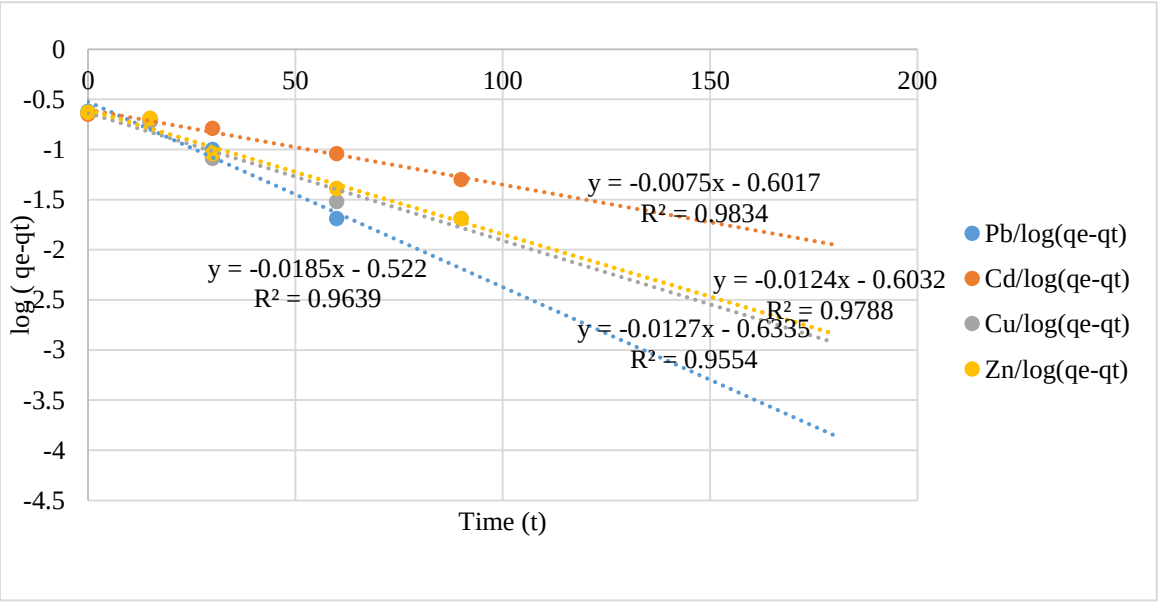


Figure 4.12. Pseudo first order kinetic on adsorption of Pb, Cd, Cu and Zn onto GA_1 adsorbent

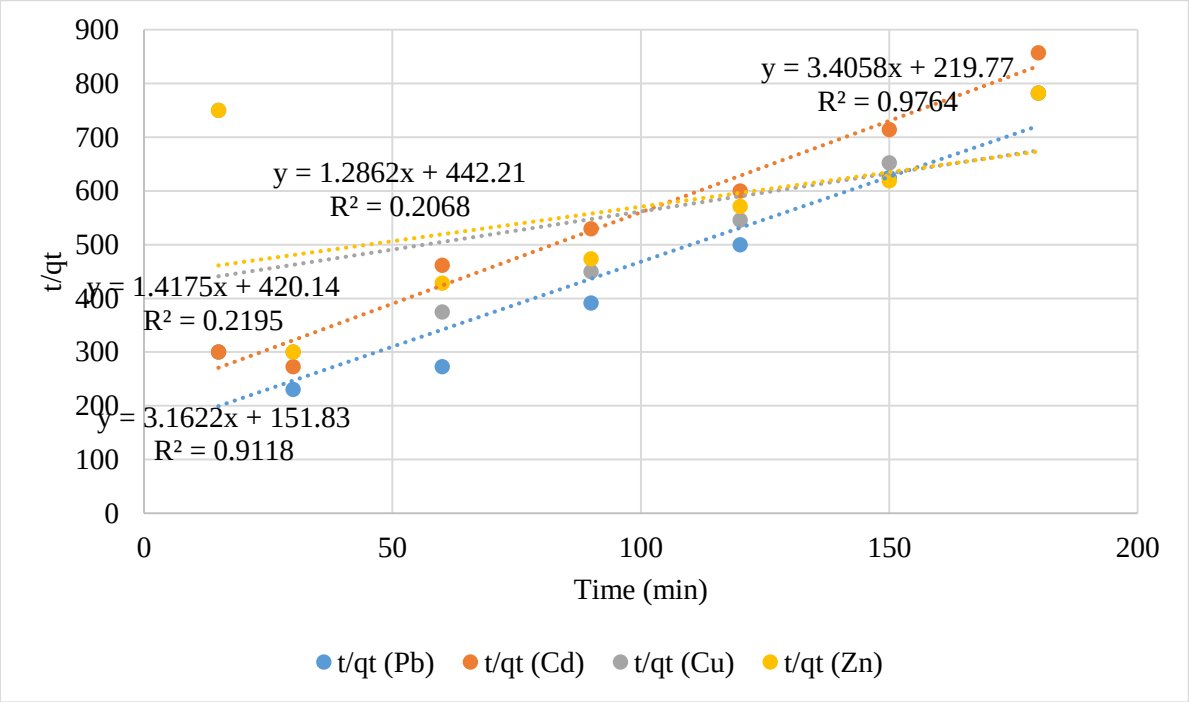


Figure 4.13. Pseudo second order kinetic on adsorption of Pb, Cd, Cu and Zn onto GA$_1$

Table 4.12. Adsorption parameters obtained from kinetic studies

Heavy metals	**Pseudo-first order model**			**Pseudo-second order model**		
	K_1 ,min^{-1}	**qe, mg/g**	**R^2**	**K_2 ,min^{-1}**	**qe, mg/g**	**R^2**
Pb	0.01551	0.24	0.9639	0.0048	0.24	0.9118
Cd	0.01618	0.22	0.9834	0.0019	0.22	0.9764
Cu	0.0271	0.23	0.9554	0.0056	0.23	0.2195
Zn	0.0271	0.23	0.9788	0.0056	0.23	0.2068

The results showed that R^2 for both Pb, Cd, Cu and Zn were greater in the pseudo-first order model than in the pseudo-second order model, as represented in table 4.12. The figures 4.12 and 4.13 also illustrate the strong linearity on the graph of $\log(qe - qt) vs\ t$ and $\frac{t}{qt} vs\ t$.

The value of R^2, which is quite close to one, indicates that the Pseudo-first order kinetic model obtained by using limestone as an adsorbent has a better applicability. This was showing that the physical processes involving adsorbent and adsorbate appear to govern the adsorption mechanism of lead, cadmium, copper and zinc.

The results from analysis were in great agreement with these reported by Javadian et al. (2015) on their study on adsorption of Pd from aqueous solution using zeolite-based geopolymer, synthesized from coal fly ash, kinetic, isotherm and thermodynamic studies as well as the report of F.F.Ali (2022) [57], on the study of limestone residues of sculpting factories utilization as adsorbent for removing Pb and Zn from aqueous solution.

4.6. Thermodynamic studies

Thermodynamic analysis on adsorption mechanism is more useful for establishing the nature and possibility of the adsorption reaction. Calculations were made for a number of thermodynamic parameters, including Gibbs free energy change (ΔG^0), Enthalpy change (ΔH^0) and entropy change (ΔS^0).

The used equations were as follows:

(i) $\Delta G^0 = -RTlnK$ (ii) $\log K = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}$ (iii) $K = \frac{q_e}{C_e}$

Where K(l/g) indicate the Langmuir constant, the absolute temperature is represented by T, while R is the gas constant expressed in J/mol K. qe is the quantity in mg/l taken of heavy metals while Ce represent the concentration of heavy metals at the adsorption equilibrium in grams per liter. The plot of ln K against 1/T allowed us to determine the values of ΔH^O, ΔS^O , and ΔG^O at various temperatures were determined and displayed in table 4.13 and figure 4.14.

The thermodynamic factors on adsorption lead, cadmium, copper and zinc onto GA_1 adsorbent were studied at temperatures 25, 30,40 and 45^0C as, where the adsorbent dose was 3.5g in 100ml of wastewater containing 10ppm heavy metals.

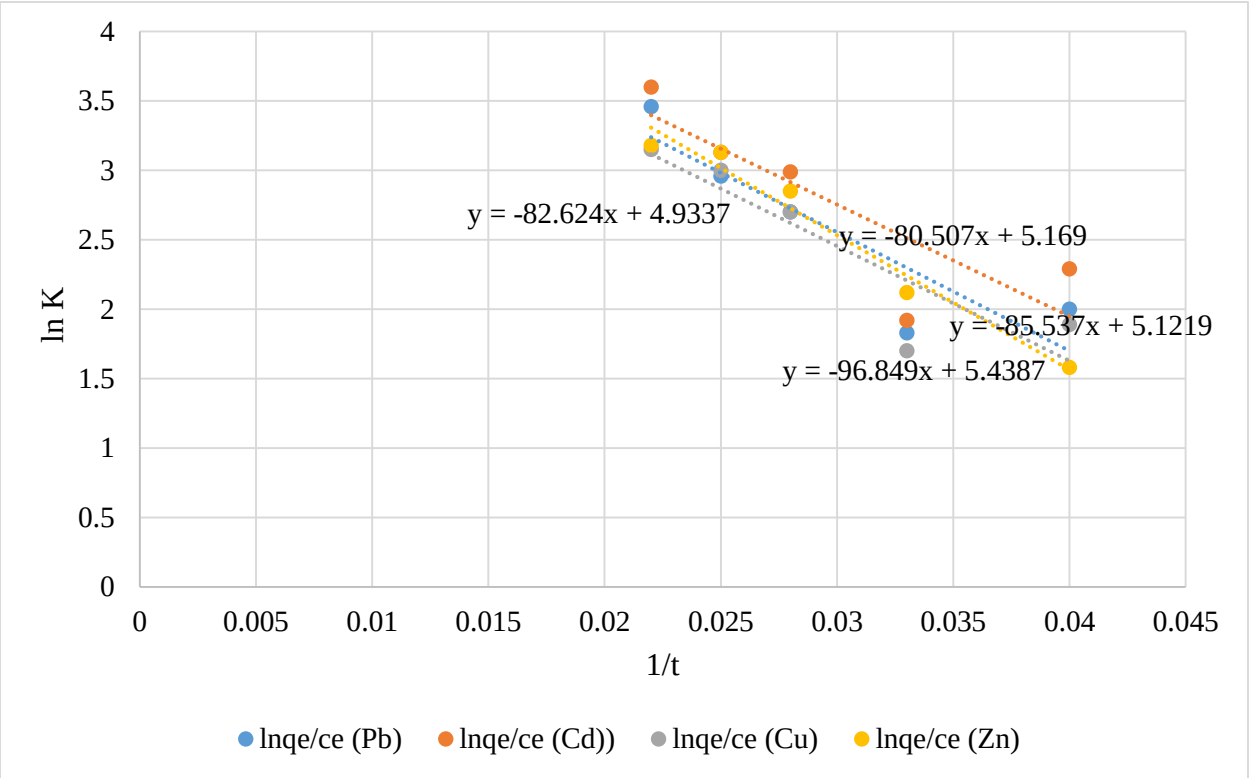


Figure 4.14. Graph of ln K vs 1/T for adsorption of Pb, Cd, Cu and Zn onto GA_1 adsorben

Table 4.13. Thermodynamic variables for Pb, Cd, Cu and Zn adsorption onto GA_1 adsorbent.

Parameter	Pb	Cd	Cu	Zn
ΔH^o (KJ mol $^{-1}K^{-1}$)	-85.53	-80.50	-82.62	-96.84
ΔS^o (KJ mol^{-1})	+5.12	+5.16	+4.93	+5.43
ΔG^o(KJ mol^{-1})/ (298K)	-4.95	-5.67	-4.68	-3.91
(303K)	-4.62	4-.83	-4.28	-5.34
(308K)	-6.91	-7.53	-6.91	-7.29
(313K)	-7.70	-8.14	-7.80	-8.14
(318K)	-9.14	-9.51	-8.32	-8.40

The fact that the standard enthalpy change was negative ($-\Delta H^{O}$) suggest that the interaction of both metals and GA_1 adsorbent was exothermic. The enhanced uncertainty at the solution interface throughout the adsorption mechanism was demonstrated by positive values of the standard entropy variation ($+\Delta S^{0}$). The obtained standard free energy change values were negative (-ΔG^{o}) indicating that the reactions were favorable and spontaneous at the temperature between 25 ^{o}C and 45 ^{o}C.

The increased standard free energy that changes as the temperature rises indicates that the adsorption is more feasible at high temperature. This validates the theoretical accuracy of the experimental results [58].

CHAPTER 5: CONCLUSION AND RECOMMENDATIONS

5.1. Conclusion

The proposed method to natural limestone for wastewater is relatively cheap and readily available. The results revealed Calcium as the dominant element, comprising more than 50 mg/g that the Gishyita and Mpenge limestone is pure.

The experimental results showed the high ability of natural limestone to absorb lead, cadmium, copper and zinc to the extent higher than 70%.

Due to its raw application cost and easy to obtain as well less complex to be used, it is a superior choice for application of natural limestone on wastewater treatment and consider It as a promising application of green chemistry principles.

5.2. Recommendations

Taking into account the results and conclusions, the following recommendations might be made:

- The efficiency of the natural limestone to remove heavy metals in surface water samples may also be investigated.
- Other mechanisms involved in heavy metal removal other than adsorption could be studied for better applications.
- The capacity of natural limestone on the removal of different nutrients like phosphate, Nitrate and ammonium as the agents of eutrophication in surface water should be studied in the next studies.

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