



The Effect of Heavy Metal Composition on the Performance of Sugarcane Bagasse as an Adsorbent in Water Treatment.

**This dissertation is submitted in the fulfilment of the
requirements for the degree of Master of Engineering.**

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PREFACE

This project was carried out under the dual support from Durban University of Technology, Department of chemical engineering and Mondi Paper in Richards Bay, under the supervision of Prof. Yusuf Isa. All the experiments were conducted at Mondi paper main laboratory under the guidance of Mr Myeza and Mr Thethwayo. The sample analyses were carried out at Mondi main laboratory under the guidance of Mr Rajesh Klirrpaul.

I Nokulunga Priscilla Buthelezi, hereby declare this research report titled “**The Effect of Heavy Metal Composition on the Performance of Sugarcane Bagasse as an Adsorbent in Water Treatment**” is my own investigation results from the experiments I have conducted under the guidance of my supervisor and senior co-workers. The results presented has not been submitted in parts or in full to any other University or any institution for any award of degree.

DECLARATION

I, **Nokulunga Priscilla Buthelezi** hereby declare that this dissertation is my own work unless stated to the contrary in the text and it has not been submitted for another degree to any other Institution.

22/04/2021

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Date

Declaration by supervisor

I, **Prof. Yusuf Makarfi Isa** as the candidate supervisor have recommended for the thesis titled Effect of heavy metal composition on the performance of sugarcane bagasse as an adsorbent in water treatment to be submitted for examination.

Supervisor signature

Date

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DEDICATION

I dedicate my dissertation to my family. A special feeling of gratitude to my late loving and caring parents Thamsanqa Buthelezi (Father) and Khonzani Buthelezi (Mother), whose words of encouragement, support, wisdom, and constructive instructions are still honored. My sister Zamashenge for being my pillar of strength and being on my side throughout the project. I also dedicate this thesis to my mentor Charles Mapfumo who has also been supportive till the completion of this project, it would have not been possible without him. All of you have been my best cheerleaders and a reason to push even harder.

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ABSTRACT

Wastewater produced by the industries is potentially harmful to the ecosystem because of various contaminants like heavy metals that find their way into soil and water supplies. Industrial waste constitutes different kinds of metal which contaminate natural water. Heavy metals can build up in the environment and enter living organisms through chain elements such as the food chain and therefore, pose a major health risk to living organisms. The situation has been worsened by the absence of broadly accepted heavy metal treatment techniques, thus this challenge continues to receive considerable attention from stakeholders including scientists and researchers. While many technologies have been proposed such as reverse osmosis, flocculation, ion exchange and so on and so forth, they continue to suffer from a number of drawbacks including generation of secondary wastes and cost ineffectiveness. Thus, in the present study, adsorption was chosen as a cost effective, efficient, and environmentally friendly treatment process.

Sugar cane milling production produces a lot of sugar cane bagasse which is considered as environmental waste if not disposed properly. It is imperative to remove heavy metals from polluted water before discharging it into the environment, rivers and lakes using sustainable techniques. Heavy metal removal from wastewater using low-cost adsorbents like sugarcane bagasse addresses two problems: removal of pollutants from water and utilization of agricultural waste.

This study evaluated the performance of sugarcane bagasse in the removal of heavy metals. Sugarcane bagasse was characterized to determine the functional groups, the porosity and surface area, crystallinity and morphology using FTIR, SEM and XRD. One factor at a time (OFAT) approach was used to evaluate the effect of operating parameters on the removal of heavy metal ions.

A 3-system component of the stock solution of synthesized wastewater namely single, binary and ternary were studied. The 3 metal ions evaluated were Copper, Chromium and Cadmium. The factors considered in the OFAT design of experiments were contact time (30-240 mins), adsorbent dosage (5-30g/L), initial concentration (50-500 mg/L), pH(2-9), and particle size (75-600 μm). It was observed that all adsorption parameters had an effect on the adsorption rate. However, an adsorption dosage had a greater impact on the adsorption rate. An increase in the adsorption dosage from (5-20 g) showed that the percentage removal efficiency for chromium, copper and cadmium increased from (40-72%, 44-75% and 39-59%) in a single metal system. In addition, the percentage removal increased from (34-62% for chromium, 47-78% for copper, and 34-62% for cadmium) in a binary metal system. Furthermore, the percentage removal increased from (38-52%, 40-59% and 24-43%) for chromium, copper, and cadmium in a ternary metal system. Adsorption capacity of the adsorbent was determined using the optimal operating parameters obtained from the OFAT design of experiments. Langmuir and Freundlich isotherms were used to analyze the adsorption data. The OFAT design of experiments resulted in producing the optimum conditions for adsorption. The optimum conditions for maximum adsorption were, contact time (180 mins), initial concentration (50 mg/L), pH (7), dosage (20 g), particle size (340-450 μm) and a mixing speed of 150 rpm. Adsorption capacities differed between the 3 system components. Maximum adsorption capacities of 38.41 mg/L were registered for copper ions and was recorded for the single component system. Stock solutions containing copper ions registered the highest adsorption capacity. There was a significant decrease in the maximum adsorption capacities for copper ions of the binary and ternary system components which were 21.45 mg/L and 1.237 mg/L respectively. This was attributed to the co-metal ion dependence in both the binary and ternary system components.

In conclusion, the study showed that sugarcane bagasse can be used as an adsorbent in the efficient removal of heavy metal ions present in wastewater.

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ABBREVIATIONS

Abbreviation	Description
Cu	Copper
Cr	Chromium
Cd	Cadmium
Zn	Zinc
Ni	Nickel
Pb	Lead
Fe	Iron
Hg	Silver
B1	Particle size <75 μm
B2	Particle size 75-150 μm
B3	Particle size 350-450 μm
B4	Particle size 500-600 μm
RO	Reverse Osmosis
NF	Nano-filtration
UF	Ultrafiltration
COD	Chemical oxygen demand
TDS	Total dissolved solids
OFAT	One factor at a time
ICP	Inductively coupled plasma
FTIR	Fourier Transform Infrared
XRD	X-ray diffraction
SEM	Scanning electron microscope

CHAPTER 1: INTRODUCTION

1.1 Background

Only 88% of South Africa's population get clean water and one of the key pollutants that pollute water is heavy metal ions (Wilkinson, 2016). Heavy metal pollution sources, which affect the environment and human health, are vast including paint, electroplating, metal processing, pigment industries and wood production (Bahaa et al., 2019). Diverse techniques for wastewater treatment for the removal of heavy metal ions have also been employed, for example chemical precipitation, ion exchange and adsorption (Ahmad et al., 2018). Adsorption is regarded as an environmentally friendly and easy to use process. It is necessary to explore suitable adsorbents since the frequency of heavy metal contamination and high processing costs of these adsorbents increase. Several studies have shown that wastewater treatment based on adsorption is an effective and low-cost purification technology if proper adsorbent is used (Ince and Ince, 2015).

Another major environmental issue is solid waste. The world production of solid waste has been reported to be around 11 billion tons of solid waste annually (Mohammed et al., 2017). Local solid waste production has been reported to be around 108 million tons per year (Greyling, 2017). Untreated solid waste occupies not only a vast territory but pollutes water and air if the waste is not properly disposed of. Solid waste disposal at landfills poses to be inefficient and easily causes contamination. Using solid waste is a way to reduce environmental pressure efficiently and make recycling possible. Most sugar mills spend lots of money on sugarcane bagasse collection, transportation, and disposal as a land-fill material (Ouadjeni-Marouf et al., 2013). The use of sugarcane bagasse as an adsorbent addresses two problems i.e. recycling of solid waste and cost effectiveness as it is locally available in plenty and has no cost.

Work has been done on the adsorption of heavy metals in wastewater using sugarcane bagasse as a potential adsorbent (Ouyang et al., 2019). However, most work reported in literature focused more on single component adsorption of heavy metal ions rather than multi-metal system adsorption process. In real life application, wastewater generated in industries often contain several metal ions concurrently (Rana et al., 2014). Therefore, this has necessitated a need of evaluating the effect of heavy metal composition on the performance of sugarcane bagasse as an adsorbent in water treatment.

1.2 Research Problem

South Africa is facing a challenge of treating the industrial wastewater before disposing it into water bodies. This wastewater contains more than one heavy metals (multi-systems) which poses health and environmental problems. Disposal of sugarcane bagasse poses environmental problems of pollution and possible water contamination. Using sugarcane bagasse as an adsorbent of heavy metal ions addresses both problems above. There are limited studies in South Africa that focus on the usage of sugarcane bagasse as an adsorbent of multiple heavy metal ions in wastewater.

1.3 Hypothesis

Sugarcane bagasse is able to remove more than one heavy metal ions present in wastewater and its performance is different to that when only a single metal is present in the waste solution.

1.4 General Objective

The aim of this study is to evaluate the performance of sugarcane bagasse in the removal of metals from multi- metal solution

1.5 Research Objectives

- To prepare and characterize the adsorbents media (sugarcane bagasse)
- To determine the effect of process parameters (i.e. contact time, dose of sugarcane bagasse, initial pH, metal concentration of water and particle size) on heavy metal removal efficiency.
- To determine the optimum process parameters for the removal of heavy metals.
- Evaluate adsorptive capacity and equilibrium isotherm of sugarcane bagasse under batch adsorption experiments.

1.6 Approach

This research was experimental in nature. Batch process was used in this research due to its simplicity to find equilibrium isotherms. Preliminary runs were done as a screening process to obtain best performance conditions for the adsorption of heavy metals in wastewater. All of the experiments for this research were done using the conditions obtained. Process parameters that were varied were initial metal concentration and pH of the synthesized water, particle size of sugarcane bagasse, contact time and sugarcane bagasse dosage. In particular, the pollutant concentration in multicomponent systems is a crucial parameter for adsorption because it can determine the occurrence of unexpected effects when different solutes are present in the same solution.

1.7 Thesis Structure

This thesis contains five chapters, and it is organized in the following manner:

Chapter 1: Introduction

This section introduces the research title; provides the background of the study, highlights the problem statement, objectives, and the scope of the study.

Chapter 2: Literature review

This section is a survey of existing studies and findings on this research area. It provides knowledge on the problem-solving strategies and shortcomings encountered by other researchers.

Chapter 3: Methodology

The methodology section provides a detail of the means and approaches taken in order to achieve the research aims and objectives. The techniques and strategies used for the design of experiments (DOE), data collection and analysis of results are explained.

Chapter 4: Results and discussion

This section provides a detail of the experimental findings and the interpretation of the results. The results generated from the experiments were compared to the findings in literature to check for validation and reliability.

Chapter 5: Conclusions and recommendations

This section summarizes the research findings according to the objectives set and demonstrate that the researcher has met the targets set at the commencement of the study. It also provides recommendations for further research in the light of the results obtained and shortcomings encountered.

CHAPTER TWO: LITERATURE REVIEW

2.1 Introduction

Wastewater is water which contains liquid waste disposed of by residential, industrial, and agricultural activities which may cover a wide range of possible pollutants. Water used in industries produces wastewater potentially harmful to the ecosystem because of various contaminants like heavy metals that find their way into soil and water supplies (Agarwal and Singh, 2017). If there is no low cost, reliable, effective technology in place, wastewater can be reversed back into the environment. A variety of industrial processes also release toxic metals and this in turn can lead to water bodies, soil and air becoming polluted. Industrial waste comprises different kinds of metal which contaminate natural water. Heavy metals found in wastewater are: Chromium (Cr), Copper (Cu), Cadmium (Cd), Lead (Pb), Zinc (Zn), Iron (Fe) which find its way to larger water bodies through wastewaters. Heavy metals can build up in the environment and enter living organisms through chain elements such as the food chain and therefore pose a major health risk to living organisms (Agrawal and Singh, 2016).

This chapter provides a broad overview about wastewater discharge in developing countries and applicability of low-cost techniques for removal of heavy metals from wastewater. The current status of the challenges surrounding wastewater generation and discharge are also discussed.

2.2 Wastewater

Wastewater is known as used water generated from point sources such as rural areas, urban areas and from non-point sources such as public and private institutions, farms, and industries. Around 90% of wastewater flows into river systems and coastal regions in developing regions such as South Africa is untreated water (Fouladgar, 2015).

Millions of gallons of liquid waste are released every day in fresh surface water bodies from rural, manufacturing, domestic and commercial sources (Ali et al., 2012). It is also estimated that some 300 to 400 million tons of liquid hazardous waste are released annually from factories to local surface water systems worldwide (Alfarra et al., 2014). This can lead to contamination of rivers, streams, and other bodies of water on surfaces and threaten well-being, food safety and the right to safe water. As a result, about two million tons of wastewater is emitted from non-point sources such as agriculture and points of sources such as factories to bodies of surface water around the world (Corcoran, 2010). Industrial wastewater contains hazardous substances such as heavy metals and industrial pollutants suspended and dissolved in it. Heavy metal emissions from mining operations is the major problem of global surface water contamination. Heavy metal pollution at threshold levels is of considerable effect on the environment and causes serious difficulties for living organisms. According to the substantiation, including but not limited to the World Health Organization, heavy metals of urgent environmental concern are lead, chromium, mercury, cadmium, copper, zinc, and iron. The pollution by heavy metals of water is a vital environmental and health problem. In fact, the government has been deeply concerned about this pollution. The development of cost-effective and cost-beneficial treatment methods for contaminated industrial wastewater remains a topic for many researchers and to discuss globally (Khulbe and Matsuura, 2018).

2.3 Heavy Metal Pollution

The heavy metals contamination is mainly caused by manufacturing unit effluent. The rapid development of industrialization has resulted in large quantities of wastewater being generated and the increased environmental processing of heavy metals (Habuda-Stanic and Flanagan, 2014). As shown on Table 2.1, diverse alkalis, arsenic, cyanides and heavy metals will be discharged to water resources by effluent irrigation from industries such as paper mills and fertilizer factories, electrical platelets, chemical, petrochemical, metal and mining sectors (Manuel, 2015). These industries release their wastewater containing harmful heavy metals without treatment (Corcoran, 2010). The massive increase in use in recent decades of heavy metals in the marine environment has led inevitably to increased flux of metal substances (Bahaa et al., 2019). The non-biodegradability of heavy metals distinguishes them from other toxic pollutants. Heavy metals, due to their mobility and toxicity and non-biodegradation, are the most harmful pollutant among all other pollutants in natural waters (Demirbas, 2008). The word heavy metal applies to any metallic chemicals with a fairly high density. The density of heavy metals is usually more than 5 g/cm (Abas et al., 2013). In addition, Srivastava et al. (2008) stated that the atomic number of heavy metals is high between 63.5 and 200.6.

Table 2. 1: Common industrial units releasing heavy metals into water bodies. *Courtesy of (Abdel et al., 2011)*

Metal	Major common industries source
Chromium	Textile, Steel, Pulp and paper, Petroleum refining, Tanning, Power plants.
Copper	Pharmaceuticals, Steel, Pesticide, Insecticides, Fungicides.
Lead	Steel works, Pulp and paper, Fertilizer, Automobile, Organic chemicals, Batteries, and paints.
Zinc	Fertilizer, Organic chemical, Pulp and paper, Steel works
Cadmium	Organic chemical, Petroleum refining, Steel works, Fertilizer, Aircraft plating and finishing, Fertilizer
Iron	From metal refining, engine parts.
Aluminium	Industries preparing insulated wiring, ceramics, automotive parts, aluminium phosphate, and pesticides.
Arsenic	Automobile exhaust/industrial dust, wood preservatives and dyes.
Mercury	Wood preservatives, leather tanning, ointments, adhesives, and paints.

2.4 Sugarcane Bagasse

In South Africa alone, 7.9 million tons of bagasse is produced per year (Wilkinson, 2016). Annually, global sugar cane production is expected to hit 540 million tons (Agarwal and Singh, 2017). For every ton of sugarcane, a total of around 280 kilograms sugarcane bagasse is produced. This can either be seen as an environmental waste or as a very useful resource in the right recovery technology. The fibrous substance that remains after sugarcane has been crushed and its juices extracted during processing of sugar are sugarcane bagasse. Heavy metal ions adsorbed in chemically modified sugarcane bagasse and the adsorption of phenol using a bagasse sugarcane derived adsorbent has been studied (Karnitz and Gurgel, 2007). It means farm waste can be used for inorganic and organic waste sorption in a variety of ways.

While sugarcane bagasse is burned in South Africa for the production of energy for sugar mills, left over is still significant (Greyling, 2017). South Africa's annual sugarcane mill output, on the other hand, is an average of about 22 million tons generating an average of 3.3 million tons of dry bagasse (Greyling, 2017). Excess bagasse is generally used for the production of furfural, pulp and paper and cogeneration but are still relevant. This contributed to the need to develop feasible and appropriate solutions for using the surplus. It constitutes about 30% to 40% of the waste. Bagasse is one of agricultural waste used in adsorbent manufacturing. Bagasse can be a cheap, attractive, and effective adsorbent for wastewater treatment. Adsorption capacity of charred xanthated sugarcane bagasse (CXSB) for the removal of specific heavy metals has been investigated (Homagai and Ghimire, 2010). Sugarcane bagasse was modified using organic compound succinic anhydride ($C_4H_4O_3$) for the uptake of Cu (II), Cd (II), and Pb (II) from a solution. The maximum adsorption capacity was determined using Langmuir model to be 114 mg/g for Cu^{2+} , 196 mg/g for Cd^{2+} and 189 mg/g for Pb^{2+} .

2.5 Wastewater Treatment

Wastewater treatment is the method of purifying water that contains industrial solid waste. This operation is highly important due to the fact that some contaminants or pollutants are difficult to manage after release from point source pollution to the environment (Adib et al., 2018).

Furthermore, wastewater treatment is essential for the following reasons (Ahmaruzzman, 2011):

1. Protecting water quality of surface water bodies; rivers and lakes.
2. Consequently protecting aquatic life; fish.
3. Protecting human health from deterioration due to direct and indirect exposure to water pollutants.
4. Ability to reuse treated wastewater in applications that do not require high water quality, leading to having more control over the waste resources; hence, conserving the water resources.

A conventional wastewater treatment process consists of a combination of physical, chemical and biological processes and operations to remove solids and organic matter from wastewater. However, there is a stage that appears before the three mentioned stages known as preliminary stage. These stages depend on the characteristics of wastewater discharge, the amount of harmfulness, and cost effectiveness. Accessibility of land for construction of treatment plants is a main factor in the process. Making polluted water fit for consumption and use again is not an easy process; hence, regarded as a challenge.

No one purification or filtration method works for all types of water pollution. In order to make water usable again after water pollution, it must be treated with a variety of filtration and purification methods. Therefore, it is important to treat heavy metals discharge from industrial wastewater, with affordable and technically feasible methods. This initiates the need for exploring cost-effective, simple and efficient removal techniques.

2.5.1 Preliminary Wastewater Treatment

The purpose of the preliminary wastewater treatment is to ensure the proper operation of the wastewater plant. This is achieved by removing from wastewater any constituents which can clog or damage pumps or interfere with subsequent treatment processes.

Preliminary treatment devices are therefore, designed to:

1. Remove or to reduce in size the large, entrained, suspended or floating solids. These solids consist of pieces of wood, cloth, paper, plastic, garbage, etc.
2. Remove heavy inorganic solids such as sand and gravel as well as metal or glass. These objects are called grit.
3. Remove excessive amounts of oil or greases.

2.5.2 Primary Wastewater Treatment

Primary wastewater treatment is aimed at the removal of fine suspended organic solids that cannot be removed in the preliminary treatment. However, some industries do not apply preliminary treatment but use primary treatment as a substitute to eliminate large suspended solid waste materials (grit and gravel) that settle down at the bottom of the tanks by gravitational force (Mungray et al., 2012). Primary treatment basically involves the process of sedimentation or settling. In the normal wastewater treatment process, sedimentation is usually carried out twice. It is carried once before the secondary treatment, referred to as primary sedimentation and then after the treatment is complete, a process known as secondary sedimentation. The design of primary treatment tanks may be rectangular or circular in shape, and in this process 30% of biological oxygen demand (BOD), and 60% of total suspended solids (TSS) can be eliminated (Ali et al., 2013). The primary wastewater treatment supports the secondary stage of treatment (Metcalf and Eddy, 2003a, El Zayat, 2014a)

2.5.3 Secondary Wastewater Treatment

At a secondary wastewater treatment stage, biologically broken down materials can be reduced into residual organic matter. For instance, the remaining 70% biological oxygen demand (BOD) of the organic compounds from the primary wastewater treatment stage are treated by microorganisms. These microorganisms comprises; bacteria, algae, fungi, protozoa, rotifers that decompose the unstable organic matter to stable inorganic forms. Other small particles of suspended solids that pass through the first stage are then settled at the bottom of the tank by using a coagulant (alum). The coagulant emboldens the colloidal materials in the wastewater to join together into trivial aggregates (Metcalf and Eddy, 2003b, Kapanji, 2010, Mihelcic and Zimmerman, 2014, El Zayat, 2014b). Secondary treatment processes are broadly classified as aerobic, anaerobic and pond processes.

2.5.4 Tertiary Wastewater Treatment

Tertiary wastewater treatment is defined as any process designed to produce an effluent of higher quality than normally found in secondary treatment. Tertiary treatment is sometimes desirable for the removal of suspended and dissolved substances, after the conventional primary and secondary treatments. This is the final stage of conventional wastewater treatment.

However, tertiary treatment is needed under the following circumstances:

1. When the quality of the effluent to be discharged does not meet the standard requirements (particularly in the developed countries).
2. When there is a necessity to reuse the wastewater (reclamation of water is quite expensive but is required in certain situations of water shortage).
3. For the removal of nitrogen and phosphorous compounds.

Most of the time at these stage, different disinfectants like chlorine, ozonation and ultraviolet radiation are used to treat wastewater (Metcalf and Eddy, 2003a)

In various developed countries, the treatment of water contaminated by heavy metals is performed using different technologies such as chemical precipitation, coagulation-flocculation, ion exchange and membrane filtration (Chiarle et al., 2000). Tertiary treatment process broadly involves the removal of suspended and dissolved solids, nitrogen, phosphorus, and pathogenic organisms. However, sometimes tertiary treatment processes may be directly carried out bypassing the other unit operations. This mainly depends on the composition of wastewater requirements. These techniques are promising technologies for wastewater treatment having toxic metals, however, they are expensive (Rao and Senthilkumar, 2012).

2.6 Heavy Metal Removal Techniques

Intake of heavy metals by living organisms leads to numerous diseases and disorders (Ali et al., 2013). Therefore, it is important to remove heavy metals from polluted water before discharging them into the environment, rivers and lakes using conventional techniques. There are many conventional methods for removal of toxic chemicals as heavy metals including the following: chemical precipitation, ion exchange process, membrane filtration, adsorption, electrochemical, photochemical oxidation, and ozonation and biological process (Sato and Qadir, 2013).

2.6.1 Chemical Precipitation

Chemical precipitation is the most widely used method for heavy metal removal from inorganic effluent. The metal ions are converted to insoluble form (particles) using precipitating agents such as calcium hydroxide, sodium hydroxide, ferric chloride or ferrous sulphate. Furthermore, precipitation of metals is achieved by the addition of coagulants such as alum, lime, iron salts and other organic polymers. The particles formed are removed by settling or filtration. Hence, large amounts of sludge and/ solid residues containing toxic chemicals produced during the process is the main disadvantage (Basri et al., 2019). The produced sludge also requires licenced disposal and further treatment. Lime precipitation can be employed to effectively treat inorganic effluent with metal concentration of higher than 1000 mg/L. Other advantages of using lime precipitation include the simplicity of the process, inexpensive equipment requirement and convenient and safe operations. Table 2.2 summarises the work done by other researchers related to removal of heavy metals by chemical precipitation.

Table 2.2: Removal of heavy metals by chemical precipitation (Fu et al., 2012).

Heavy metals	Initial metal conc (mg/L)	Precipitant	Optimum Ph	Removal efficiency (%)
Ni	50	Alkali	2.5	98.4
Ni	50	Alkali	11	92.8
Ni	100	FeSO ₄	3	99.9
Cu, Zn, Cr, Pb	100	Lime	7-11	99.37-99.6
Cu, Cr	48.51	Ca(OH) ₂ and NaOH	8.7 and 12	98.56
Cu, Cd	50	Pyridine based thiol legand	4.5	99.99 99.88
Zn	200	Sulfate reducing bacteria	6.8	-
Cd, Cu, Pb, Ni, Zn	-	Sodium decanoate	4-8	>90
Cu	100	1,3,5 Hexahydrotriazine Dithio-carbamate (HTDC)	3-9	99.6
Fe	194	1.3 Benzenediamedoet Hanethiol dianion	4.5	>90
Cu	25	Ca(OH) ₂	12-13	>99

The unit operations typically required in this technology includes neutralization, coagulation or flocculation, solid/liquid separation and dewatering. The precipitation method is simple and economical. However, method may not be a viable option for certain end-users since it is not versatile. In addition, chemical precipitation requires a large amount of chemicals to reduce metals to an acceptable level for discharge. Other drawbacks are its slow metal precipitation, poor settling, the aggregation of metal precipitates, and the long-term environmental impact of sludge disposal (Febrianto and Kosasih, 2009). Furthermore, disadvantages of precipitation methods is that metal concentration of treated water cannot be reduced below the solubility of the precipitate. Therefore, the use of other techniques such as adsorption is advisable in order to protect the environment.

2.6.2 Ion Exchange

Ion exchange is a process in which there is an exchange of ions between the liquid phase and a porous solid. The exchange occurs between the ions of insoluble exchange material (ion-exchange material) and the ions of different species in solution (i.e wastewater for advanced treatment). In ion exchange systems, naturally occurring inorganic zeolites and synthetically produced organic resins are usually employed. An organic ion exchange resin is made up of high-molecular weight polyelectrolytes that can exchange their mobile ions for ions of similar charge from the surrounding medium. Each resin has a distinct number of mobile ion sites that has set the maximum quantity of exchanges per unit resin. Most of the resins used are synthetic because their characteristics can be tailored to specific applications. Ion exchange resins are as cation exchangers, which have positively charged mobile ions available for exchange. Both anion and cation resins are produced from the same basic organic polymers. They differ in ionisation groups attached to the hydrocarbon network. It is this functional group that determines the chemical behaviour of the resin (Esmaili and Foroutan, 2015). Resins can be broadly classified as strong/weak cation exchangers or strong/weak base anion exchangers. Ion exchange is used for water softening, demineralization and separation and recovery of salts, including salts of organic acids and bases. It is regarded as another method used successfully in industries for the removal of heavy metals from effluent. Commonly used matrices for ion exchange are synthetic organic ion exchange resins. The resin is a polymer that has been functionalized by the addition of either acidic or basic groups. For example, sulfonated polystyrene contains SO_3^- group that attach to cations from solution, and hence, can be used as a cation exchange resin (Esmaili and Foroutan, 2015).

The particular choice of acidic or basic groups allows the designer to modify the strength of interaction and enhance selectivity of the resin when a solution is passed over a cation-exchange resin, the cation in the solution equilibrates with the cations that were attached to the resin and hence effectively become adsorbed onto the resin. The disadvantage of this method is that it cannot handle concentrated metal solution as the matrix gets easily fouled by organics and other solids in wastewater. Moreover, ion exchange is nonselective and is highly sensitive to the pH of the solution. In addition, a disadvantage of this method is high cost of resin and high cost of disposing of regeneration solutions (Gaikwad, 2010). Table 2.3 summarises the work done related to heavy metal removal using ion exchange method.

Table 2.3: Heavy metal removal using ion exchange (Thakare and Jana, 2015, Carro et al.,

Heavy metal	Initial metal conc.	Resin	Optimum pH	Removal efficiency (%)
Cu, Zn, Cd	-	Amberlite IR-	-	-
Pb	-	Purolite C100	-	99.17%
Cu	50–150 mg/L	Indion 225H	6.3–6.5	-
Ni, Pb	800, 1,000, 1,250 mg/L	Amberjet 1,200 Na	-	98%, 99%
Hg, As	-	-	-	98.56%
Ni	1,800, 2,800, 3,800 mg/L	Acidic cation exchange resin	3–7	97%
Cd, Pb	0.1 to 6 mmol/L	Sargassum muticum loaded with calcium	5	-

2015).

Electrolytic recovery or electro-winning is one of the many technologies used to remove heavy metals from process water streams. This process uses electricity to pass a current through an aqueous metal-bearing solution containing a cathode plate and an insoluble anode.

Positively charged metallic ions cling to the negatively charged cathodes leaving behind a metal deposit that is strippable and recoverable. A noticeable disadvantage is that corrosion could become a significant limiting factor, where electrodes could frequently have to be replaced.

The synthetic resins with strong acid (H^+) and basic (OH^-) functional groups serve as an ion exchange. The cation exchangers (with H^+ or Na^+) can replace the positively charged ions (Ca^{2+} , Mg^{2+}) in water with hydrogen ions. The anion exchange (with OH^-) can remove negatively charged ions (SO_4^{2-} , NO_3^- and CO_3^{2-}). The wastewater is first passed through a cation exchanger. For cation exchange acid (H_2SO_4 , HCl), while for anion exchange resins, alkali $NaOH$ are used. For an effective removal of dissolved solids by ion exchange, the wastewater should not contain high concentration of suspended solids as they block the ion exchange beds (Gaikwad, 2010).

2.6.3 Electrodialysis/ Membrane Separation

Electrodialysis is a membrane separation in which ionized species in the solution are passed through an ion exchange membrane by applying an electric potential. The membranes are thin sheets of plastic materials with either anionic or cationic characteristics (Figure 2-1). Membranes are widely used for concentration of solutions of dissolved solids, as well as suspensions of particulates (Abdullah and Yusuf, 2019). A tubular membrane that is permeable to the solvent but not to the solute can be used to remove the solvent from a solution in the same manner as cross flow filtration. When a solution containing ionic species passes through the cell compartments, the anions migrate towards the anode and the cations towards the cathode, crossing the anion exchange and cation exchange membranes.

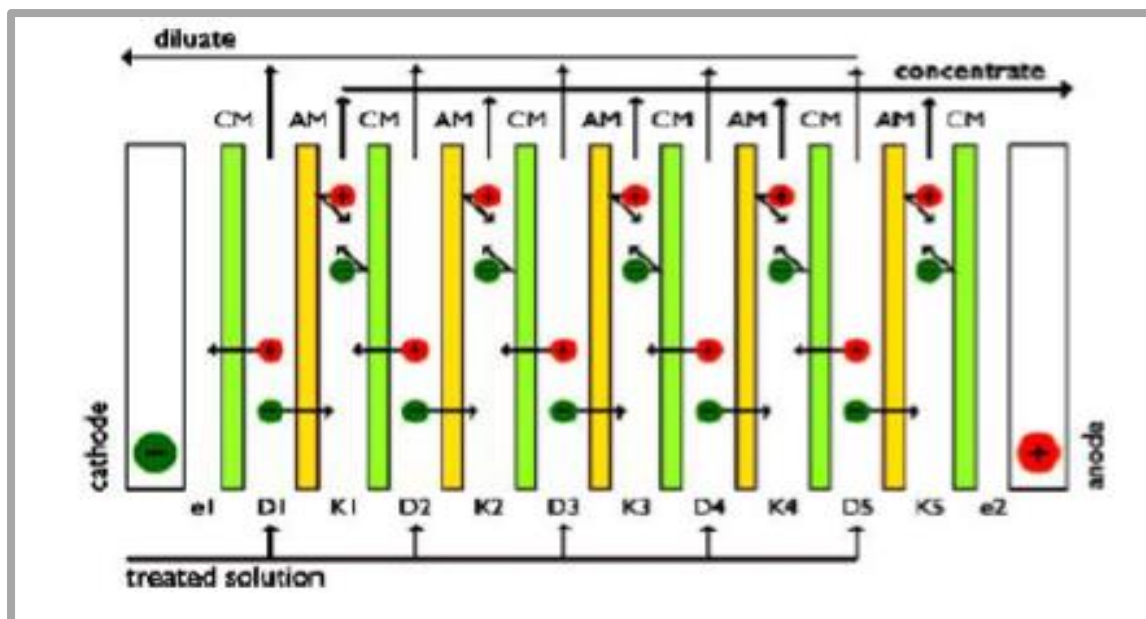


Figure 2. 1: Electro dialysis principles adapted from Chen, Wang, and Chang (2009) CM – cation exchange membrane, D-dilute chamber, e1 and e2-electrode chambers, AM-anion exchange membrane and K-concentrate chamber.

Membrane processes operate on the basis of mechanisms such as: pressure driven which, includes reverse osmosis (RO), ultrafiltration and nanofiltration (NF); concentration driven, which includes diffusion dialysis; electrically driven, which includes electro dialysis and finally, temperature difference driven, which includes membrane distillation (Abdullah and Yusuf, 2019). In the electro-dialysis process, ionic components of a solution are separated through the use of semipermeable ion-selective membranes. This process may be operated in either continuous or a batch mode. Membrane filtration (UF, RO, and NF) is used to simultaneously remove colour, COD, heavy metals, and total dissolved solids (TDS) from wastewater. Membrane separation processes offer various advantages such as a compact system, easy control of operation and maintenance and low ion needs for chemicals (Juang and Shiau, 2000). However, in spite of the advantages, membrane separation has the drawbacks of poor removal of low molecular weight (organic) materials (ultrafiltration) and high energy consumption (Reverse osmosis).

Additional problems associated with the electrodialysis process for wastewater purification include chemical precipitation of salts with low solubility on the membrane surface. Another limitation of membrane process is flux decline caused by membrane fouling, which may result from plugging of organic and inorganic materials in the membrane pores. This fouling of membranes lowers the economic efficiency of the separation processes by reducing the rate of production of treated water and softening the membrane life, to reduce the membrane fouling, activated carbon pre-treatment, possibly preceded by chemical precipitation and some form of multi-media filtration may be necessary (Khulbe and Matsuura, 2018).

2.6.4 Membrane filtration

Membrane filtration has received considerable attention for the treatment of inorganic effluent since it is capable of removing not only suspended solid and organic compounds, but also inorganic contaminants such as heavy metals. Depending on the size of the particle that can be retained. Various types of membrane filtration such as ultrafiltration, nanofiltration and reverse osmosis can be employed for heavy metal removal from wastewater, Unique specialties enables UF to allow the passage of water and low-molecular weight solute, while retaining the macromolecules, which have a size larger than the pore size of the membrane. The main advantage of this process is regeneration of sludge (Abdullah and Yusuf, 2019).

2.6.5 Reverse Osmosis Process

Reverse osmosis (RO) is by far the most widely used membrane process. In a reverse osmosis plant, water passes through a membrane, while dissolved minerals and other solids are rejected in the retentate. Table 2.3 demonstrate the summary of the study that was conducted by other researchers. Reverse osmosis is used to generate deionized water, process feed water, purify boiler feed water, recover wastewater from waste streams and desalinate sea water or brackish water for drinking and irrigation.

Table 2.4: Removal of heavy metals by reverse osmosis method (Dialynas and Diamadopoulos, 2009).

Membrane	Heavy metal	Initial concentration Mg/L	Removal efficiency (%)
RO	Cu, Ni	-	99.5
RO	Ni, Zn	44-169	99.2, 99.8
RO	Cu	-	95
	Ni		
	Cr		
RO	Pb	-	100
	Ni		100
	Cr		89
	Cu		49

In a reverse osmosis process, the feed water is pressurized to provide an adequate pressure gradient to overcome the difference in osmotic potential between the briny retentate and the purer permeate. Under the applied pressure gradient, water flows through the membrane against the concentration gradient. The membranes are usually designed as spiral-wound modules and are operated in cross flow (Bakalar et al., 2009).

The reverse osmosis process depends upon a semi-permeable membrane through which pressurized water is forced. Reverse osmosis is the opposite of the natural osmosis process of water. Osmosis is the name for the tendency of water to migrate from a water saline solution to a stronger saline solution, gradually equalizing the saline composition of each solution when a semi-permeable membrane separates the two solutions (Bakalar et al., 2009).

Consequently, in reverse osmosis water is forced to move from stronger saline solution to a weaker solution, again through a semi-permeable membrane. Because molecules of salts are physically larger than water molecules, the membrane blocks the passage of salt particles.

The end results are desalinated water on one side of the membrane and highly concentrated saline solution of water on the other side. The recovery of water from RO plants depends on the feed water quality, the production specifications, and the need to prevent membrane fouling. Highly pure water is usually not obtained in a single stage. The membrane typically rejects 96% to 98% of the salts per stage, and several stages may be used to achieve the desired purity, with recycle or retentate. Hence, the disadvantage of this method is that it is expensive (Bakalar et al., 2009).

2.6.6 Ultrafiltration

Ultrafiltration is a membrane filtration process similar to reverse osmosis, using hydrostatic pressure to force water through a semi-permeable membrane, ultrafiltration technologies can be used in a variety of ways in wastewater treatment and water reuse systems. Common applications for ultrafiltration systems are food and beverage processing, pharmaceutical use, municipal, borehole and surface water treatment (Bakarat and Schimdt, 2010). In filter mode, feed water flows inside the ultrafiltration membrane fibre, in either a crossflow or dead-end filtration configuration, depending on the feed water quality. Filtrate is collected into the central core tube and passed out to the process. In the backwash mode, filtrate backwash flows from the central core tube to inside the fibre tubes and out to the drain. In most systems, the backwashing cycle is controlled by a timer or differential pressure switch. In table 2.5, the removal efficiency of heavy metals obtained by other scientists using ultrafiltration method is demonstrated..

Table 2.5: Removal of heavy metal efficiency by ultrafiltration (Tanhaei et al., 2014) .

UF Type	Heavy metals	Complexing agent	pH	Removal efficiency (%)
Micellar enhanced UF	Cu, Ni	SDS, TX114, TX100 Brij35, TX405	11	-
Micellar enhanced UF	Cd, Zn	SDS		99
Polymer enhanced UF	Hg	Polyvinylamine	-	99
Polymer enhanced UF	Co	PVA and sulfonated PVA	5.93 6.5	31.81 99.98

In applications where complex contaminants are present in the feed water, or additional treatment is required, chemicals may be used during the backwashing process. Usually, sodium hydrochlorite and hydrogen peroxide are used to help flush the membrane surface impurities. Ultrafiltration dramatically reduces use of pre-treatment chemicals (Shahrin et al., 2019).

Advantages of ultrafiltration includes:

1. Product quality is stable even during feed water quality variations.
2. Single step treatment reduces operating costs and increases efficiency.
3. Low pressure feed and backwash operation.
4. Increased efficiency of RO system design and operation contributing to the reduced capital and operational costs.
5. Reduce labour requirements.

In spite of the advantages, this process has drawbacks. On the contrary this method uses more electricity. May need pre-treatment and requires replacement of membranes.

2.6.7 Coagulation and Flocculation

Coagulation comes from the Latin word “coagulare” which means “to agglomerate” in water treatment. Coagulation is the destabilization of colloids by neutralizing the forces that keep them apart. Cationic coagulants provide positive electric charges to reduce the negative charge (zeta potential) of the colloids. As a result, the particles collide to form large particles (flocs). Hence, coagulation is the result of the addition of chemical reagents to water suspension where the dispersed colloidal particles are assembled in larger aggregates called flocs or microflocs (Pang et al., 2011a).

Coagulation is an elementary step, but it is essential to the physico-chemical treatment process of water and wastewater. This is the first step in the elimination of colloidal particles and its main function is to stabilize the particles. This stabilization is essentially the neutralization of the electrical charge present on the surface of the particle thus facilitating the agglomeration of the colloids. Colloids are insoluble particles suspended in water. These particles are usually less than 1 μm in size and they have poor settling characteristics (Johnson and Kirby, 2008).

Coagulation is always considered along with flocculation and is used to remove particles which cannot be removed by sedimentation or filtration alone. In table 2.6, the removal of heavy metals by coagulation/ flocculation is summarized. Coagulation and flocculation methods are responsible for the colour and turbidity of water. They include clays, metal oxides, proteins, microorganisms, and some organic compounds.

Table 2.6: Shows heavy metal removal efficiency by coagulation or flocculation method (Pang et al., 2011b).

Heavy metal	Coagulant/flocculant	Initial metal conc.	Optimum pH	Removal
	Aluminium sulphate		Alum- 6.2–7.8	
Fe, Zn	Polyaluminium Chloride	25–45 mg/L	PACL-8– 9.3	99%
	Magnesium chloride	-	MgCl ₂ - 8.7–10.9	-
Co, Ni, Cu	Chitosan montmorillonite system	20–100 mg/L	6.8	-
	Sodium dodecyl Sulphate	11.2 mg/L	6–9	99%
Cr, Ni, Zn	Tanfloc	20 mg/L	Cu-6 Zn-7	75%

Coagulation-flocculation can be employed to treat wastewater laden with heavy metals. The important property which they all have is that they carry a negative charge and this, along with the interaction between the colloidal particles and the water, prevents them from aggregating and settling in still water (Tang et al., 2014).

The particles can be aggregated by adding either multi-valent ions or colloids having an opposite (positive) charge, and these are added as chemical coagulants e.g., aluminum, and ferric salts which are present as the ions. The flocculation step can only operate on water/wastewater where the particles are already destabilized. It is a logical step following coagulation.

During the flocculation step an increase of the particles present in water phase results in the formation of flocs. The types of bond between the destabilized particles and flocculants are mainly ionic bonds and hydrogen bonds.

Flocculation can also be described as the action of polymers to form bridges between the flocs and bind the particles into large agglomerates or clumps. Bridging occurs when segments of polymer chain absorb on different particles and help particles aggregate. The general approach of this technique includes pH adjustment and involves the addition of ferric/alum salts as the coagulant to overcome the repulsive forces between particles (Johnson and Kirby, 2008).

In spite of its advantages, coagulation-flocculation has limitations such as high operational cost due to chemical consumption. The increased volume of sludge generated from coagulation-flocculation may hinder its adoption as a global strategy for wastewater treatment.

This can be attributed to the fact that the sludge must be converted into stabilized products to prevent heavy metals from leaking into the environment. To overcome such problems, electrocoagulation may be a better alternative than the conventional coagulation, as it can remove the smaller colloidal particles and produce just a small amount of sludge. However, this technique also creates a flock of metallic hydroxides, which requires further purification making the recovery of valuable heavy metals impossible. Thus, there is a need for development of low-cost alternatives for wastewater treatment (Johnson and Kirby, 2008).

2.7 Adsorption

Adsorption is a mass transfer process of adsorbate to adsorbent materials. For instance, toxic heavy metals like Chromium, Cadmium, Cobalt, Lead and Nickel are examples of adsorbates whilst industrial by-products, abundant clay or ore and agricultural waste are examples of adsorbent materials (Babel and Kurniawan, 2003). Adsorption has emerged as a promising technique for metal removal. The adsorption of heavy metals from contaminated water allows for the attachment of heavy metal ions onto the surface of solid materials or adsorbents (Gupta and Jain, 2011). This process will occur in two phase interfaces such as liquid-liquid, liquid-gas, or liquid-solid interfaces. The adsorption capacities depend on physical and chemical properties of the adsorbent as well as the adsorbate residence time, the concentration of the adsorbate in the liquid solution and experimental conditions such as temperature and solution pH (Abas et al., 2013).

Adsorption methods have been mostly used and therefore most widely studied in industry (Chiarle et al., 2000). The adsorbent option is the starting point for choosing an adsorbent. Some industrial wastewater systems may be used with several adsorbents. Activated carbon, which has proven useful for extracting heavy metals, is a well-known adsorbent. Nonetheless, it is not possible to apply activated carbon for wastewater treatment due to its high prices and regeneration costs, as a result of high losses in the real process (Febrianto and Kosasih, 2009). Activated carbon was used to adsorb contaminants from wastewater (Carvalho et al., 2011) and other researchers reported on the use of zeolites in wastewater treatment (Qiu and Zheng, 2007). In addition, there has been evidence of the use of other adsorbents such as synthetic polymeric adsorbents (Zabkova and Otero, 2006) and silica-based adsorbents as well as of industrial waste (Lam et al., 2006).

2.7.1 Types of Adsorption

At molecular level, adsorption is due to attractive interactions between a surface and the species being adsorbed. There are two types of adsorption:

2.7.1.1 Physical Adsorption

The effect is the intermolecular attraction forces between adsorbate and adsorbent molecules. In this case, purely physical forces of molecular attraction that retain the adsorbing on the surface are called Van Der Waals forces. This is a phenomenon easily reversible. The energy of interaction between the adsorbate and adsorbent has the same order of magnitude but is usually greater than the energy of condensation of the adsorptive. Therefore, no activation energy is needed (Febrianto and Kosasih, 2009).

2.7.1.2 Chemical Adsorption

It is a result of chemical interaction between the solid and the adsorbed substance. It is also called activated adsorption, irreversible and it is particularly important in catalysis. Therefore, the energy of chemisorption is considered like chemical reaction (Febrianto and Kosasih, 2009). It may be an exothermic or endothermic process ranging from very small to very large magnitudes. The elementary step in chemisorption often involves large activation energy. According to IUPAC's recognized definition, chemisorption is adsorption where the forces concerned are called valence forces of the identical type with the one operating in the development of chemical compounds.

2.7.2 Mechanism of Adsorption

Adsorption is a complex mechanism that may occur due to several mechanisms which could differ from one adsorbent to the other based on the type of the adsorbent, its origin and processing (Rao and Senthilkumar, 2012).

Those complex mechanisms could be ion exchange, chelation adsorption due to physical forces, ion entrapment in the capillaries and spaces of the cell wall of the adsorbent, formation of complexes between the hydroxides functional groups (El Zayat, 2014a) and carboxylic functional groups of the adsorbent and positively charged metal ions, and co-precipitation of the insoluble metal ions hydroxide on the surface of the adsorbent (Wong and Lee, 2003).

2.7.3 Removal of heavy metals using different adsorption materials

Adsorption method is a relatively low-cost method. Adsorption has certain advantages over conventional methods such as they minimize chemical and biological sludge, low-cost, high efficiency, regeneration of adsorbents and possibility of metal recovery. Adsorbents which have been already used for heavy metal removal are activated carbon, zeolites, manganese oxide, agricultural waste products. Activated carbon is a widely used adsorbent for heavy metal removal. Activated carbon has well developed pores and high internal surface area for adsorption and is prepared from agricultural waste. Agricultural waste : biosorption process is eco-friendly for removal of heavy metals from wastewater. Removal efficiencies obtained using different types of activated carbon and agricultural waste is presented in table 2.7 and 2.8 below.

Table 2.7: Removal of heavy metals by activated carbon (Kosa et al., 2012, Sankararamakrishnan et al., 2014)

Membrane	Heavy metal	pH	Removal efficiency (%)
Activate carbon (waste coconut button)	Hg and Cu	Pb (II), Cu (II): pH 6.0	Pb (II) >90
		Hg (II): pH 7.0	Hg (II) >95
			Cu (II) >95
Moso and bamboo activated carbons	Cu, Cr and Cd	5.81-7.86 and	Pb (II) > 99.9
		7.10-9.82	Cu (II) >100
			Cr (III) >100
			Cd (II) >96.4
Activated carbon prepared from grape	Cd (II) Pb (II)	6-5.5	98.8

Table 2.8: Removal of heavy metals by agricultural wastes (Singh and Singh, 2012)

Adsorbent	Heavy metal	Removal efficiency (%)
Black tea waste	Cu (II)	>99
Rice Husk	Cr (IV)	93-94
Sugarcane bagasse	Cr (III)	41.5
	Cr (IV)	80.7

2.7.4 Summary of different methods used and its advantages and disadvantages.

The different methods have their own advantages and disadvantages. Hence, when selecting a method to be used it is advised to take into consideration their pros and cons. Table 2.7 provided below presents the different techniques used in heavy metal wastewater treatment associated with advantages and disadvantages.

Table 2.9: summary of heavy metal removal techniques and its advantages and disadvantage

Treatment Technologies	Advantages	Disadvantages
Oxidation	Rapid process for toxic pollutants removal	High energy costs and formation of by products
Io exchange	Good removal of a wide range of heavy metals.	Adsorbents requires regeneration or disposal.
Chemical precipitation	Low cost for high volume. Process is often improved by high ionic strength. It is a reliable process well suited to osmotic control.	Stoichiometric chemical addition requirements .High water content sludge must be disposed of. Part per billion (ppb) effluent contaminant may require two-stage precipitation and poor settling.
Membrane filtration	Good removal of heavy metals	Concentrated sludge production and expensive
Adsorption	Flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants	Adsorbents require Regeneration
Coagulation/flocculation	Economically feasible	High sludge production and formation of large parties.
Electrochemical treatment	Rapid process and effective for certain metal ions	High energy costs and formation of large particles.
Ozonation	Applied in a gaseous state. alteration of volume	Short half life
Photochemical Irradiation	No sludge production Effective at lab scale	Formation of by-product Require a lot of dissolved O ₂
Electrokinetic coagulation	Economically feasible	High sludge production
Fentons reagents	Effective and capable of treating variety of wastes and no energy input necessary to activate hydrogen peroxide	Sludge generation

2.8 Sugarcane Bagasse as an Adsorbent

Sugarcane bagasse is composed of cellulose (40-50%), hemicellulose (25-30%) and lignin (20-25%)(Gurgel and de Freitas, 2008). Those three organic polymers that constitute sugarcane bagasse are a huge source of hydroxyl and phenolic groups whose sorption properties can be enhanced by chemical modification (Nghah and Hanafiah, 2008). These three polymers are also responsible for the absorptive properties of sugarcane bagasse.

Research was done to explore the adsorption properties of sugarcane bagasse. Adsorption capacity of charred xanthated sugarcane bagasse (CXSB) for the removal of specific heavy metals has been investigated. In that research, the sugarcane bagasse (SCB) was washed with deionized water for the removal of any acids until neutralization is attained, that is why it is called charred (Gupta and Jain, 2011). Then it was xanthated by adding carbon disulphide (CS_2) in the presence of an alkali. The maximum adsorption capacities reached (mol/kg), were 1.95 for Cd (II), 1.58 Pb (II), 2.52 for Ni (II), 2.40 for Zn (II) and 2.91 for Cu (II). Those adsorption capacities were considered higher than several other bio-sorbents stated in literature. The batch equilibrium experiments showed that the optimum pH for Cd (II), Pb (II), Ni (II), Zn (II), and Cu (II) bio sorption using CXSB was 5, 4, 4, 6 and 5, respectively. In another work, sugarcane bagasse was modified using organic compound succinic anhydride($C_4H_4O_3$) for the uptake of Cu (II), Cd (II), and Pb (II) from a solution. The maximum adsorption capacity in was determined using Langmuir model to be 114 mg/g for Cu^{2+} , 196 mg/g for Cd^{2+} and 189 mg/g for Pb^{2+} .

2.9 Factors Affecting Adsorption Capacity

2.9.1 Solubility and Initial Concentration of Adsorbate

The adsorption capacity of a metal decreases with the increasing solubility of the metal species (solute) in a solvent (Horsfall and Spiff, 2005). The initial concentration of heavy metals has an impact on the sorption capacity because it acts as a driving force to overcome the resistance of the metal of the mass transfer from the liquid phase to the solid phase (Ahmaruzzman, 2011). In general, it is claimed by some researchers that the higher the initial concentration of the heavy metals, the more the metal uptake by the adsorbent (Ahmaruzzman, 2011).

2.9.2 Contact Time

Contact time affects the adsorption capacity, where the time required for the adsorption process to reach equilibrium differs based on the adsorbent nature and the available adsorption sites (Ahmaruzzman, 2011). An increase in the present uptake of Pb^{2+} , Cd^{2+} , Ni^{2+} , was reported using modified straw (Nano-cellulose), with the increase in time until equilibrium was reached and no further increase was observed (Kardam and Raj, 2014). It was reported that the adsorption of Cu^{2+} , Cd^{2+} and Pb^{2+} ion using modified sugarcane bagasse increased with contact time until equilibrium (Farooqi et al., 2007).

2.9.3 The pH of the Solution

The amount of metal uptake by adsorbents is greatly affected by the pH of the solution due to the consequent change in the distribution of the surface charge of the adsorbent as well as its degree of ionization and the speciation of functional group (El Zayat, 2014a). In general, the adsorption capacity of heavy metal ions increases with the increase in pH (Ahmaruzzman, 2011). This is attributed to the fact that at low pH the adsorbent is protonated by H^+ ions and the surface charge the adsorbent is positive while the charge of the metal species is positive; hence creating forces of repulsion (Ding et al., 2012).

Additionally, at low pH the concentration of the H^+ ions is high therefore the competition between the H^+ ions and the metal ions over the active sites on the surface of the adsorbent reduces the adsorption (Zabkova and Otero, 2006). However, a relatively small amount of metal uptake takes place due to proton H^+ exchange with heavy metal ions (Pansini and De Gennaro, 1991). On the other hand, when pH increased, the surface functional groups were activated and the functional groups are deprotonated (Soetaredjo and Kurniawan, 2013).

Consequently, the surface charge of the adsorbent becomes negative while the predominant metal ions are positive (Ahmaruzzman, 2011).

Therefore, adsorption increases due to electrostatic forces of attraction as well as due to a decrease in the H^+ ions (Soetaredjo and Kurniawan, 2013). Consequently, leading to a decrease in the competition between the metal ions and the H^+ ions on the available active sites on the surface of the adsorbent (Habuda-Stanic and Flanagan, 2014). However, when pH further increases, both the predominant metal ions and the adsorbent are negatively charged, leading to a decrease in the adsorption capacity (Ahmaruzzman, 2011).

As adsorption takes place, the pH of a solution drops due to the release of the H^+ ions in the adsorption process indicating that ion exchange is a major mechanism of adsorption. Moreover, the pH has an impact on the solubility of heavy metals, as the pH of the solution increases, the solubility of the metal decreases eventually as explained before the adsorption increases (Manuel, 2015).

2.9.4 Particle Size

As the particle size decreases, the specific surface area increases, which is the surface area of the adsorbent available for the adsorption of the solute; consequently, increasing the adsorption capacity of the adsorbent (Ahmaruzzman, 2011). It was reported that there was an increase in the uptake of Pb^{2+} when the particle size of modified rice straw was reduced (Abdel et al., 2011).

2.9.5 Properties and Dose of the Adsorbent

The nature of the adsorption process, such as the rate and the maximum adsorption capacity is related to the physical and chemical characteristics of the adsorbent, such as porosity, mechanical strength, and rigidity of the adsorbent material (Febrianto and Kosasih, 2009). The dose of the adsorbent has a great effect on the adsorption capacity (Chiarle et al., 2000). It was reported that increasing the limestone, adsorbent dose from 0.5 g to 2 g had in turn led to an increase in the removal efficiency of Cd^{+2} by a factor of 3.5 (Ya and Zhou, 2009).

2.10 Adsorption Isotherm

Adsorption isotherms are characterized by many mathematical structures often based on empirical fitness and simplifying the physical characteristics and adsorption processes (Febrianto and Kosasih, 2009). Researchers forecast the potential adsorption capacity for a sorption device which can aid in determining the feasibility and the necessary dose of bio-sorbent in the treatment process for a particular application and selects the most appropriate sorbent for that case. Isotherm models also simulate the relation between the equilibrium concentration of heavy metals and the adsorption capacity of a sorbent (Fianko and Osaе, 2007).

Therefore, it is necessary to analyze the isothermic data to create an equation that accurately represents the results and can be used for design purposes and for the optimization of an operating procedure. Langmuir and Freundlich models are the most commonly used isotherm models in the literature. Some of the reasons for extensive use of those models are simplicity and simple interpretability.

The isotherm of a single solution adsorption system is also defined (Horsfall and Spiff, 2005). At the same time linear regression has been frequently used to evaluate the model parameters as the Temkin, Langmuir- Freundlich (Sips isotherms), Flory-Huggins, Polanyi-Dubinin-Manes (PDM), Hill isotherm, Redlich-Peterson and Dubinin –Radushkevish can also be used to model experimental data.

The amount of adsorbate that may be collected on an adsorbent depends on the temperature and adsorbate levels. Usually, the volume of adsorbed material is produced as a function of a constant temperature concentration and the resulting process is called adsorption isotherm (Metcalf and Eddy, 2003a). In case of granular activated carbon, it is normally powdered to reduce adsorption times.

The amount of adsorbate remaining in a solution is measured at the end of the test period. The adsorbent phase concentration after equilibrium is calculated using equation 2-1.

The adsorbent phase concentration information calculated using equation 2-1 is used to formulate adsorption isotherm as shown herewith:

$$Q_e = \frac{V(C_o - C_e)}{m} \quad 2.1$$

Where Q_e is the adsorption efficiency (mg adsorbate/g adsorbent), C_o is the initial concentration of heavy metals (mg/L), C_e is equilibrium concentration of heavy metals (mg/L), V is the volume of the wastewater (L) and m is adsorbent weight (g).

2.10.1 Langmuir and Freundlich Adsorption Isotherm

The Langmuir isotherm also called the ideal localized monolayer model was developed to represent chemisorption (Wang and Xu, 2009). Langmuir (1918) theoretically examined the adsorption of gases on solid surfaces and considered sorption as a chemical phenomenon. Langmuir reported the data regarding adsorption between gases and solids (Langmuir, 1918).

The formula of isotherms comes from the following theories,

- a) Collect similar surface of adsorbent material,
- b) Molecules of adsorbent material do not attract each other,
- c) Uniform mechanisms of adsorption,
- d) Monolayer made at the highest adsorption process, and
- e) Molecule of adsorbate adsorbed at the open place of adsorbent.

The Langmuir equation refers to the distribution of a substance over the solid surface at fixed temperatures as molecules are enclosed on a solid surface. Isotherms are based on the presumption that adsorption is limited to single layer coverage, all sites of surface are similar and can only accept one adsorbed molecule, the potential for an adsorbed molecule to be present on a given sites is independent of its surrounding site occupancy and adsorption is reversible (Wong and Lee, 2003) Langmuir isotherm describes monolayer adsorption or is a monolayer type adsorption (Langmuir, 1916).

Even, on an adsorbent region, Langmuir isotherm assumes homogenous sites of sorption and energy (Grassi et al., 2012). Langmuir isotherms have two hypothing, namely the presence on the surface of a sorbent of a fixed number of active sites, of all processing uniform energy for sorption, and reversible sorption (Yang and Lua, 2003).Langmuir isotherm was derived from the above hypothesis that it has no appeal between the maximum adsorption and a mono-layer of adsorbent materials.

The adsorption of Langmuir is effectively used for the pull of metal ions and is characterized as follows (Kirbiyik et al., 2012):

$$Q_E = \frac{q_M \times K_L \times C_E}{1 + K_L C_E} \quad 2.3$$

Linear equation of Langmuir is:

$$\frac{1}{q_E} = \frac{1}{q_M} + \frac{1}{q_M K_L} \times \frac{1}{C_E} \quad 2.4$$

Where Q_E is the mass of heavy metals absorbed per gram of adsorbent (sugarcane bagasse) [mg/g], C_E is equilibrium concentration of heavy metals in wastewater, milligram of heavy metals per litre (mg/L), K_L is Langmuir constant, litre per milligram of heavy metal [L./mg] and q_M is maximum coverage, milligram of heavy metal per gram of adsorbent.

When the Langmuir model is used to describe the adsorption process, the good model for test results does not necessarily mean that the underlying assumptions are defined by the sorbent (El-Gendy et al., 2011). Even when the model matches the experimental results, it is impossible that all sites will become energetically equivalent (Weber and Van Vliet, 1981). Such divergence also limits the definition of values A and B, even though the value of a does not reflect an adsorption potential for the sorbent to be examined.

Freundlich isotherm model is a multilayer type of adsorption. This multilayer shows heterogeneous surface adsorbent, that energy of adsorption is not equivalent for all adsorbent sites (Günay et al., 2007). The equation shows as follows:

$$q_E = K_F C_E^{\frac{1}{n}} \quad 2.5$$

Where in this case q_E is the mass of Cu, Cr and Cd adsorbed per gram of sugarcane bagasse, K_F is the Freundlich constant related with adsorption capacity (mg/g), C_E is the equilibrium Cu, Cr and Cd concentration in wastewater in milligram per liter (mg/L), n is the heterogeneity coefficient (dimensionless). For linearization of the data, the Freundlich equation is written in logarithmic form.

And linear Freundlich linear formula:

$$\log(q_E) = \log(K_F) + \frac{1}{n} \log(C_E) \quad 2.6$$

CHAPTER THREE: MATERIALS AND METHODS

3.1 Introduction

This chapter presents the experimental procedure of extracting heavy metal ions contained in wastewater using a low-cost adsorbent, sugarcane bagasse. The chapter outlines the chemicals and equipment used, the process parameters measured, the experimental setup and the analytical methods employed for data analysis. Synthesis of wastewater stock solutions was done followed by experimental work which included batch experiments that evaluated the process parameters that affect the extraction of heavy metal ions present in wastewater. Characterization of the adsorbent was done to determine the functional groups responsible for the adsorption process.

3.2 Materials and Reagent Used

3.2.1 Equipment Used

The following laboratory apparatus were used during the experimental procedure: conical flasks, beakers, Petri dish, measuring cylinder, pipette, funnels, and laboratory shovel. The instruments used throughout the experiment are listed in table 3.1.

Table 3. 1: List of instruments used during the whole experiment.

Item Number	Instrument	Purpose
1	Oven	Removal of moisture from sugarcane bagasse (drying).
2	Digital weighing balance	To weigh the samples of sugarcane bagasse dose.
3	Wood crusher machine	To crush sugarcane bagasse.
4	Orbital shaker	To agitate the adsorbent with aqueous metal ion solution.
5	pH meter	To measure the pH.
6	Sieve shaker	Particle size classification
7	Whatman filter paper	To filter or separate adsorbent from solution.
8	Inductively Coupled plasma (ICP)	To measure residual metal ion concentrations and to check the concentration of the prepared solution

3.2.1.1 Digital Weighing Balance

The digital mass balance systems are extremely sensitive devices used to measure substances. The digital mass balance (AS 220/C/2) manufactured by Radwag manufacturer was used to weigh the samples or sugarcane bagasse dose.

3.2.1.2 Wood Crusher Machine

The wood crusher (model by Thomas) was used to grind sugarcane bagasse to produce particles that ranged from 75 to 600 μm with average humidity of up to 50 percent. The crusher production is between 2000 and 2500 kg / hour.

3.2.1.3 Orbital Shaker

The orbital shaker (SSL1 model manufactured by Stuart) offered a smooth orbital shaking with an orbit of 16 mm and a speed range of 30 to 300 centimeters, which was suitable for agitating the adsorbent with aqueous metal ion mixtures. The frame has four horizontally securing bars with plastic-coated horizontally securing handles for shaking the sample bottles.

3.2.1.4 pH Meter

A digital pH meter (A215) manufactured by Stuart was used to measure the pH of the solution. It uses rotary controls for mode and pH calculation. An unintentional movement of the calibration controls does not affect the sample measurement through the inappropriate design feature. The large display made it easy to see the simple liquid crystal display (LCD) readings during laboratory experiments.

3.2.1.5 Inductively Coupled plasma (ICP)

Inductively coupled plasma optical emission spectrometry (ICP-OES), is an analytical technique that was used for the detection of trace metals (ppb) and to measure residual metal ion concentrations. It is a type of emission spectroscopy that uses the inductively coupled plasma to produce excited atoms and ions that emit electromagnetic radiation at wavelengths characteristic of a particular element. The intensity of this emission is indicative of the concentration of the element within the sample. Unlike atomic absorption spectroscopy, which can only measure a single element at a time ICP-OES has the capability to scan for all elements simultaneously. This allows rapid sample processing. The model of the ICP-OES that was used is AAC/14, by Varian manufacturer.

3.1.2.6 Sugarcane Bagasse

Grinded sugarcane bagasse was used as an adsorbent material which would adsorb the metal ion concentrations. The sugarcane bagasse was grinded and crushed into small particles that ranged from 75 to 600 μm by the wood crusher machine.

3.2.2 Chemicals Used

All chemicals used were analytical grade for heavy metal solution (Chromium sulphate, copper sulphate and cadmium sulphate). Reagent grade concentrated sulfuric acid and NaOH were used to adjust pH values of samples. De-ionised water for wastewater synthesis and during the sugarcane bagasse preparation (final washing).

3.2.3 Chemicals Utilized for Inductively Coupled Plasma Analysis

- Water: Deionized distilled (grade III)
- Argon: 99,9999% purity ('Argon 5.0')
- Nitric acid: Concentrated, AR grade
- Nitric acid, dilute: 1:1 HNO₃ (AR grade)
- Hydrochloric acid, dilute: 1:1 HCL grade
- Calibration standard solutions: prepared from standard stock solution of chromium, cadmium, and copper metals.

Agricultural waste that was used as a bio sorbent is sugarcane bagasse.

3.3 Sugarcane Bagasse Collection, preparation, and characterization.

3.3.1 Collection and preparation of the adsorbent

Sugarcane bagasse was collected from UCL Company limited (PTY) in a plastic bag and stored for preparation. This bio sorbent was initially prepared and then pre-treated according to the method reported (Horsfall and Spiff, 2005).

Sugarcane bagasse was washed with deionized water to remove impurities that might block the pores and interfere in the adsorption process. Sugarcane bagasse was then dried under sunlight and was then reduced in small pieces using a wood crusher. Subsequently, the sugarcane bagasse was grinded using crusher and sieved using a mechanical sieving system, so the particle size used ranged between 75 µm-600µm, which is smaller than particle size used by other researchers because as the particle size decreases, the surface area increases; consequently, the adsorption capacity increases. The fine particles of sugarcane bagasse were then first rinsed with deionized water then distilled water after.

Then dried in an oven at 80 °C until the moisture content is constant and kept in desiccators. Samples were then divided so that part of each bio-sorbent was left untreated and the other part was subjected to pre-treatment.

3.3.2 Characterization of the adsorbent

In this study the primary material that was used as an adsorbent was sugarcane bagasse. The adsorbent was collected from UCL company in Dalton. Samples of the bagasse were characterized with X-ray diffraction (XRD), Fourier transformed infrared spectroscopy (FTIR), scanning electron microscope (SEM)

3.3.2.1 FTIR for adsorbent characterization –To identify functional groups of sugarcane bagasse

The functional groups present on the surface of the biomass was qualitatively detected by Fourier Transform Infrared spectroscopy (FTIR) using a Perkin Elmer spectrum spectrophotometer. The spectrum was obtained from a wavelength range of 4000 to 400cm⁻¹.

3.3.2.2 X- Ray Diffraction (XRD) -To measure crystallinity of sugarcane bagasse

A Bruker D8 advance X-Ray Diffraction system using the Xpert data collector software was used to identify the crystalline nature and mineralogical composition of the biomass.

3.3.2.3 Scanning Electron Microscope (SEM) -To examine and analyse the material microstructure morphology.

The scanning electron microscope (SEM) is used to analyse the sugarcane bagasse microstructure morphology and the porosity of the adsorbent.

3.4 Wastewater (Stock Solution) Synthesis

All aqueous solutions were prepared in distilled water. Solutions containing Cu (II), Cd (II) and Cr (II) were prepared using analytical grade copper sulphate, cadmium sulphate and chromium sulphate respectively, supplied by Monitoring and Control Laboratories (MCL) chemical company. Dilute HCL and sodium hydroxide (NaOH) were used for pH adjustment that ranged from 2-9. Three systems were used to synthesize the wastewater feed.

3.4.1 Single metal system.

In this system, three different types of feeds were prepared using three various metal ions. These various metal ions are explicitly copper (Cu^{2+}), chromium (Cr^{2+}) and cadmium (Cd^{2+}) metal ions. Each feed contained a separate type of metal ion. This implies that each feed was prepared using 100% of each metal ion salts.

3.4.2 Binary metal system

In this system, three types of feeds were prepared once again using three various metal ions. However, in this system, two different metal ions were combined in each feed. For instance, Copper (Cu^{2+}) and chromium (Cr^{2+}) ions were combined to form a binary (Cu - Cr) feed solution. Subsequently, chromium sulphate and cadmium sulphate solutions were also combined to form another binary (Cr-Cd) feed solution.

Furthermore, cadmium sulphate and copper sulphate ions were combined to form the last binary feed solution referred to as (Cd-Cu) solution. One ratio of metal salts was used to prepare each feed. The ratio consisted of 50% of one metal salt combined with 50% of another metal salt. For instance, 50% of copper sulphate was combined with 50% of chromium sulphate to form a 100% (Cu-Cr) solution. Hence, three combination ratios of 50%:50% (Cu-Cr), 50%:50% (Cu-Cd), 50%:50% (Cd-Cr) were established and used to prepare the feed solution.

3.4.3 Ternary component system

This was the last system used to prepare the ultimate feed solution. In this system, all three metal salts were combined together; copper (Cu^{2+}); chromium (Cr^{2+}) and cadmium (Cd^{2+}) to form a ternary (Cu-Cr-Cd) feed solution. Similar to the binary component system, one ratio of metal salt solutions was used. The combination ratio prepared was 33.3%:33.3%:33.3% (Cu-Cr-Cd).

3.6 Experimental Set-up

3.6.1 Synthetic Stock Solution

A total of 7 synthetic wastewater feeds were prepared using Cu, Cr and Cd salts and stored in a vessel. Subsequently, sugarcane bagasse was prepared, characterized, and stored in plastic bags ready to be utilized during the batch adsorption experiments. Sugarcane bagasse and the wastewater feed were then agitated in a mixer. Consequently, the adsorption process then took place while maintaining the pH of the solution that ranged from 2-9. The pH was adjusted using an acid or base solution. Filtration of the treated wastewater was then done using filter papers. The filtrate was then collected and sent for analysis while the adsorbent which is sugarcane bagasse containing the heavy metals was collected in a tank using a laboratory shovel.

The schematic diagram denoting the experimental design is illustrated in Figure 3.1- 3.6.

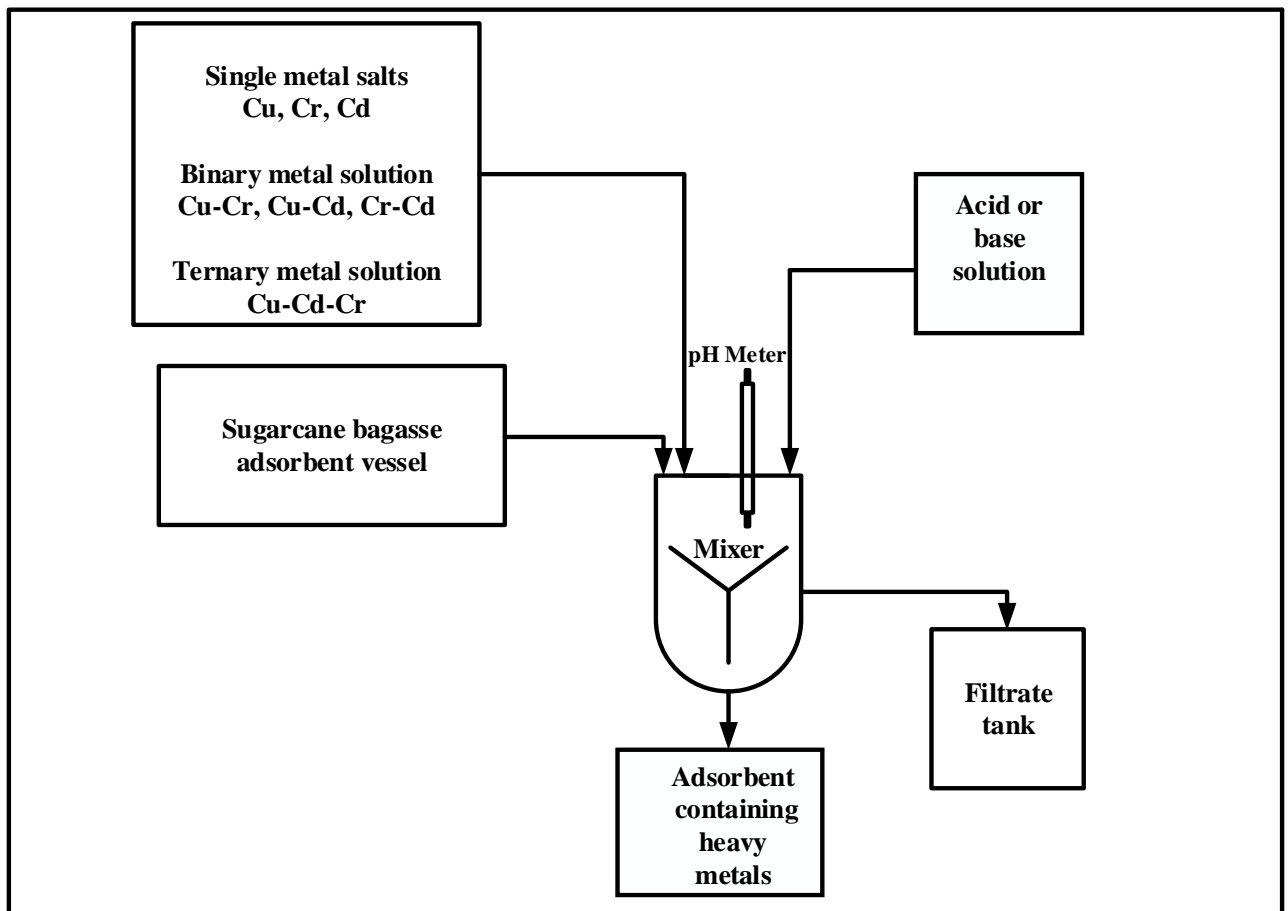


Figure 3. 1: Schematic process flow diagram for heavy metal sorption from wastewater using sugarcane bagasse.

3.6.2 Operating variables

1. Initial copper, chromium, and cadmium concentration
2. Particle size
3. Contact time
4. Initial pH
5. Adsorbent dosage

3.7 Experimental Approach

3.7.1 Preliminary Runs for Screening Process

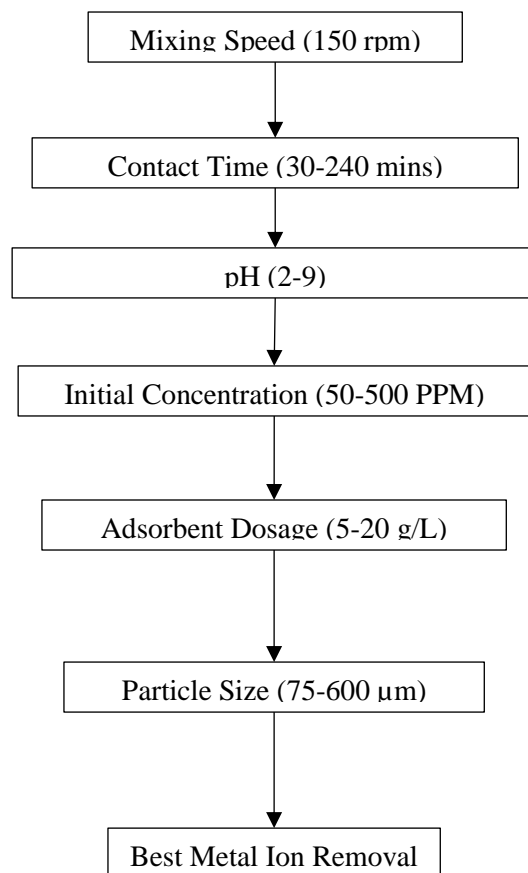


Figure 3. 2: Experimental work program on sugarcane bagasse diagram

3.7.2 Experimental Work Program Description

Screening process was conducted to determine the best optimum conditions for heavy metal ion removal. According to Srivastava et al. (2015), chromium is considered as one of the most frequent metal pollutants. From the superfund priority list of hazardous substances, chromium ion is affirmed as one of the top 20 contaminants present in the environment (Srivastava et al., 2008).

Therefore, in this process, chromium operating parameters range were used as the basis of the intact batch experiments (Agrawal and Singh, 2016).

Those ranges were as shown in figure 3.2:

- Sugarcane bagasse particle size (75 μm -600 μm)
- Initial concentration (50-500 ppm)
- Initial pH (2-9)
- Contact time (30-240 min)
- Adsorbent dosage (5-20 g/L)

3.7.3 Batch Adsorption Experiments

3.7.3.1 Effect of Contact Time

The effect of contact time was investigated to determine the optimum conditions for maximum adsorptive removal of heavy metals over the contact time that ranged from 30-240 mins by allowing the adsorbent to adsorb the heavy metal ions contained in the wastewater solution. Optimum contact time for the adsorption of Cu, Cr and Cd was assessed over a range of 30 mins, 60 mins, 90 mins 120 mins, 150 mins, 180 mins and 210 mins during the screening process. The effect of contact time was investigated under a fixed mixing speed of 150 rpm.

3.7.3.2 Effect of Solution pH

The effect of solution pH was investigated to determine the optimum conditions for maximum adsorptive removal of heavy metals over the initial pH range of 2-9 by allowing the adsorbent to adsorb a desired concentration of heavy metal ions in the wastewater solution. Selected values of solution pH were 3, 5, 7 and 9. The effect of solution pH was done under a constant mixing speed of 150 rpm while maintaining the optimum contact time determined from the subsequent batch experiment.

3.7.3.3 Effect of initial concentration

The effect of initial concentration was investigated to determine the optimum conditions for maximum adsorptive removal of heavy metals over the initial concentration that ranged from (50-500 PPM) by allowing the adsorbent to adsorb a desired concentration of heavy metal ions in the wastewater solution. Optimum initial concentration for the adsorption of the heavy metals was assessed over a range of 50 ppm, 250 ppm and 500 ppm during the screening process. The effect of initial concentration was done at a constant mixing speed of 150 rpm while maintaining the optimum solution pH and the optimum contact time that were determined from the subsequent batch experiments.

3.7.3.4 Effect of adsorption dosage

To determine the optimum dosage required for the maximum adsorption removal of heavy metals, different adsorbent doses ranging from 5 to 20 g/L were used by allowing the adsorbent to adsorb a certain amount of heavy metal ions in the wastewater solution. The impact of sugarcane dose on the removal of Cu, Cr and Cd metal ions was investigated by varying its amount from 5 g/L, 10 g/L, 15 g/L and 20 g/L during the screening process.

The effect of adsorbent dosage was studied at a constant mixing speed of 150 rpm while maintaining the optimum solution pH, the optimum contact time and the optimum initial concentration that were determined from the subsequent batch experiments.

3.7.3.5 Effect of Sugarcane Bagasse Particle Size

To determine the optimum particle size of the adsorbent required for the maximum adsorption removal of heavy metals, different adsorbent doses ranging from 75-600 μm were used by allowing the adsorbent to adsorb an amount of heavy metal ions in the wastewater solution. The impact of the sugarcane bagasse particle size on the removal of Cu, Cr and Cd metal ions was investigated by varying its amount using the following sets of range <75 μm , 75-150 μm , 350-450 μm , and 500-600 μm during the screening process. The effect of particle size of the adsorbent was done at a constant mixing speed of 150 rpm while maintaining the optimum solution pH, the optimum contact time, the optimum initial concentration, and the optimum adsorbent dosage that were determined from the subsequent batch experiments.

3.7.3.6 Adsorptive Efficiency of Sugarcane Bagasse

Linearized Langmuir and Freundlich isotherm equations outlined in chapter two were used to estimate the potential and adsorption capacity of sugarcane bagasse under batch adsorption experiments and for the design purposes of practicability of adsorption techniques.

3.8 Analytical Methods

3.8.1 Determination of pH of the Solution and Calibration Method

The pH of the solution was measured accurately using a pH meter. The pH meter was calibrated before the pH measurements were made. The pH meter was calibrated using buffer solution 4.0, 7.0 and 10. In order to ensure the quality of the results obtained in the laboratory, the calibration was done by running standards.

3.8.2 Determination of Heavy Metal Concentrations

3.8.2.1 Preparation of Standard Solutions

Mixed standard solutions contained these metal ions: cadmium, chromium, copper prepared from the respective metal salt solutions. This was achieved by mixing 20 ml of the metal stock solution using a pipette with 1 L of water containing 2 ml of nitric acid.

3.8.2.2 Sampling and Sample Preparation for Heavy Metal Analysis

Samples were collected in a plastic container including caps to avoid contamination. Sample containers were thoroughly cleaned with distilled water. Samples were preserved immediately after sampling by addition of 10 ml of concentrated AR grade nitric acid per litre of sample. After acidification samples were stored at approximately 4 °C.

3.8.2.3 Analytical Procedure

The table in 3.2 shows the heavy metals, recommended analytical wavelengths and typical upper limit concentration for calibration

Table 3. 2: Wavelengths and upper concentration limits

Element	Wavelength	Upper concentration limit/ppm
Cadmium (Cd)	228.802	50
Copper (Cu)	327.395	50
Chromium (Cr)	267.716	50

3.8.2.4 Analysis of Samples

The instrument was calibrated. Each sample run was then started with the analysis of the blank, in order to check the sample preparation, reagents and procedures for contamination. A thistle funnel was subsequently dipped into the center of the sample then the sample was introduced to the plasma and analysed each element present in the sample, rinsing for an appropriate time with deionized water between the samples.

CHAPTER FOUR: RESULTS AND DISCUSSION

4.1 Introduction

This chapter discusses the results obtained from the characterization of sugarcane bagasse as an adsorbent for the removal of heavy metals (copper, chromium, and cadmium) including FTIR, XRD and SEM. The experimental results obtained from the performance of sugarcane bagasse in the removal of heavy metal ions present in wastewater were also discussed. It also outlines the experimental design employed using the one-factor-at-a-time (OFAT) approach in order to identify the optimal operating parameters for the best performance of the adsorbent in removing the heavy metals ions. Adsorption capacities of the adsorbent for each metal was determined so as to establish the isotherms.

4.2 Adsorbent characterization

4.2.1 FTIR Analysis

The FTIR analysis was utilized to determine the functional groups on the surface of sugarcane bagasse responsible for adsorption of chromium, copper, and cadmium. It is significant to know the functional groups present on the adsorbent since the adsorption capacity is largely inclined by the chemical structure of the adsorbent. Functional groups are by far the greatest vital characteristics prompting the surface behavior of the adsorbent. Functional groups present on the surface of sugarcane bagasse are represented on figure 4.1. These organic groups were depicted based at different wavelengths as shown in table 4.1.

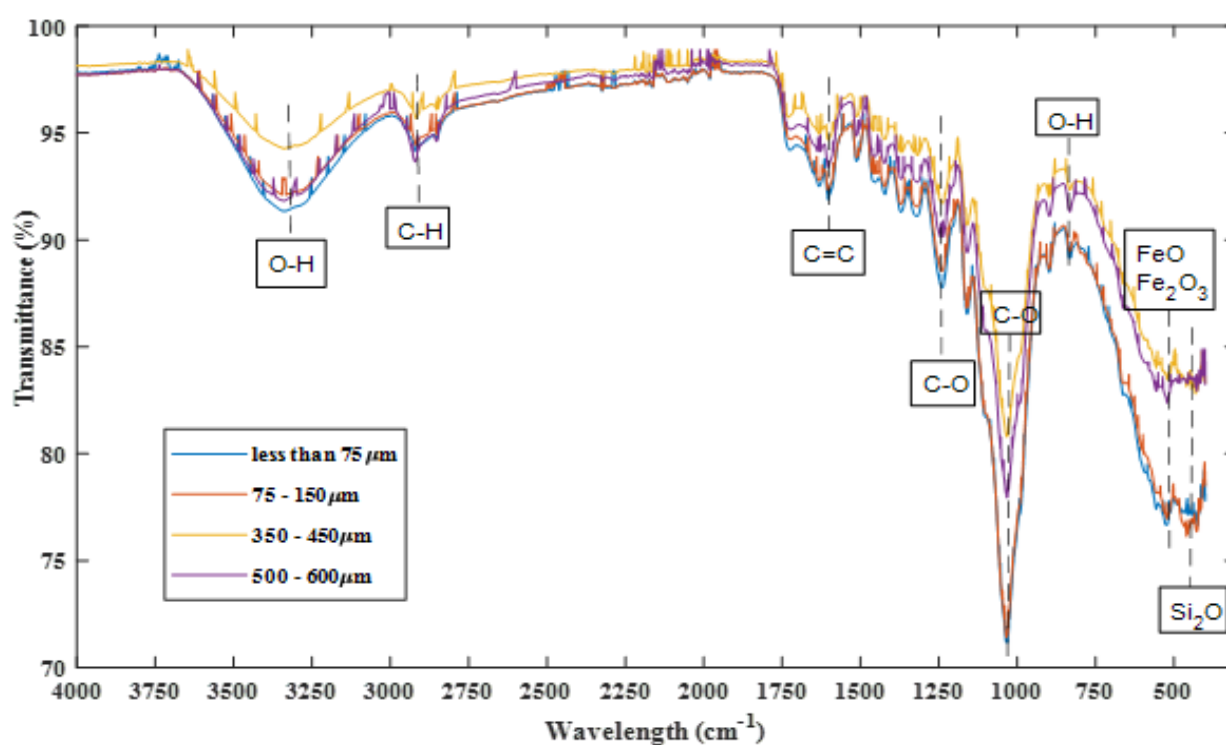


Figure 4. 1:FTIR spectra of raw sugarcane bagasse adsorption of Cr (II), Cu(II) and Cd(II) heavy metals

Table 4. 1: Functional groups found in sugarcane bagasse at different wavelength

Functional group	Wavelength (cm ⁻¹)
O-H for Al-OH, Si-OH	3320
C-H stretching	2920
C=C stretching	1512
C-O aromatic ring stretching	1281
C-O stretching	1035
O-H deformation linked to Al ³⁺ , Mg ²⁺	800
FeO, Fe ₂ O ₃ stretching	510
Si-O-Si bending	420

The defining peaks identified in the FTIR spectra of sugarcane bagasse occurred at different wavelengths. The spectrum displayed an intense broad band at 3320 cm⁻¹ which contributed to the stretching vibration of structural O-H group hydrogen bonded with inter-lamellar water or O-H groups in adjacent layers. Zhang et al. (2011) also reported that the broad spectral band closer to what was found is due to the O-H stretching of intramolecular hydrogen bonds for cellulose (Júnior et al., 2009). Another band was detected at a wavelength of 2920 cm⁻¹ was due to C-H stretching. In contrast the peak at 1512cm⁻¹ is due to the C=C stretching vibrations resulting from the aromatic rings of lignin (Zhang et al., 2011).

The high intensity band of 1281 cm⁻¹ is due to C-O aromatic ring stretching or C-O stretching vibration of cellulose, lignin and hemicellulose as supported by (Júnior et al., 2009, Putra et al., 2014) . Furthermore, adsorbent intensity at 1035 is correspondingly related to C-O stretching of cellulose, hemicellulose, and lignin. The peak at 800 cm⁻¹ may be assigned to the glycosidic bonds in cellulose as reported by (Chao et al., 2014) and to the O-H deformation linked to Al³⁺, Mg²⁺. The minor peak at 510 and 420 cm⁻¹ is related to the FeO, Fe₂O₃ stretching and Si-O-Si bending (Lima et al., 2014).

Thus, the FTIR spectra of bagasse indicates that the surface of the biomass is rich in polymeric hydroxyl, carbonyl and aromatic rings as confirmed from the above analysis which play a major role in the binding of chromium, copper, and cadmium ions (Chao et al., 2014).

4.2.2 XRD analysis

X-Ray diffraction is a rapid analytical technique primarily used for phase identification of a crystalline material and can provide information on unit cell dimensions. The analysed material is finely ground, homogenized and average bulk composition is determined. X-ray diffraction peaks are produced by constructive interference on a monochromatic beam of x-ray diffracted at specific angles from each set of lattice planes in a sample. The peak intensities are determined by distribution of atoms within the lattice. Consequently, the X-ray diffraction pattern is the fingerprint of the periodic atomic arrangement in a given material. Figure 4.2 below stipulates the results of the sugarcane bagasse obtained from X-ray diffraction for different particle size classes.

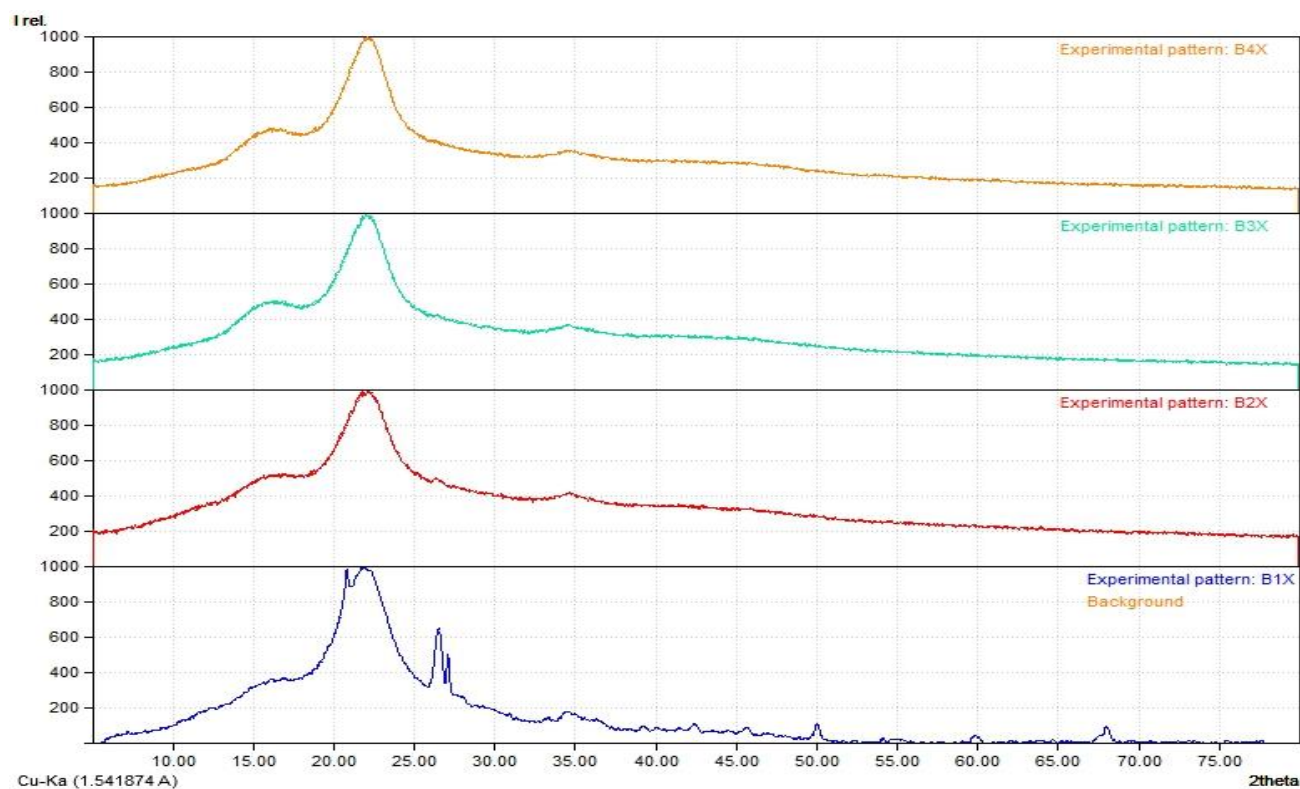


Figure 4. 2: XRD for sugarcane bagasse adsorbent.

From the XRD patterns, the mineralogical compositions of the sugarcane bagasse sample were determined. The XRD patterns allow the interpretation of the basal space (d-spacing) of the bagasse. It also gives the indication for the determination of the crystallinity index of any substance (French and Cintrón, 2013).

The XRD patterns indicate that the sugar bagasse is mainly amorphous in nature as it contains broad peaks/humps and lower intensity for the B2, B3 and B4 which has the following particle size distribution 75-150 μm , 350-450 μm , and 500-600 μm , respectively. B2, B3 and B4 have the same graphics pattern as indicated in figure 4.2 while B1 (<75 μm) shows a mixture of crystallinity and amorphous structure contained in it.

The XRD patterns of the sugarcane bagasse fibre reveals the main diffraction peaks at 2θ angles: 15.6° and 22° which confirmed the typical cellulose-I structure (Anggono et al., 2019), while B1 shows other diffraction peaks at 2θ angles: 26.41° , 27° , 34.56° , 39.26° , 42.38° , 45.56° and 50° indicating presence of crystalline structure.

The crystalline peaks observed in the B1 graphics pattern as opposed to B2, B3 and B4 may be attributed to the disruption of the hemicellulose or lignin component of the sugarcane bagasse (Liu et al., 2019), as the particle size of B1 is smaller than that of the other.

The most dominant minerals found has represented by the peaks in the diffractogram are Cristobalite [SiO_2], Bementite [$\text{Mn}_7\text{Si}_6\text{O}_{15}(\text{OH})_8$], Rhodonite [MnSiO_3], Cadmium ditantalum tris (diphosphate) [$\text{Ta}_2\text{Cd}(\text{P}_2\text{O}_7)_3$] and caesium disulphate [$\text{Cs}_2\text{S}_2\text{O}_7$]. Other minerals present are Potassium nitrate, Panunzite [(K, Na)AlSiO₄], Boehmite [AlO(OH)], Koritnigite [AsZnO₅], Potassium, Lasalite, Barium indium nitride and Anorthite.

4.2.3 SEM analysis

It was necessary to determine the microstructure morphology of sugarcane bagasse. The scanning electron microscope (SEM) was used. The porous nature of sugarcane bagasse is desirable as the metal ions can easily penetrate the pores of sugarcane for efficient adsorption.

Figure 4.3 and 4.4 represents results of SEM at different magnifications as shown below.

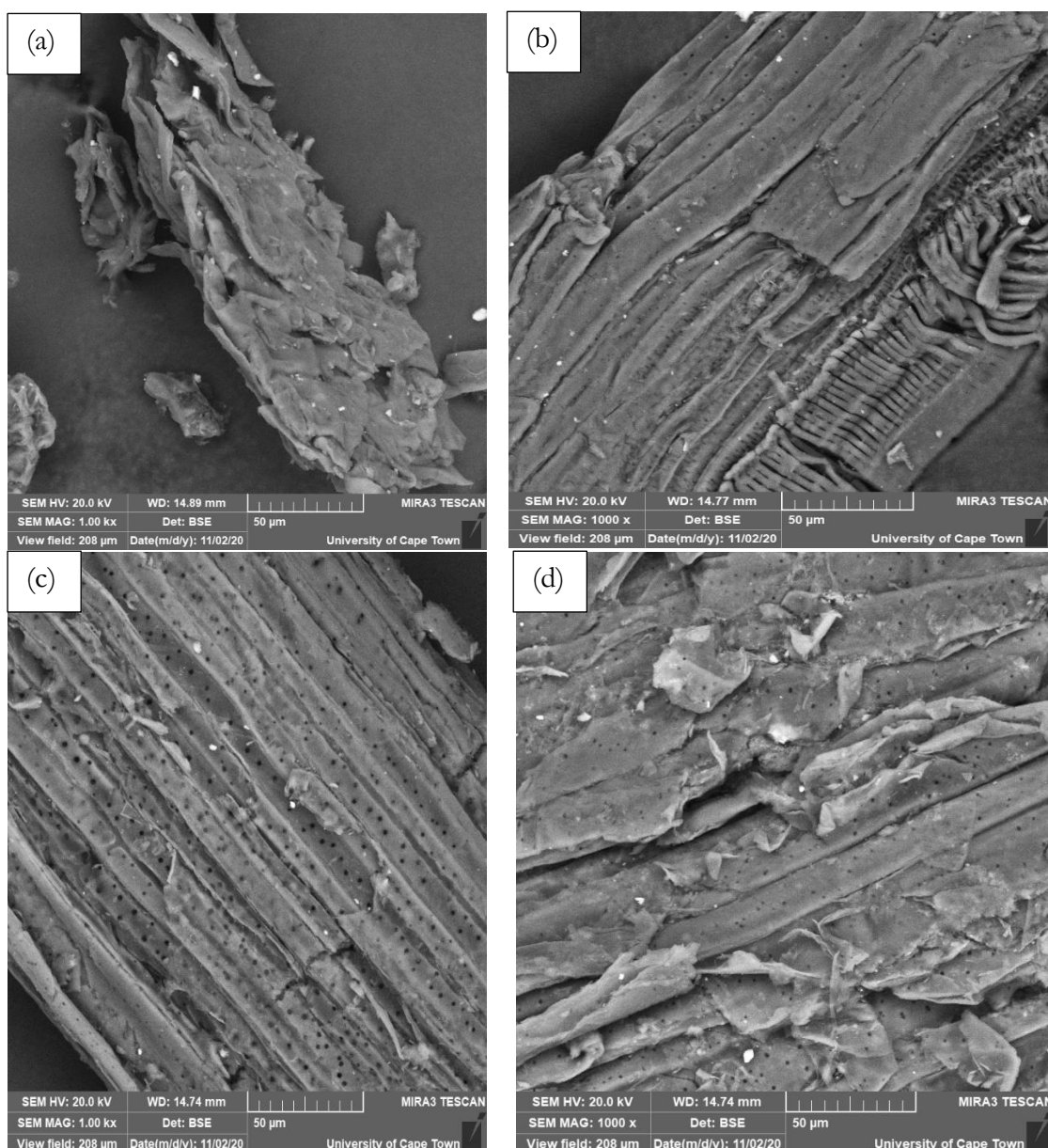


Figure 4. 3: SEM images for Sugarcane bagasse at 1000 magnification (a) B1 (b) B2 (c) B3 (d) B4

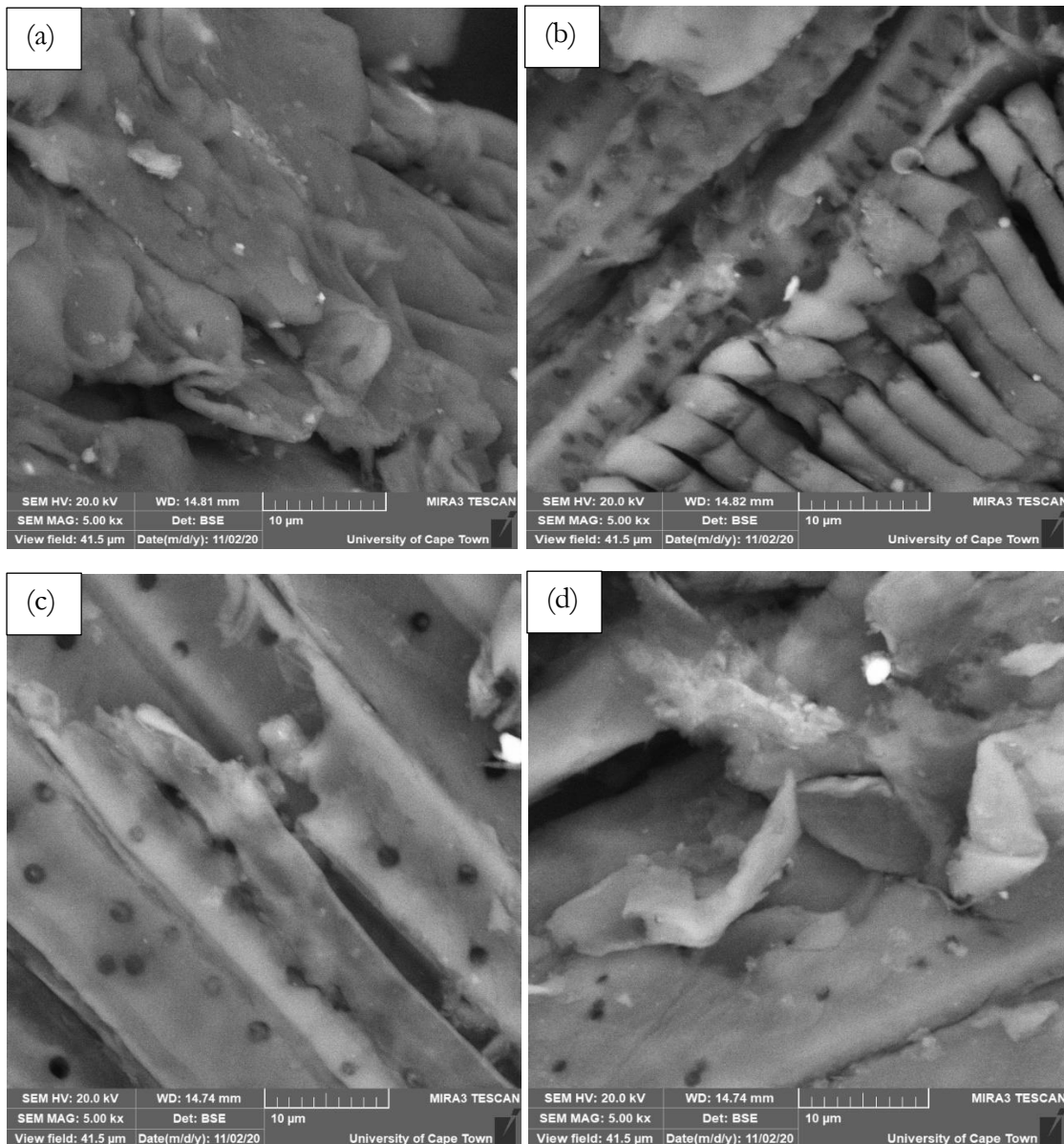


Figure 4. 4: SEM images for Sugarcane bagasse at 5000 magnification (a) B1 (b) B2 (c) B3 (d) B4

Figure 4.3 shows the micrograph at a magnification of 1000 while Figure 4.4 shows a micrograph with a magnification of 5000 for the sugarcane bagasse obtained from the SEM unit. Figure 4.4 shows the micrographs of sugarcane bagasse. The smooth and formless nature in Figure 4.4 (a) representing the sugarcane bagasse with the particle size class of less than 75 μm reveals the amorphous structure to be the main structure of sugarcane bagasse.

Figure 4.4 (b) (sugarcane with particle size class of 150-350 μm) however, indicate the presence of thin rod-like structure which usually indicates/confirms crystallinity in any sample while the sugarcane bagasse in Figure 4.4(c) have smooth surface with small cracks.

Figure 4.4(d) shows that sugarcane bagasse contained the fibre and the pith at a particle size of 500-600 μm . Fibre surface is formed by parallel stripes and is partially covered with the residual material. In contrast, pith is more fragile and fragmented structure containing pits, which are small pores connecting neighboring cells on the surface of the wall. The sugarcane bagasse has a tight structure with some pores on the surface. The presence of dark spot on the surface of the sugarcane bagasse demonstrated in Figure 4.4(b), (c) and (d) represents the pores and this is more profound in figure 4.4(c) which epitomizes the SEM of sugarcane bagasse at a particle size of 350-450 μm .

4.3 EXPERIMENTAL DESIGN AND OPERATING PARAMETERS

There are a number of factors that affect the performance of sugarcane bagasse as an adsorbent in the removal of more than one heavy metal ions from synthetic wastewater. In order to identify the best operating parameters that can be used for the optimization of the performance of the adsorbent batch experiments based on OFAT methods were conducted. Three system components of the stock solution were established namely single, binary and ternary. The following variables were investigated for each system component, in order to determine how these factors influence the performance of sugarcane bagasse:

- Contact time
- Dosage
- Initial pH
- Initial Concentration
- Particle Size

4.3 Operating Parameters for Single Metal System

4.3.1 The Effect of Contact Time

A preliminary study was performed on the effect of contact time on copper, cadmium, and chromium adsorption by sugarcane bagasse adsorbent. Figure 4-1 outlines the results obtained.

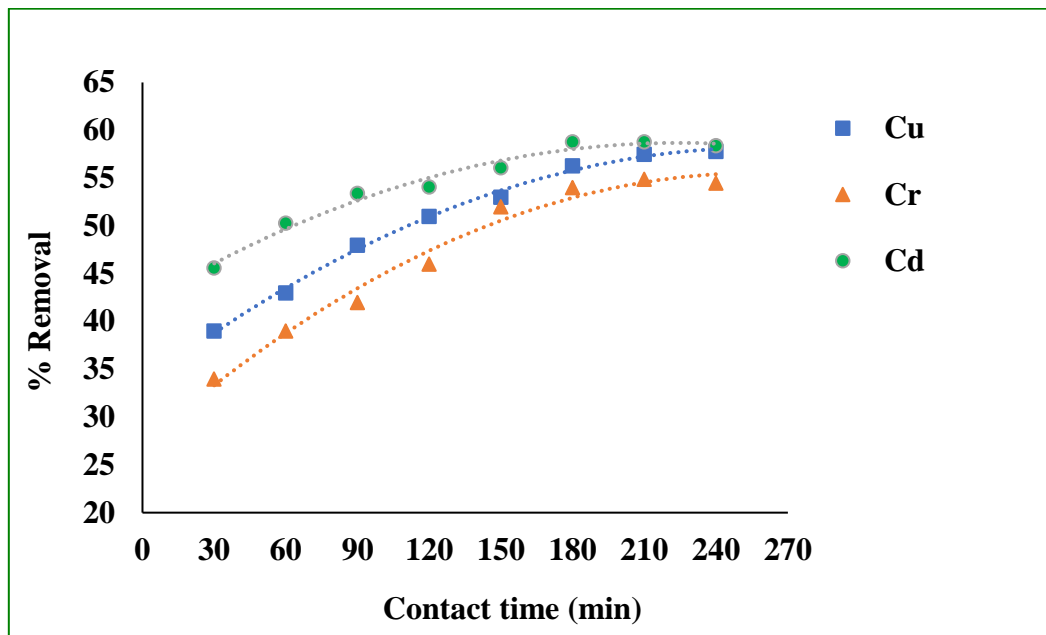


Figure 4. 5: Effect of contact time on the adsorption for a single metal system at a mixing speed of 150 rpm, adsorbent dosage of 20g/L, initial metal concentration of 50 ppm, pH of 7 and particle size 350-450 μm .

As shown in Figure 4.5, the first 30 to 180 minutes demonstrated higher removal efficiencies, and after 180 minutes no further significant change was observed. The greater removal efficiency between 30 to 180 min is attributed to the existence of more contact surface areas of the adsorbent as contact time increases between the adsorbent and the metal ions. As the contact time increases, the surface of the adsorbent continues to wear out of the porous areas as the agitation cycle increases leading to reduced contact surface areas which results in no significant removal (Mungray et al., 2012).

The removal efficiency at this point is mainly regulated by the adsorption potential of metals from the outside to the inside by adsorbents. The optimum contact time for the single component system was 180 mins. This optimum contact time was then used in the following batch experiments. It was observed that when varying contact time from 30 to 240 mins, cadmium had a greater removal efficiency (45.6-58.4) as compared to copper (39-57.8) and chromium (34-54.5) in a single metal system.

4.3.2 The Effect Of pH

The pH plays a vital role in the adsorption process and research has shown that it is one of the critical parameters. The main guiding force that regulates metal adsorption by adsorbents is an acidity or alkalinity of a solution (Ahmad et al., 2018). Solution pH has an important impact on metal ion solubility, ionization rates in relation to reaction and adsorbents counter-concentration of the functional group. It was of essence to evaluate its effect in the adsorption of Cu (II), Cr (II) and Cd (II) during the adsorption process, as it affects the solubility of the metal ions, concentration of the counter ions on the functional group of the adsorbent and the degree of ionization of the adsorbate during reaction. The active sites on an adsorbent can either be protonated or deprotonated depending on the pH.

Adsorption experiments were performed at a pH range of 3-9 as shown in Figure 4.6 because at higher pH levels above 10, Cu (II), Cr (II) and Cd (II) would be converted into their hydroxide forms and get precipitated.

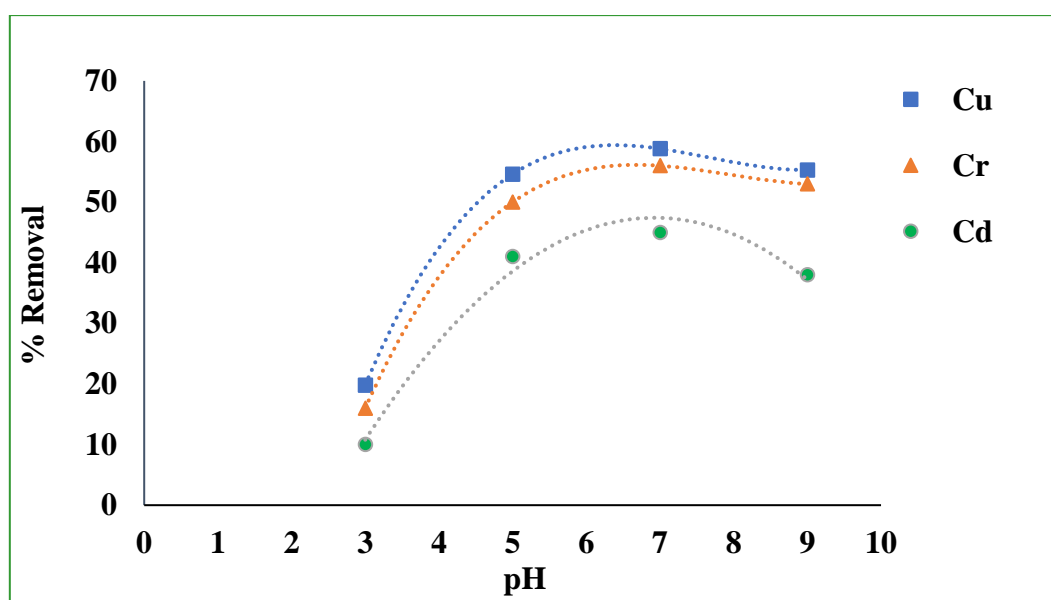


Figure 4. 6: Effect of pH on the adsorption for a single metal system at a contact time of 180 mins; initial metal concentration of 50 ppm, mixing speed of 150 rpm; particle size 350-450 μm , adsorbent dosage of 20 g/L.

Figure 4.6 displays the role of pH in adsorbing single metal ion solutions containing copper, chromium, and cadmium ions. It was noted that Cu (II) had a greater removal efficiency as compared to Cd (II) and Cr (II). The adsorption uptake for Cu (II) was enhanced from (19.8% to 58.8%), Cr (II) from (16% to 56%) and Cd (II) from (10% to 38%) respectively.

Sugarcane bagasse contains lignocellulosic matter which provides strong attractive force for the binding of pollutant ions because of its numerous and varied functional group. It was found that at a lower pH (3), the removal efficiency of Cu (II), Cr (II) and Cd (II) was 19.8%, 16% and 10%). The adsorption is slow at lower pH value because the functional groups on the adsorbent are more protonated and, hence, they are less available to retain the metals.

This implies that the adsorbent surfaces remain positively charged and because of the rivalry between metal-ions and hydrogen ions positively charged for the active positions of the adsorbent ions (Öncel, 2008). As a result adsorption efficiency was low. At lower pH, the positively charged ion Cu (II), Cr (II) and Cd (II) species may compete with H^+ and can be adsorbed at the surface of the adsorbent by ion exchange mechanism. A higher pH value tends to govern the electrostatic attraction between cations and surface locations, which decreases the challenging impact of hydrogen ions and gives the adsorbed surface a higher affinity for copper, chromium, and cadmium adsorption. The optimum pH for the single component system was pH value of 7. This optimum pH value was used further in the following batch experiments.

4.3.3 The Effect of Initial metal Concentration

The initial concentration of the metal stock solution is a constraint that governs the movement of resistance between the adsorbents and the polluted solution. The effect of initial metal concentration was investigated by varying Cu (II), Cr (II) and Cd (II) concentration from 50 ppm to 500 ppm while all other parameters were kept constant for instance, pH was at 7, adsorbent dosage 20g/L, constant time 180 min, particle size 350-450 μm . Figure 4-3 displays the results obtained.

It was necessary to investigate the effect of initial metal concentration in adsorption because normally wastewater contains different ion concentration.

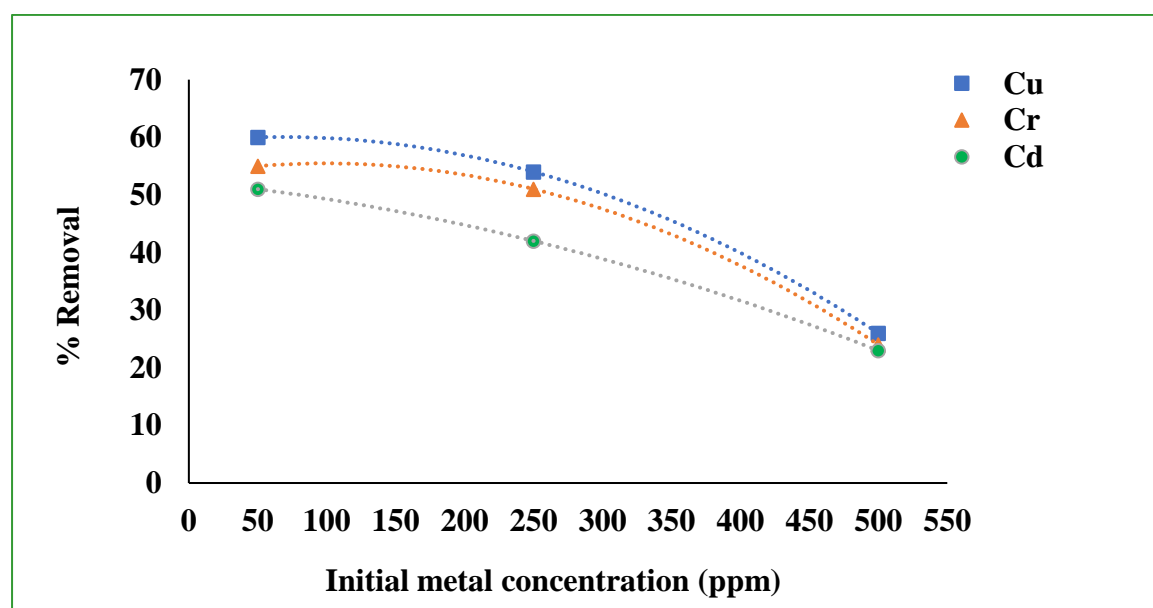


Figure 4. 7: Effect of initial metal concentration on the adsorption for a single metal system (pH of 7; contact time of 180 mins; mixing speed of 150 rpm, adsorbent dose 20 g/L, and particle size of 350-340 μm)

As shown in Figure 4.7, the removal efficiency was observed to be higher at lower metal concentration 50ppm which was 60%, 55% and 51% for Cu (II), Cr (II) and Cd (II). This may be because dilute contaminants are easier to carry in contrast to the concentrated form from liquid into solid phases(Muwanga and Barifaijo, 2006). The percentage removal of Cu (II), Cr (II) and Cd (II) showed a decrease with an increase in ion concentration. The percentage removal for Cu (II) decreased from 60% (50 ppm) to 26% (500 ppm), Cr (II) from 55% (50 ppm) to 24% (500 ppm) and for Cd (II) from 51% (50 ppm) to 23% (500 ppm) respectively. The decrease is due to the fact that the adsorbent has a fixed number of active sites and at higher concentration, the active sites becomes saturated. The optimum initial concentration for the single metal system was 50 ppm. The optimum initial concentration was used in further batch experiments.

4.3.4 The Effect of Adsorbent Dosage

The synthesized water was prepared to imitate the concentration and pH of actual wastewater. The effect of the adsorbent dosage was investigated by varying adsorbent mass from 5 to 20 g/L as outlined on Figure 4-8. Adsorbent mass is an important variable because it relates to the number of active sites available and consequently affect the overall efficiency of the water treatment system.

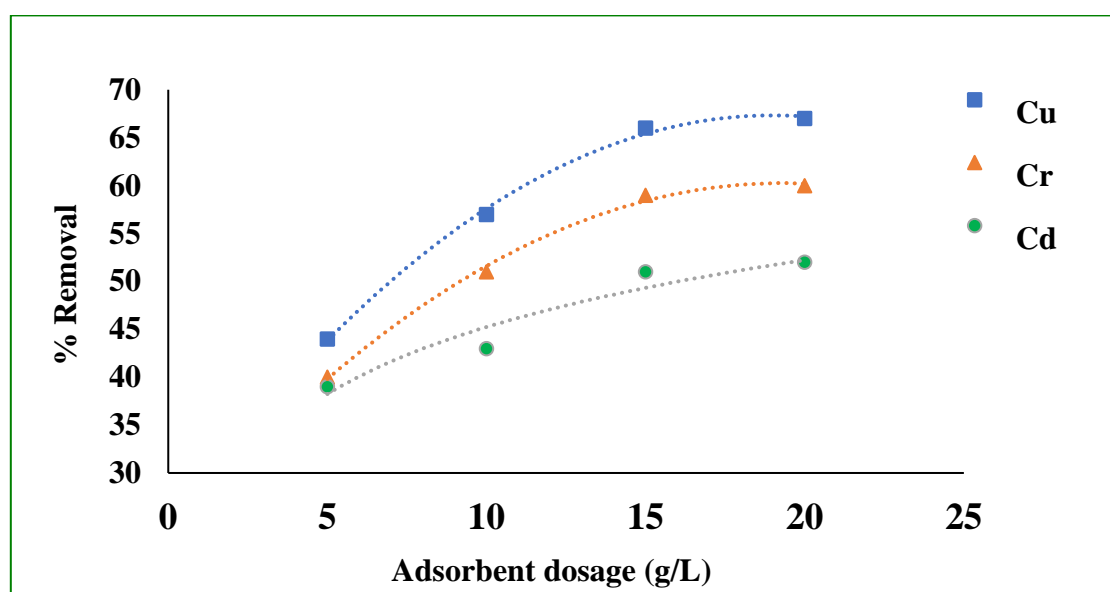


Figure 4. 8: Effect of adsorbent dosage on the adsorption for a single component system (pH of 7; contact time of 180 mins; mixing speed of 150 rpm, and initial metal concentration of 50 ppm)

As shown in figure 4.8, the percentage removal increased from (44 % to 67%) for Cu (II), from (40% to 60%) for Cr (II) and from (39% to 52% for Cd (II). An increase in the removal efficiency as the dosage increases is due to an increase in the availability of exchangeable sites with the increase in the adsorbent dosage. With increasing dosage of adsorbents, there is more surface area for copper, chromium and cadmium adsorption (Mozammel et al., 2002). The optimum adsorbent dosage for the single component system was 20 g/L. The optimum adsorbent dosage was used in further batch experiments.

4.3.5 The Effect of Particle Size

From Figure 4.9, it is clear that the increase in particle size passes through a maximum and decreases as particle size increases. The decrease in particle size increases the metal adsorption in a fixed adsorbent dose. The increase in adsorption by smaller particles was due to greater exposure to pores and the larger surface area for mass adsorption in the adsorbent per unit mass (Pansini and De Gennaro, 1991). The optimum sugarcane bagasse particle size range for the single metal system was 350-450 μm . The optimum particle size range was used in further batch experiments.

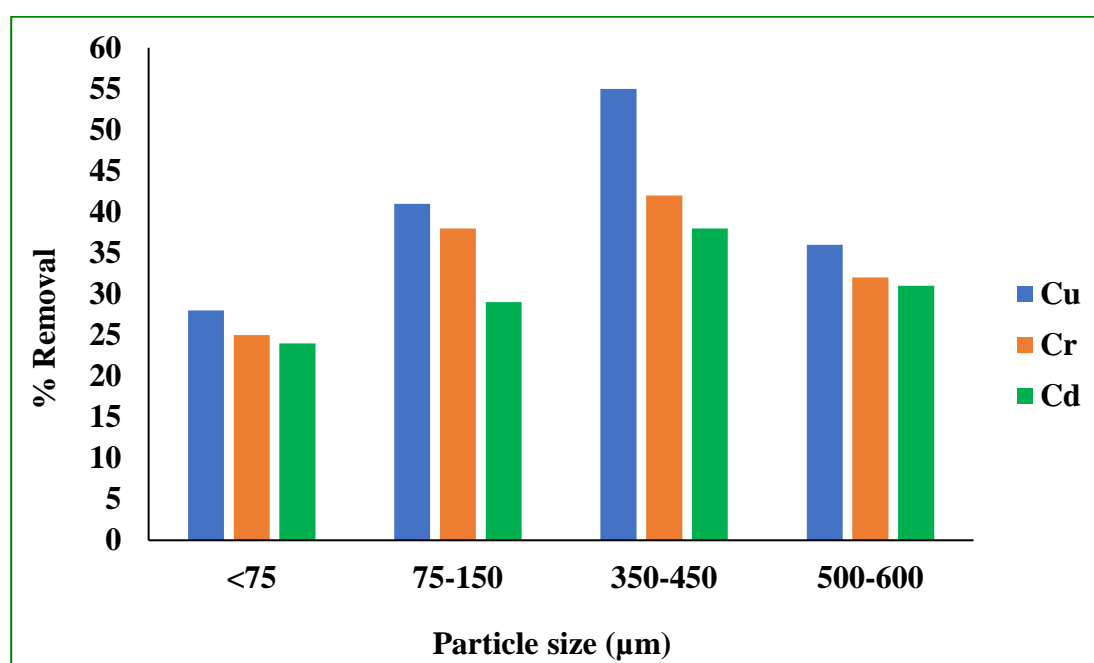


Figure 4. 9: Effect of particle size for a single component system (pH of 7; contact time of 180 mins; mixing speed of 150 rpm; adsorbent dosage of 20 g/L and initial concentration of 50 ppm)

Referring to figure 4.9, the particle size range of 350-450 μm denoted to have higher removal efficiency of Cu (II), Cr (II) and Cd (II) which is in contrast with what other researchers have reported.

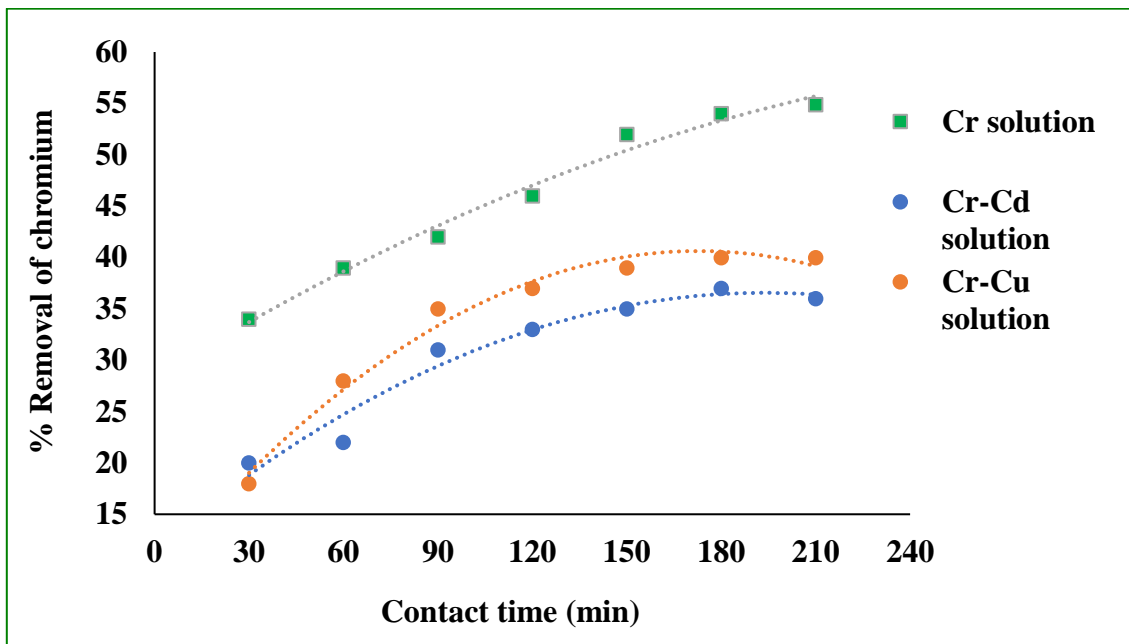
The adsorbent with the smaller particle ($< \mu\text{m}$) size was expected to have higher removal efficiency as compared to that with larger particle size. This deviation might be due to the fact that the adsorbent with the particle size had more of carboxylic functional groups and high level of silica that acted as an adsorption site including C-O aromatic ring, C-H and Si-O-Si compared to the adsorbent with different particle size class ($<75 \mu\text{m}$, $75\text{-}150 \mu\text{m}$, and $500\text{-}600 \mu\text{m}$). This implies that the surface of the adsorbent with the particle size of $350\text{-}450$ was rich in polymeric hydroxyl, carbonyl and aromatic rings which play a major role in binding of Cr, Cd, Cu ions. In addition, the results obtained from SEM reveals that sugarcane bagasse at a particle size class of $350\text{-}450 \mu\text{m}$ is more porous as compared to other particle size classes which constituted a greater removal efficiency. This means that heavy metals had a larger surface area hence better ion removal.

4.4 Operating Parameters for Binary System Component

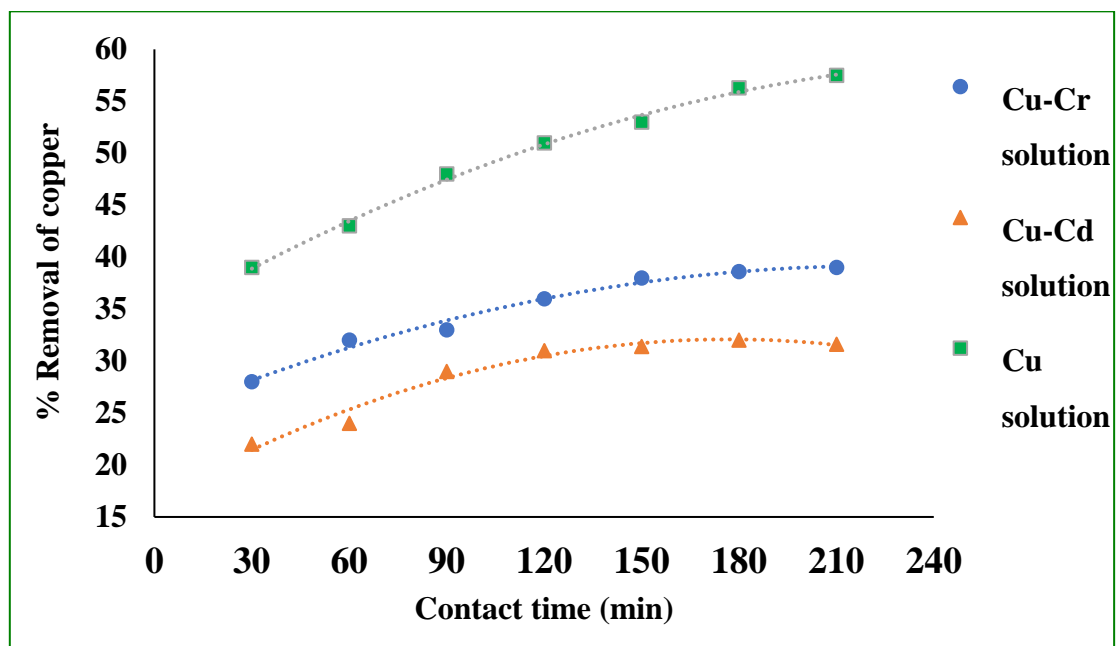
The batch experiments for operating parameters were repeated similarly as to that of the single component systems. For binary stock solutions, it was seen that generally the removal efficiencies for individual metals were lower compared to single ion systems due to metal-to-metal competition within binary metal ion system components (Perez-Marin and Zapata, 2007). Generally, it was observed that the removal efficiency for Cu (II) ions was greater compared to Cd (II) and Cr (II).

4.4.1 The Effect of Contact Time

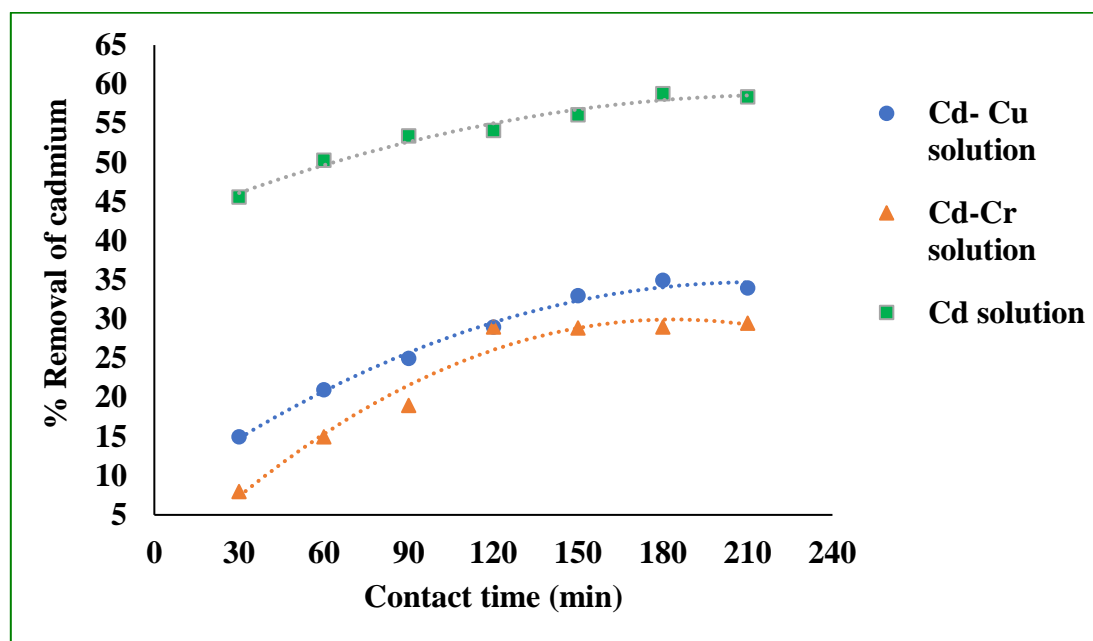
Figure 4.10 (a), (b) and (c) outlines the effects of contact time on the removal efficiency of Cu (II), Cr (II) and Cd (II) respectively in the presence of other metal ions. The maximum removal efficiency for Cr (II), Cu (II) and Cd (II) in a single metal system was found to be 54.9%, 57.5% and 58.4% respectively. It was observed that the maximum removal efficiency for the binary metal system was significantly lower compared to single metal system.



(a)



(b)



(c)

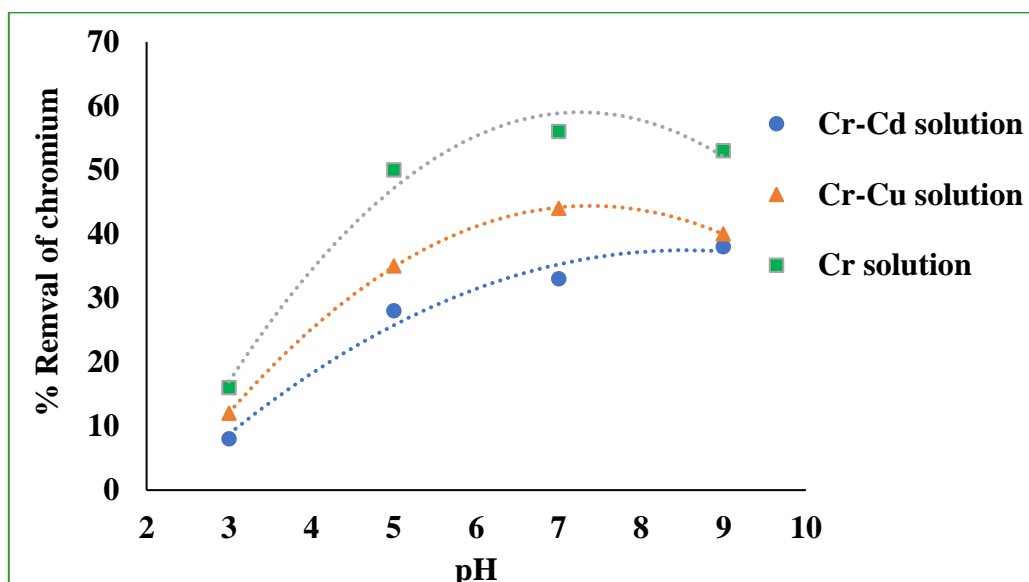
Figure 4. 10: Effect of contact time on the adsorption for individual metal ions, chromium (a), Copper (b) and cadmium (c) in the binary component system. [Mixing speed of 150 rpm]

From figure 4.10, Cr (II) showed a higher affinity to sugarcane bagasse with a maximum removal efficiency of 40% as compared to Cu (II) and Cd (II) which registered maximum removal efficiencies of 39% and 34% in the presence of other metal ions. It was noted that chromium was better removed in Cr-Cu (40%) solution as compared to Cr-Cd (37%). However, copper was better removed in a Cu-Cr (38.6%) solution as compared to Cu-Cd (32%) solution. Furthermore, cadmium was better removed in a Cd-Cu (35%) solution as compared to Cd-Cr (29.5%) solution. The results also showed that there was a weak competition in the adsorptive capacity of Cr (II) in the presence of Cd (II), whereas the capacity of adsorption of Cu(II) was reduced by the presence of Cd(II). Cu (II) was comprehended not to be greatly influenced by the presence of Cd (II) and Cr (II) ions in the binary metal solution in terms of removal efficiency. The removal efficiency for Cd (II) was smaller compared to Cu (II) and Cr (II) under all values in the presence of other metal ions.

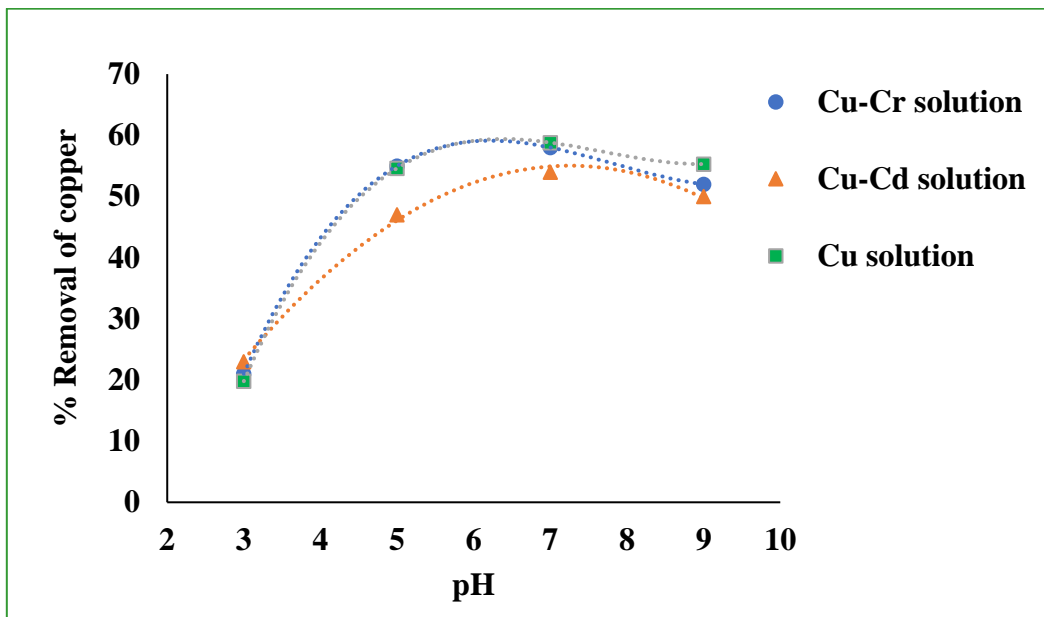
The removal efficiency of the individual metal in the binary metal system followed this order, for Cu (II) in binary metal system Cu-Cd and Cu-Cr it was [Cu>Cd, Cu>Cr]. For Cd (II) in the binary metal system Cu-Cd and Cd-Cr it was [Cu>Cd, Cr>Cd]. Moreover, for Cr (II) in the binary metal system Cu-Cr and Cd-Cr it was [Cu>Cr, Cr>Cd]. Similar to what was observed in single metal system, the removal rate was relatively increasing for all the metal ions and then slowly decreased as time increased for all binary component systems. This study has chosen an optimum contact time of 180 minutes to remove the two metal ions maximally and was used for further batch experiments. The adsorption during the initial phases is due to the abundance of active sites on the surface of the adsorbent which is saturated and consumed over time (Juang and Shiau, 2000).

4.4.2 The Effect of pH

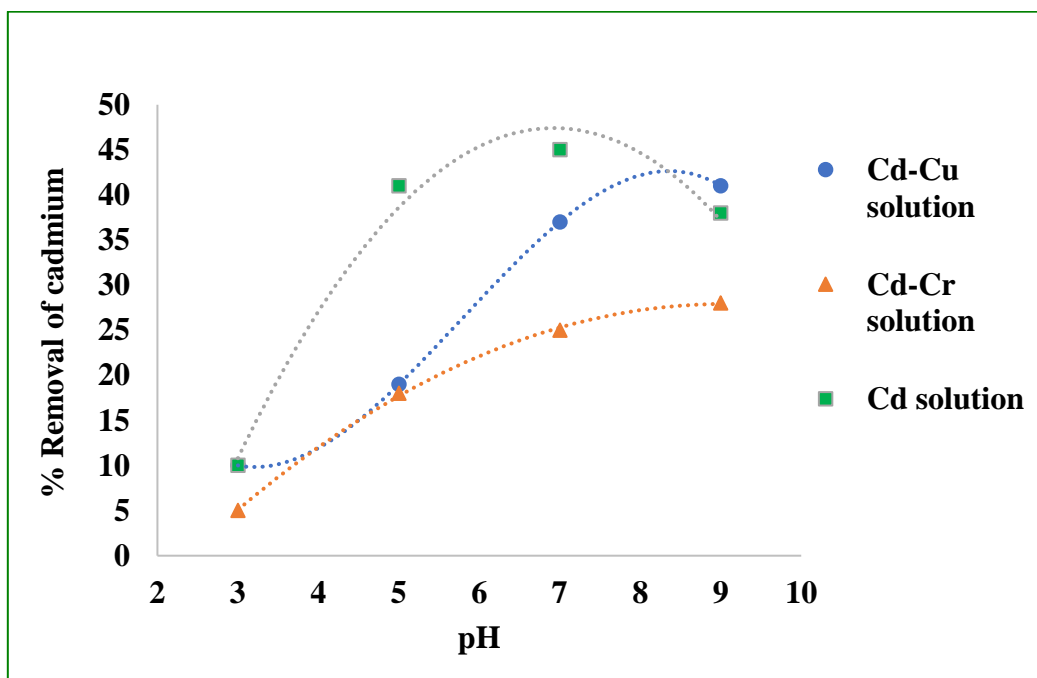
Figure 4.11 (a-c) results show that the pH of the liquid strongly influences the removal of the two metal ions from the solution. At a pH range of 3-7, it was observed that Cr (II) did not have a great effect on the removal of copper as compared to Cd (II).



(a)



(b)



(c)

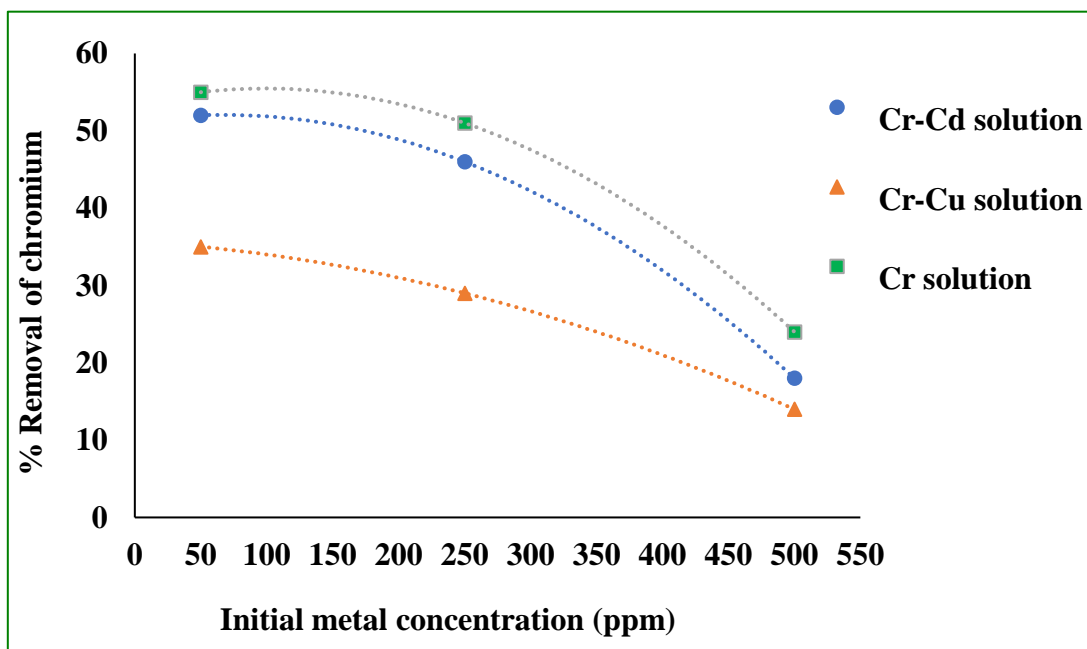
Figure 4. 11: Effect of pH on the adsorption for individual metal ions, Chromium (a), copper (b) and cadmium (c) in the binary component system. [Mixing speed of 150 rpm, contact time of 180 mins]

As shown in figure 4.11, Cu (II) removal percentage from the binary metal system Cu-Cr solution had almost the same efficiency. This could imply that some of the metal were adsorbed on the same site and that Cu (II) removal was not hindered by the presence of the other metals. Copper had a greater effect (44%) on chromium adsorption than did on cadmium (37%). Cadmium removal efficiency was reduced by 8% when copper was also in a solution whereas chromium removal efficiency was reduced by 12% when copper was present. It was observed that maximum removal efficiency for all the binary systems was 52% for Cu (II) metal ions.

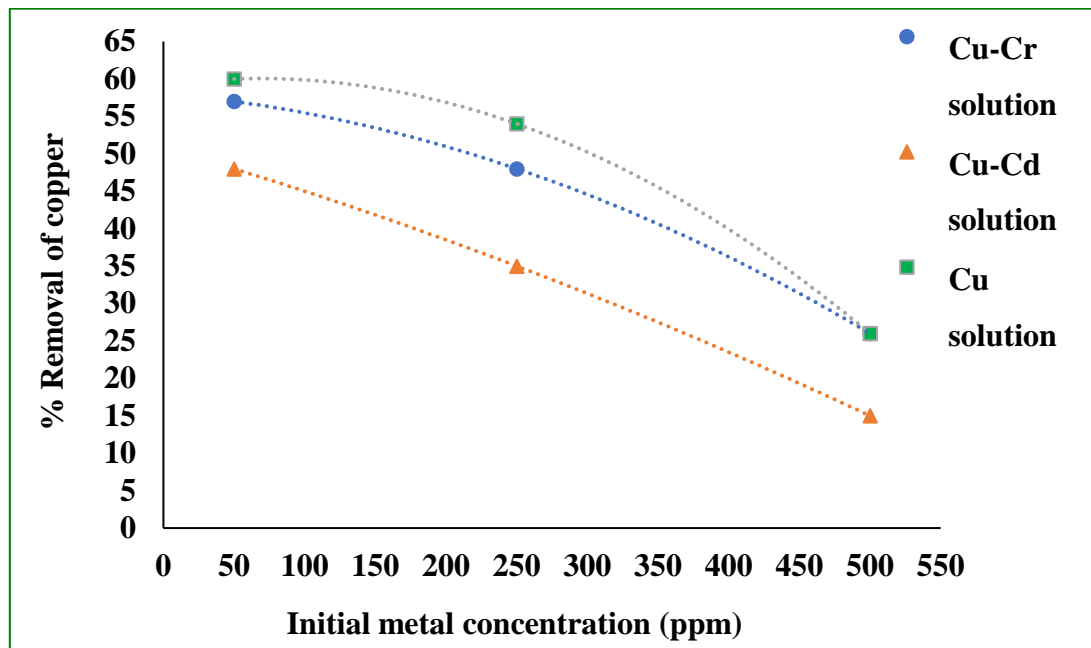
This was a significant decrease as compared to the single component system where a maximum removal efficiency of 55.3% for Cu (II) was recorded. This clearly showed that the presence of other metal ions in the solution did affect the removal efficiency of the metal ion to be extracted. These results indicated that although the metals did compete for the binding sites of the adsorbent, there was a decrease in the number of active sites when both metals were present. A general trend for all three-metal ion removal was observed. It was seen that the increase in pH led to the increase in metal ion removal efficiency up till a maximum value and then started to decrease as pH continued to increase. This was attributed to the fact that the adsorption in acidic medium was weak and increased with increasing pH. With values greater than pH of 7.0, the hydroxide species of metal ions may be precipitated leading to decrease in the removal of the metal ions. The adsorption was weak with a low pH, as large amounts of protons rival metal cations in the active sites on bagasse sugarcane(Kara, 2005). Therefore, for further batch experiments, the optimum pH value of 7.0 was selected as an ideal removal.

4.4.3 The Effect of Initial Metal Concentration

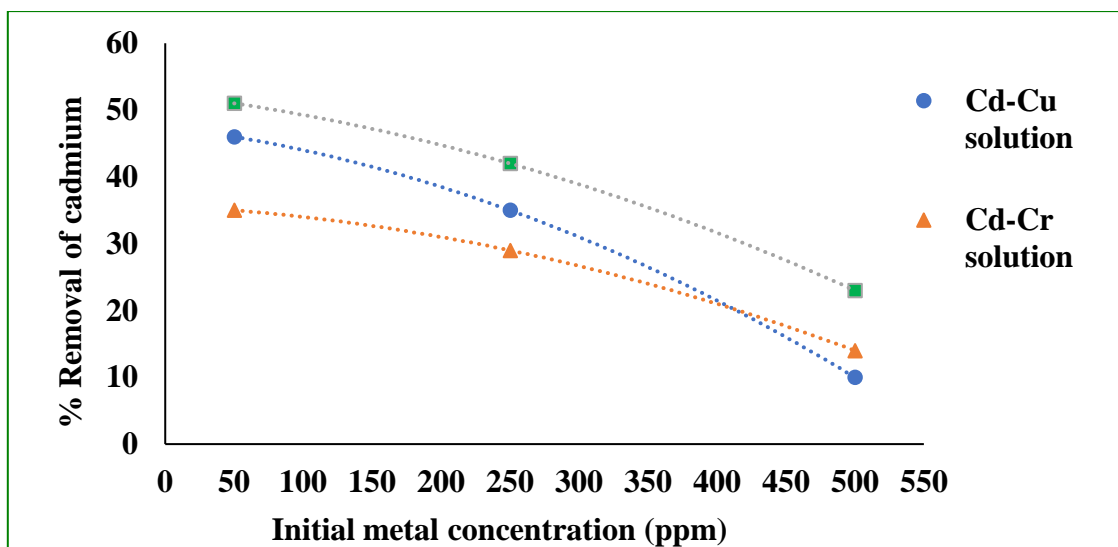
Figure 4.12 (a-c) displays how initial metal concentration affects the removal efficiency of a metal ion in the presence of another metal ion. Though the removal efficiency for Cu (II), Cd (II) and Cr (II) in binary solutions were slightly lower than that in the single metal system, it was however observed that for Cu (II) metal ion, the presence of chromium did not significantly affect the removal of Cu (II). This was shown by the similarities of both the maximum and minimum removal efficiencies for both the single (maximum = 60% and minimum = 26%) and binary (maximum = 57% and minimum = 26%).



(a)



(b)



(c)

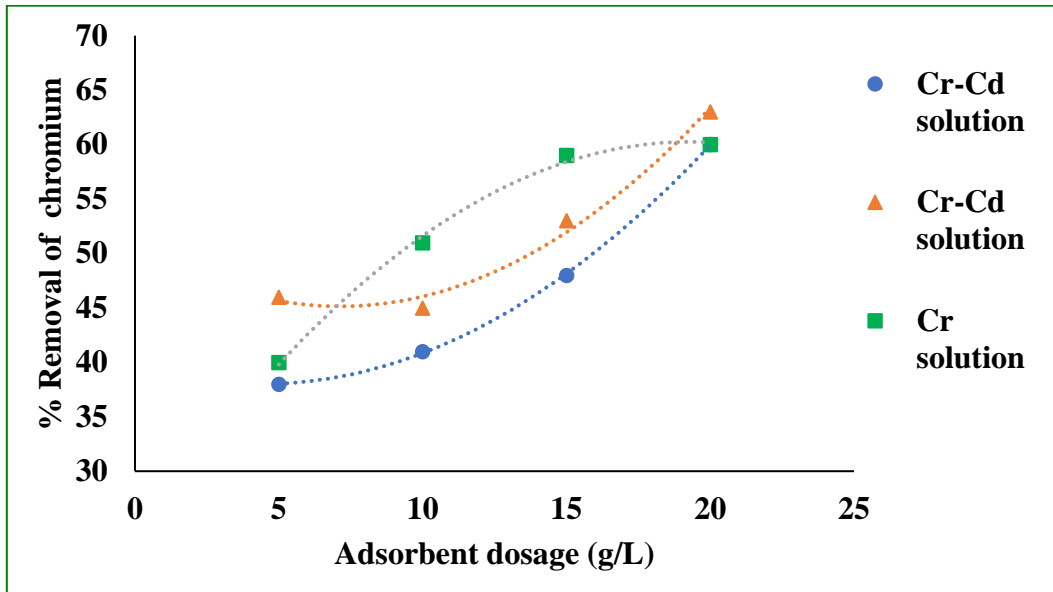
Figure 4. 12: Effect of initial concentration on the adsorption for individual metal ions chromium (a), Copper (b) and cadmium (c) in the binary component system. [Mixing speed of 150 rpm, contact time of 180 mins, pH of 7.0]

Figure 4.12 exhibits that Cu (II) had higher affinity to sugarcane bagasse and its adsorption was not affected by the of chromium metal ion. This is attributed to the fact that Cu (II) demonstrates effective competition for sorption sites in the presence of Cd (II) and Cr (II).

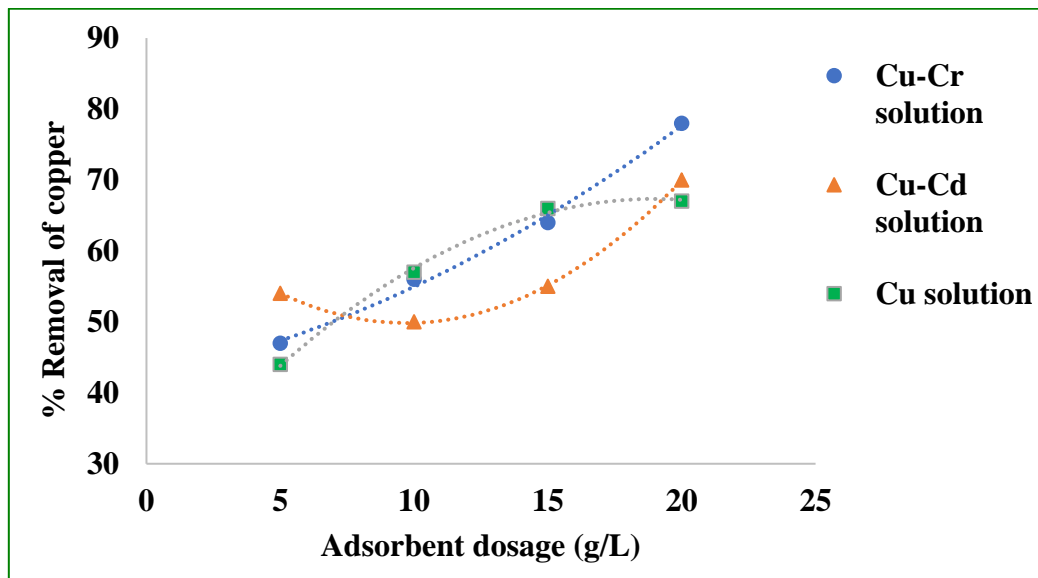
Maximum percentage of chromium was found to be 52% in the presence of cadmium. It showed a lower percentage removal (35%) in the presence of Cu (II). Whereas maximum percentage removal of Cu (II) was determined to be 57% in the presence of Cr (II). It showed a lower percentage removal 48% in the presence of Cd (II). Subsequently, removal efficiency of Cd (II) was found to be at a maximum of 46% in the presence of Cu (II) and at minimum 35% in the presence of Cr (II). It was generally observed that with the initial metal concentrations of 50, 250 and 500ppm the rate of removal of the two-metal ion generally decreased. This decrease is due to the fact that all adsorbents at higher concentrations are saturated in a fixed number of active sites (Karnitz and Gurgel, 2007). The initial concentration of 50 ppm for these three binary samples was considered optimal and used in further batch experiments.

4.4.4 The Effect of Adsorbent Dosage

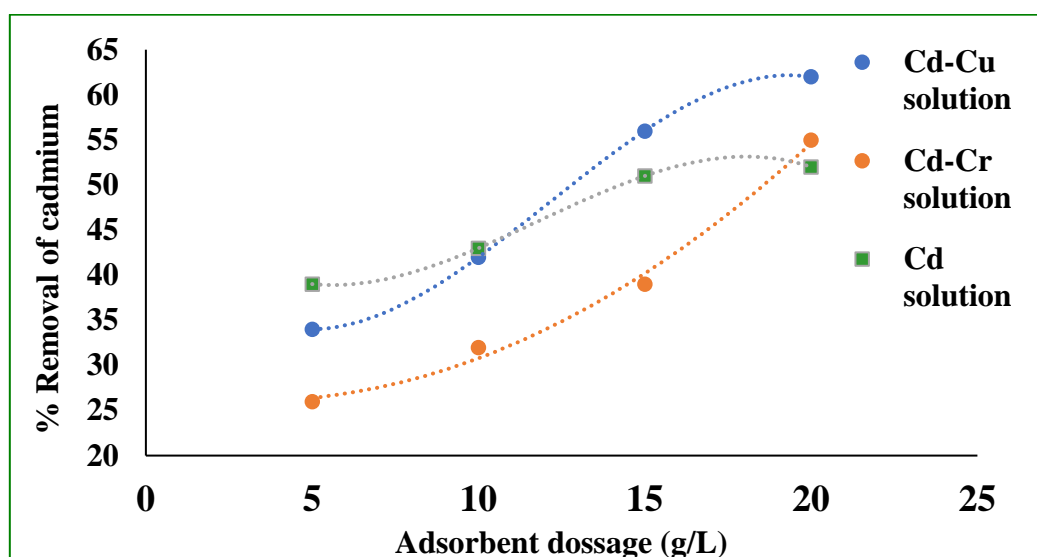
The effect of varying the adsorbent dosage at an initial metal concentration of 50 ppm, mixing speed of 150 rpm, contact time of 180 min, and particle size of 350-450 was investigated. Figure 4.13 (a-c) outlines how adsorbent dosage affects the removal efficiency of a metal ion in the presence of another metal ion. It was observed that removal efficiency increases with increasing adsorbent dosage for the given initial metal concentration.



(a)



(b)



(c)

Figure 4. 13: Effect of initial concentration on the adsorption for individual metal ions, copper (a), Chromium (b) and cadmium (c) in the binary component system. [Mixing speed of 150 rpm, contact time of 180 mins, pH of 7.0, initial concentration of 50 ppm]

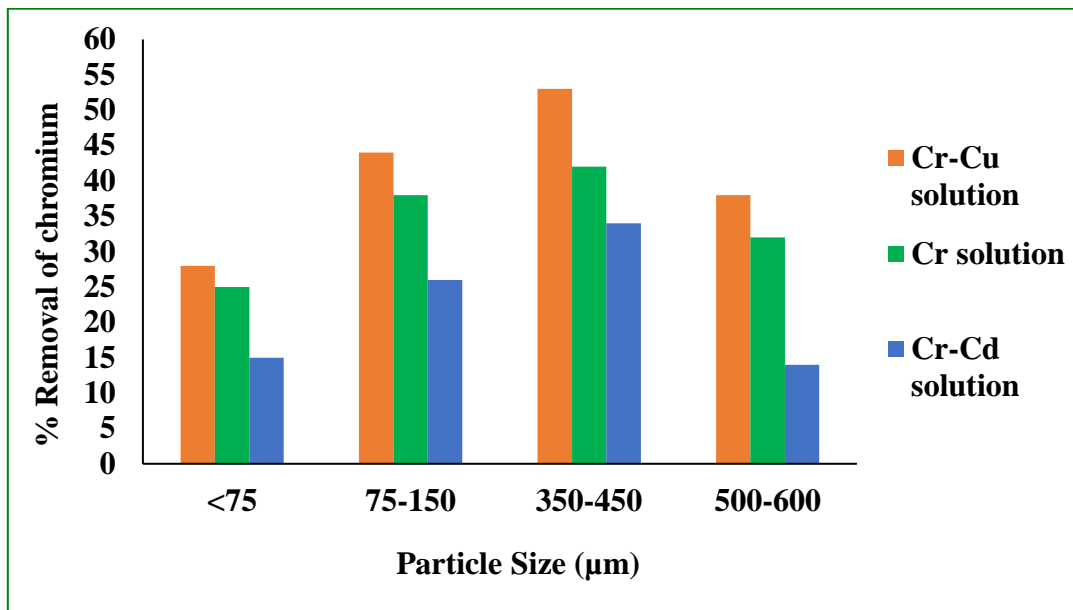
Referring to figure 4.13, it was perceived that by increasing the adsorbent dosage from g to 20g/L, the removal efficiency increased from 44% to 67%, 40% to 60% and 39% to 52% for Cu (II), Cr (II) and Cd (II) in a single metal system. This is to be expected because, for a fixed initial metal concentration, increasing adsorbent dosage provides a greater surface area of adsorption sites. Maximum removal efficiency for all binary metal system was obtained to be 78% for Cu (II). Minimum removal efficiency for all binary metal system was found to be 55% for Cd (II). Cadmium appeared to have a greater effect as the contaminant than copper and chromium. The removal efficiency of Cu (II) and Cr (II) initially decreased as the adsorbent dosage increased to 10 g/L. This was contrary to the literature. The decrease in the removal efficiency could be due to aggregation or overlapping of adsorption site caused by overcrowding of the adsorbent particles. In addition, it could be that the capacity of adsorbent available was not fully utilized at an adsorbent dosage of 10 g/L in comparison to other adsorbent dosage.

Subsequently, at an adsorbent dosage of 15 to 20 g/L an increase in removal efficiency was observed. The increase in the removal efficiency can be attributed to the contact surface increase resulting in more active sites on the surface of sugarcane bagasse (Farooqi et al., 2007). Generally, the removal efficiency for Cu (II), Cd (II) and Cr (II) in binary solutions were slightly lower than that in the single metal system. This is attributed to the competition for adsorption sites posed by the presence of other metal ions in the solution.

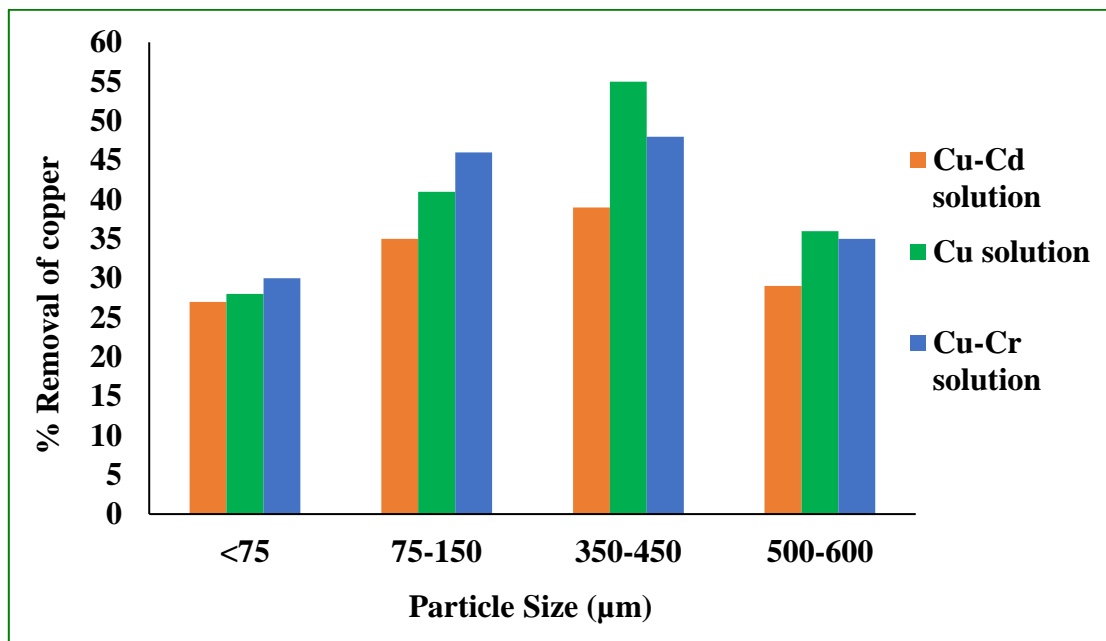
Comparing binary system to single system it was seen that all results for both component systems demonstrated that increased sugarcane bagasse dosage from 5 g/L to 20 g/L led to an increase in the percentage of removal of both metal ions. Nonetheless, Cr (II) was better adsorbed in the presence of Cd (II) as compared to the presence of Cu (II) but Cu (II) was better adsorbed in the presence of Cr (II) as compared to the presence of Cd (II). Furthermore, Cd (II) was better removed in the presence of Cu (II) as compared to the presence of Cr (II). The adsorbent dosage of 20 g/L for these three binary component systems was considered optimal and used in further experiments.

4.4.5 The Effect of Particle Size

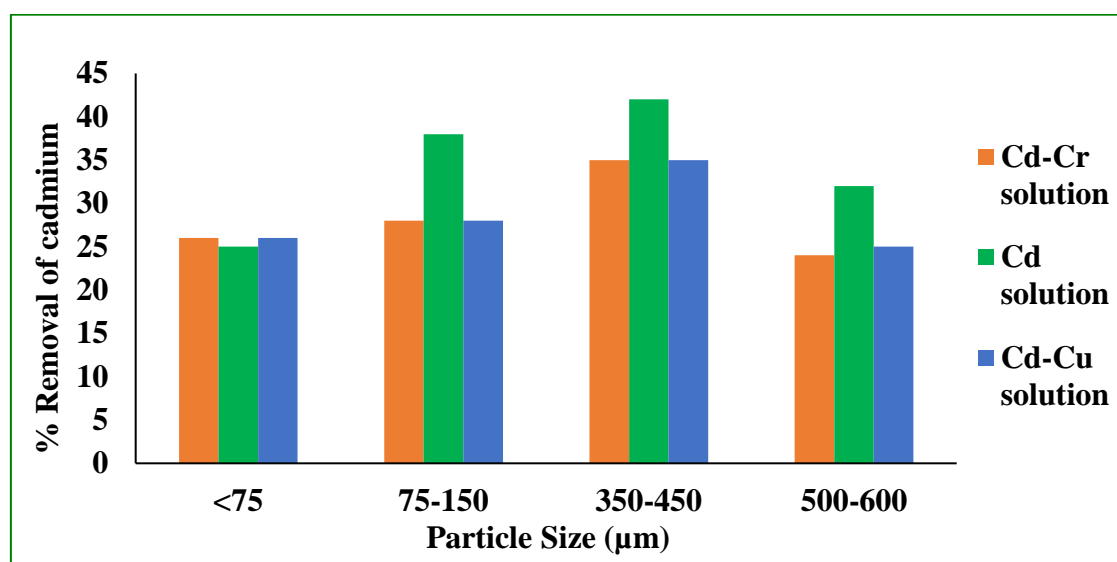
Figure 4.14 (a-c) outlines how particle size affects the removal efficiency of an individual metal ion in the presence of another metal ion. Cu (II) was not greatly influenced by the presence of Cd (II) and Cr (II) ions in the solution in terms of removal efficiency.



(a)



(b)



(c)

Figure 4. 14: Effect of initial concentration on the adsorption for individual metal ions, chromium (a), Copper (b) and cadmium (c) in the binary component system. [Mixing speed of 150 rpm, contact time of 180 mins, pH of 7.0, initial concentration of 50 ppm, adsorbent

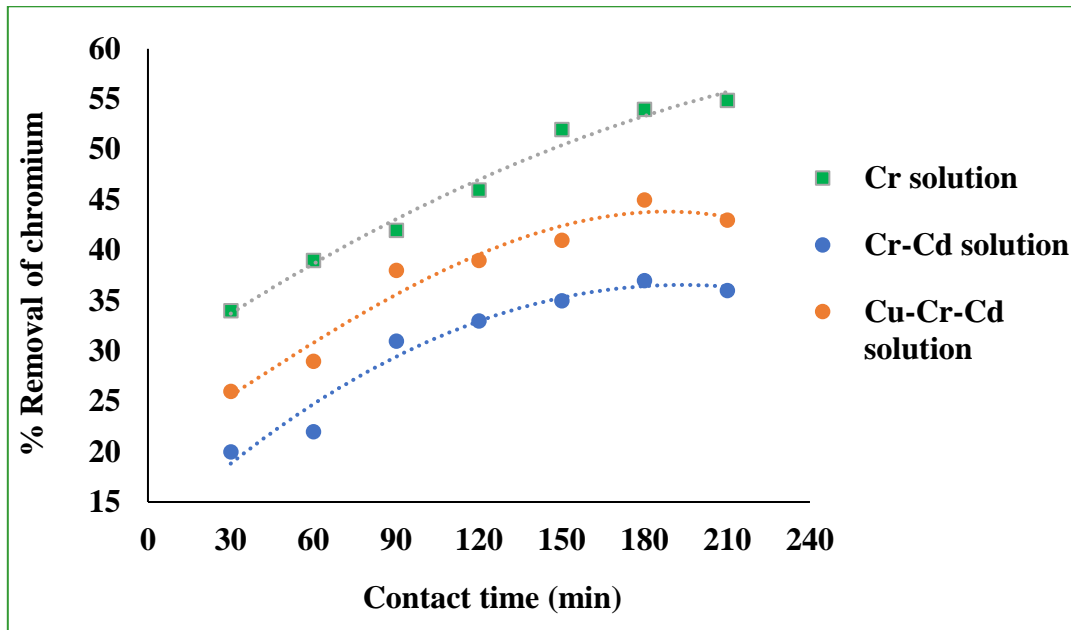
Generally, the removal efficiency for Cu (II), Cd (II) and Cr (II) in binary solutions were slightly lower than that in the single metal system. This is attributed to the competition for adsorption sites posed by the presence of other metal ions in the solution. Increase in the particle size led to the increase in the removal of the metal ions up until to a maximum value of removal efficiency. The greater percentage removal by smaller particle sizes could be attributed to the fact that smaller particles had a large specific adsorptive surface, but also the surface area decreased as particle size increased (Lam et al., 2006). Breaking larger particles tends to create small splits and channels on the sugarcane bagasse particle surface, resulting in more efficient diffusion because the particles are smaller hence resulting in increased removal efficiency. The particle size range of 350-450 μm for these three binary samples was considered optimal and used in further experiments.

4.5 Operating Parameters for Ternary System Component

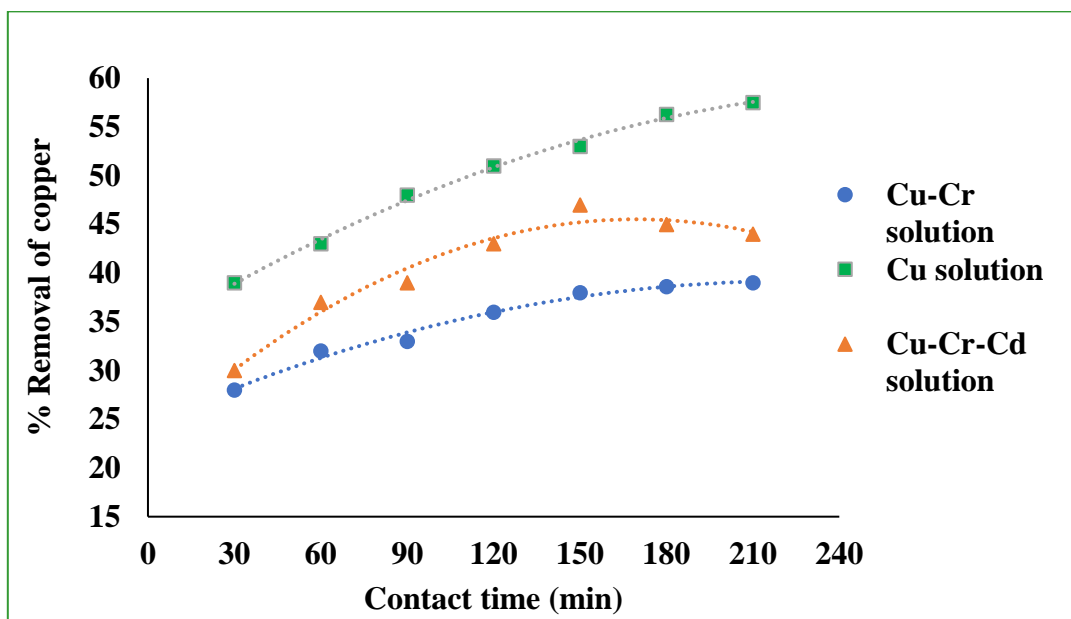
The batch experiments for the operating parameters were repeated similarly as to that of the single and binary metal systems. For ternary stock solutions, it was seen that generally the removal efficiencies for individual metals were lower compared to single and binary ion systems due to more increased metal to metal competition within ternary metal ion system components (Perez-Marin and Zapata, 2007). Generally, it was observed that the removal efficiency for Cu (II) ions was greater compared to Cd (II) and Cr (II). The removal efficiency of the individual metals followed this order, (Cu > Cr > Cd)

4.5.1 The Effect of Contact Time

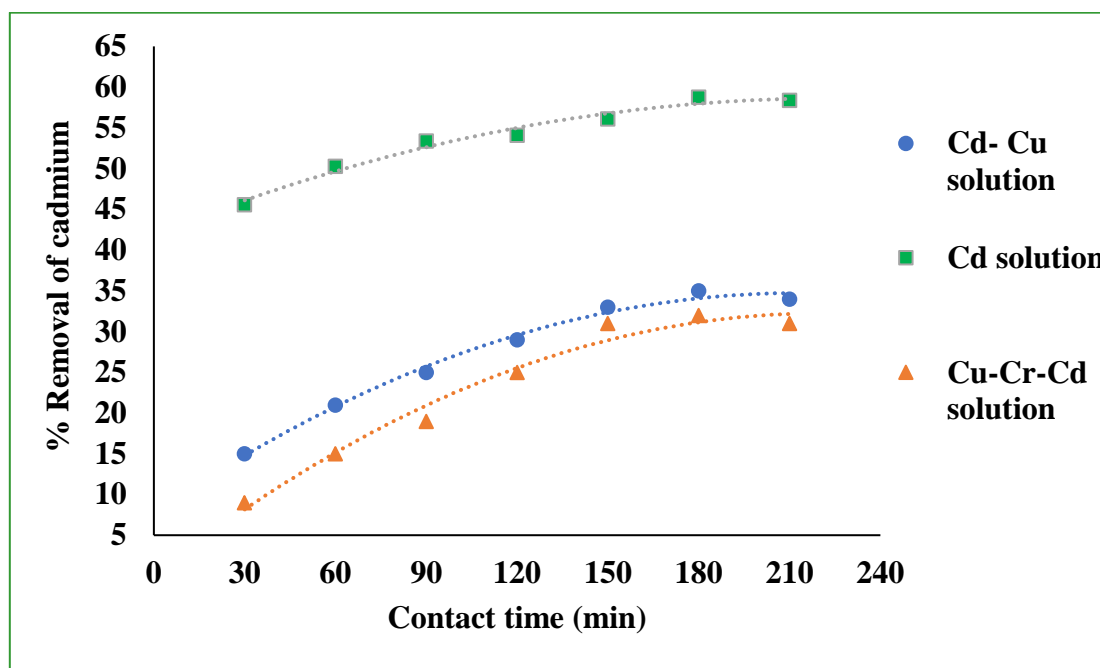
Figure 4.15 (a) outlines the effects of contact time on the removal efficiency of individual metal ions in the presence of two other metal ions. Generally, the removal efficiency for Cu (II), Cd (II) and Cr (II) in ternary solutions were much significantly lower than that of the single component system but slightly higher than that of the binary. This was contrary to what other researchers reported (Abdullah and Yusuf, 2019, Agrawal and Singh, 2016, Febrianto and Kosasih, 2009). However, researchers like Anteck & Zdarta (2018) outlined a similar phenomenon but they didn't manage to explain what could have caused such phenomenon to occur.



(a)



(b)



(c)

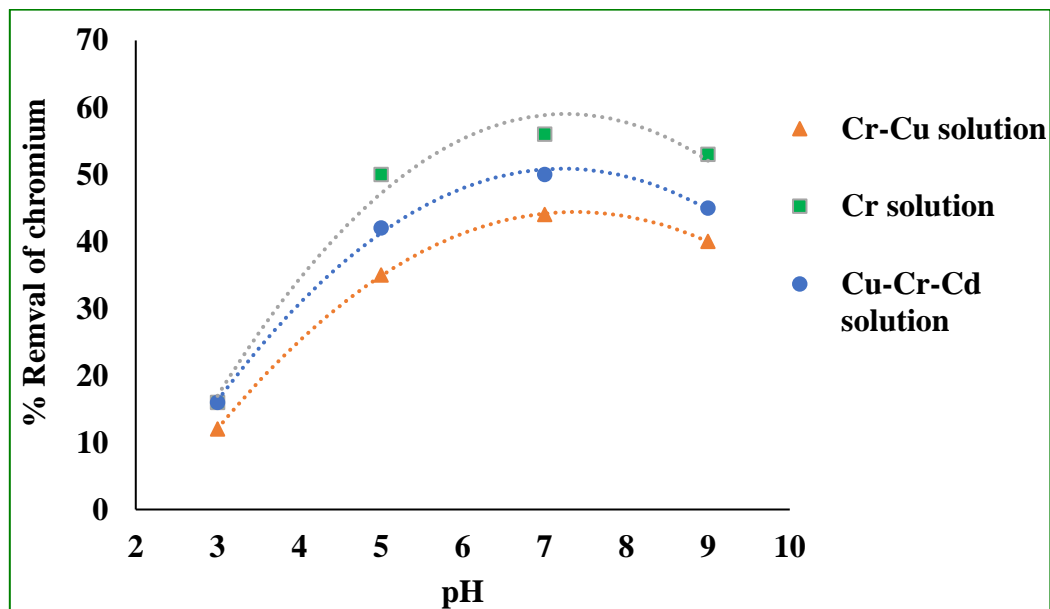
Figure 4. 15: Effect of contact time on the adsorption for individual metal ions, copper (a), Chromium (b) and cadmium (c) in the ternary component system. [Mixing speed of 150 rpm]

As displayed on figure 4.15 it was observed that at an optimum contact time (180 min), the removal efficiency of Cu (II) in a ternary metal system was reduced by 11.3% and 17.7% compared to single and binary metal system efficiency. Whereas the removal efficiency for Cr (II) in a ternary metal system has been shown to be reduced by 9% and 17% in comparison to single and binary metal system efficiency. Furthermore, it was observed the removal efficiency for Cd (II) was reduced by 24% and 21% in comparison to single and binary metal system efficiency. Based on the results obtained, it was observed that each metal appeared to have an effect as the contaminant of the other.

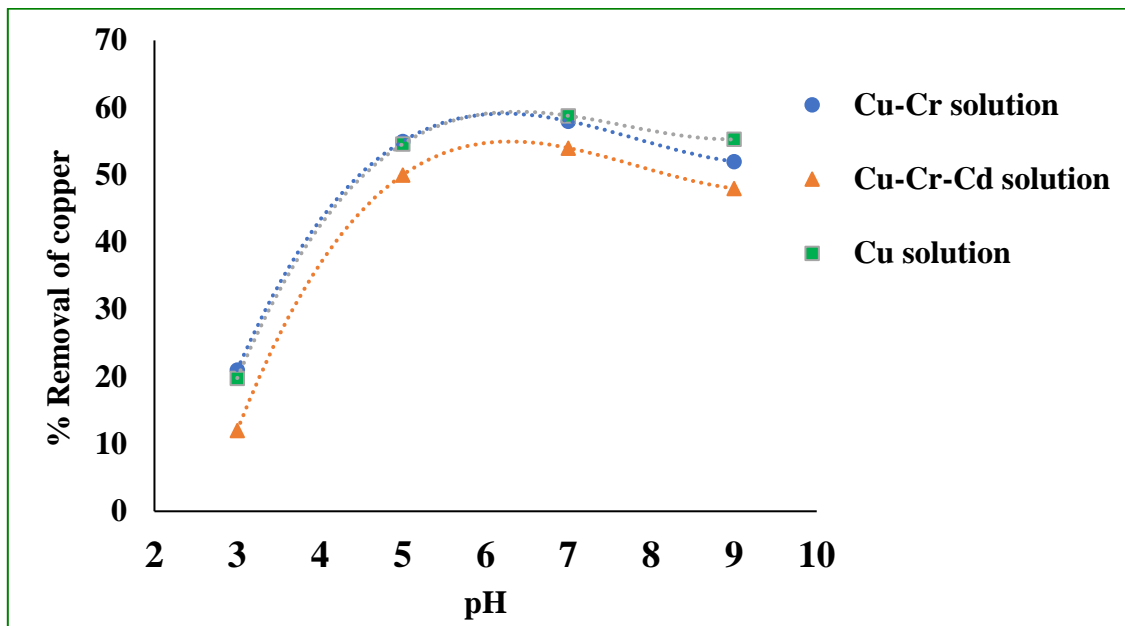
However, adsorption of Cd (II) showed to be greatly hindered in the presence of Cu (II) and Cr (II). The exquisite reduction on the removal efficiency of each metal ion in the ternary metal system is due to the competition for adsorption sites between the metals adsorbed. The contact time of 180 mins for the ternary samples was considered optimal and used in further experiments.

4.5.2 The Effect of pH

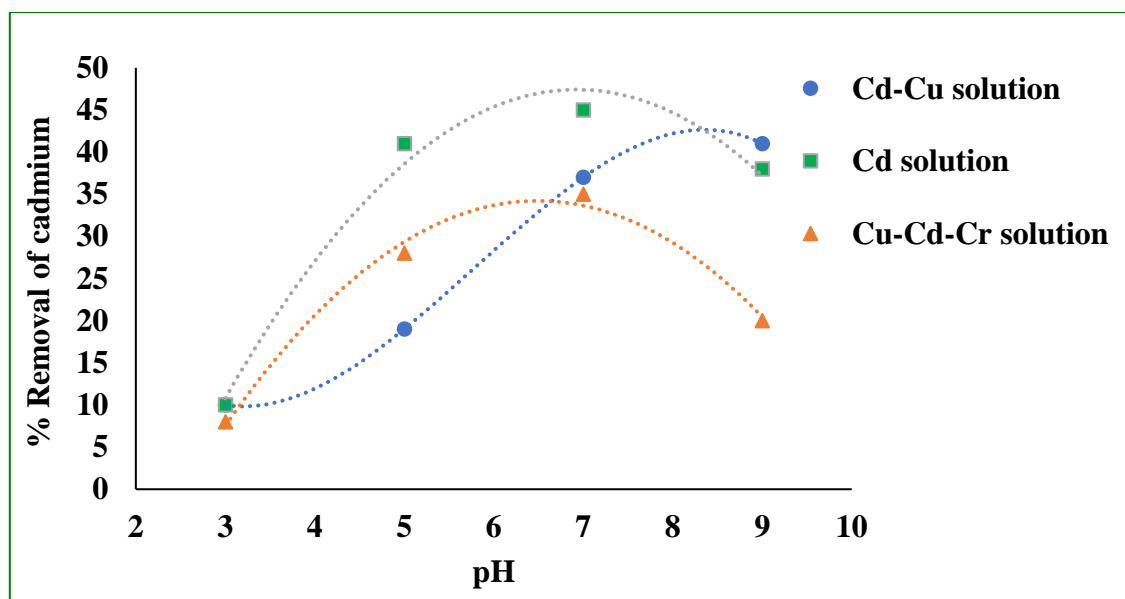
The pH is one of the parameters that plays a vital role in the adsorption process. It influences the solubility of heavy metals and affects the concentration of the counter ions on the functional groups hence, it is imperative to take it into account during adsorption process. In addition pH affects the solubility of metal ions, concentration of the counter ions on the functional groups of the adsorbent and the degree of ionization of the adsorbate during reaction. Figure 4.16 (a-c) outlines the effects of pH on the removal efficiency of an individual metal ion in the presence of two other ions. Commonly, the removal efficiency for Cu (II), Cd (II) and Cr (II) in ternary solutions were much significantly lower than both of the single and binary component system.



(a)



(b)



(c)

Figure 4. 16: Effect of pH on the adsorption for individual metal ions, copper (a), Chromium (b) and cadmium (c) in the ternary component system. [Mixing speed of 150 rpm, contact time of 180 mins]

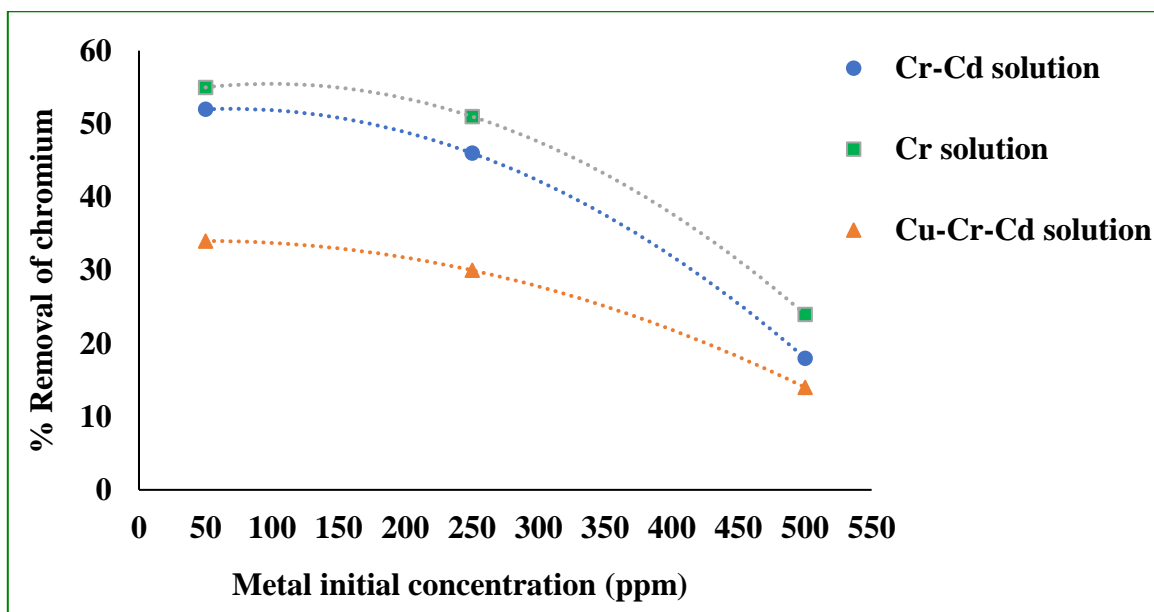
The results presented on figure 4.16 shows that there was a reduction on the removal efficiency for Cu (II), Cd (II) and Cr (II) in ternary metal solution.

It was noted in all figures that the maximum removal efficiency for all the ternary systems was 48% for Cu (II) metal ion as compared to both the single (55.3%) and binary (52%). It was denoted there was a reduction of 12%, 10% and 4.8% for Cr (II), Cd (II) and Cu (II) on the adsorption uptake in a ternary metal system compared to their respective single metal solution. It was perceived that the adsorption efficiency increased with an increase in pH. However, after an optimum pH of 7, the adsorption efficiency started to decrease. Sugarcane bagasse contains the hydroxyl functional groups which are active sites for metal binding. At lower pH (3) these functional groups become protonated and, hence, they are less available to retain the metals. As a result, the adsorption of Cr (II), Cu (II) and Cd (II) decreases. At high pH values (9), the quantity of H⁺ ion is reduced, while most active adsorbents are de-protonated. This advances the metal uptake. It was comprehended that removal efficiency of Cd (II) was prominently affected by the presence of Cu (II) and Cr (II) as it had the highest the highest reduction percentage of 12% compared to Cu (II) and Cr (II) which was registered to be 4.8% and 10%. This is attributed to the presence of two other metal ions resulting in increased competition for adsorption sites.

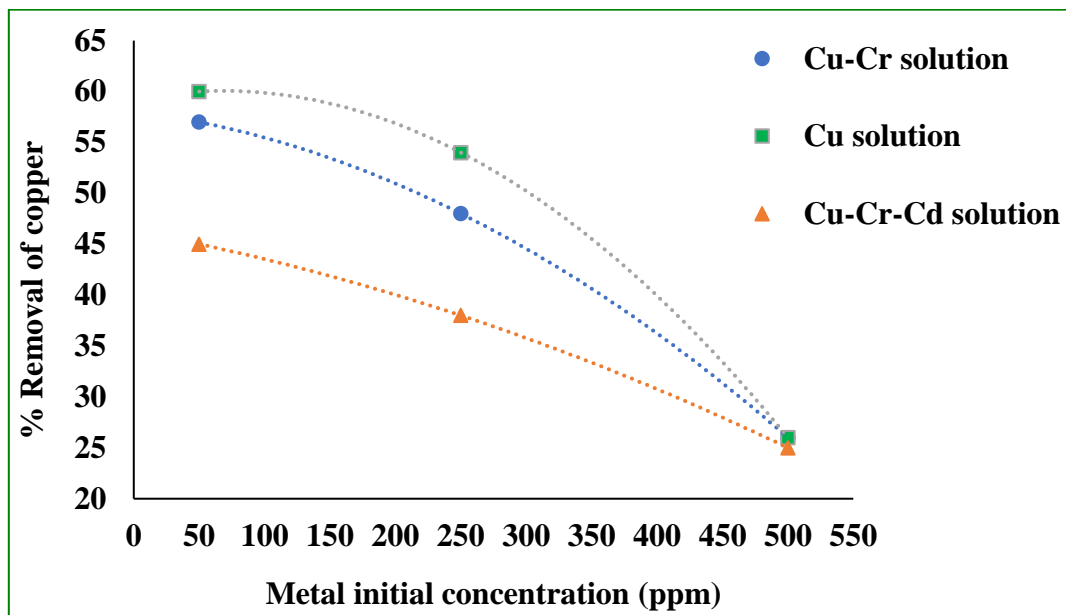
Furthermore, the metal ion-binding mechanism of adsorption on sugarcane is attributed to its abundance of hydroxyl groups from cellulose in which aqueous medium favours ion exchange of complexation with metal ion. The pH of 7 for the ternary samples was considered optimal and used in further batch experiments. The dependence of Cd (II), Cr (II) and Cu (II) was linked with both the surface functional group and the metal ion species predominant in aqueous solution. The species Cd²⁺ and Cd(OH)⁺ are predominant at pH lower than 7, while the groups on the surface are protonated and cannot bind to metal ions in solution. Besides, at very low pH, the surface groups are associated with the hydronium ions (H₃O⁺), negatively affecting the interaction with metal cations. When pH increases, the surface affinity with the metal also increases and adsorption is improved.

4.5.3 The Effect of Initial Metal Concentration

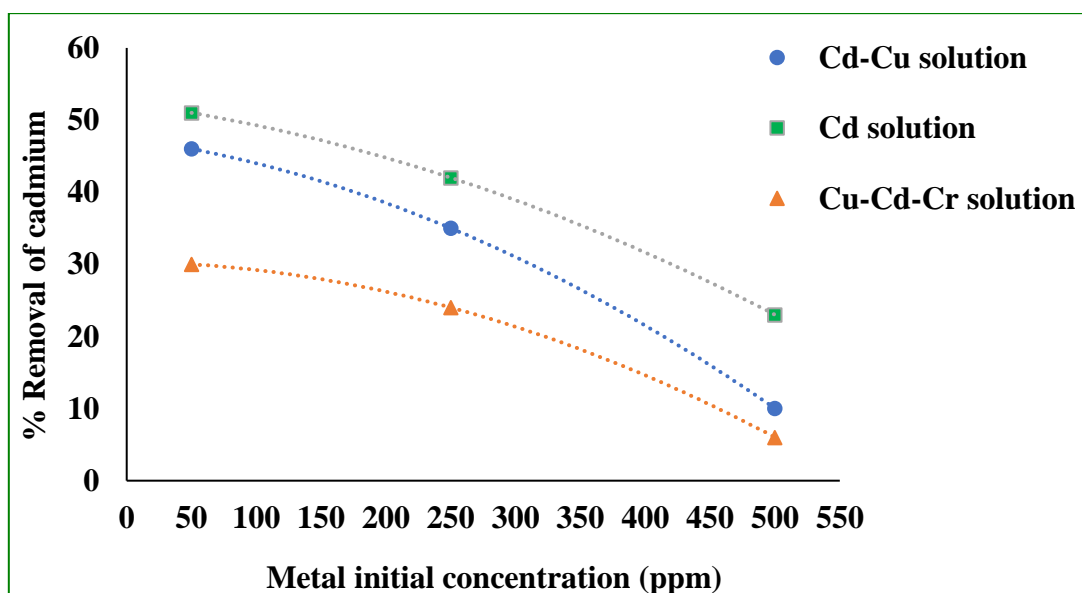
Figure 4.17 (a-c) outlines the effects of initial metal concentration on the removal efficiency of individual metal ions in the presence of two other metal ions. It was observed that the removal efficiency in the ternary system was much lower as compared to the single and binary systems. This was confirmed by the maximum and the minimum removal efficiencies of 45% and 25% respectively for Cu (II) metal ions in ternary solution as compared to 60% and 26% for single system and 57% and 26% for binary system. This decrease is due to the fact that all adsorbents at higher concentrations are saturated in a fixed number of active sites (Karnitz and Gurgel, 2007).



(a)



(b)



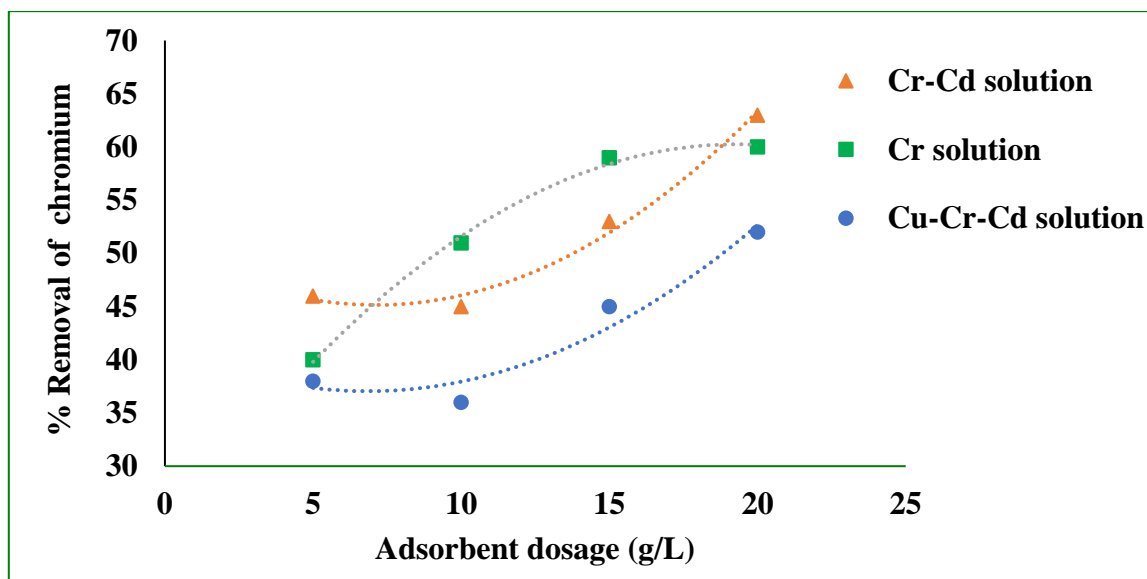
(c)

Figure 4. 17: Effect of initial concentration on the adsorption for individual metal ions, chromium (a), Copper (b) and cadmium (c) in the ternary component system. [Mixing speed of 150 rpm, contact time of 180 mins, pH of 7]

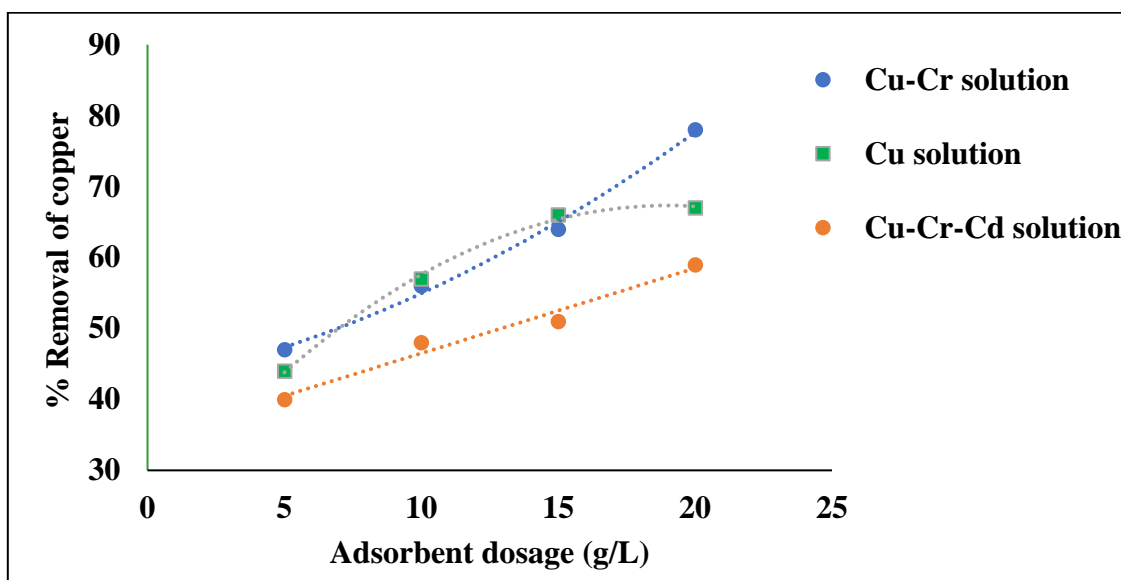
From figure 4.17, it can be seen that the ternary metal system followed the same trend as the binary and single metal system. The increase in initial metal concentration from 50 ppm to 500 ppm resulted in reduction of removal efficiency for Cu (II), Cr (II) and Cd (II). It was observed that each metal in a ternary system appeared to have an effect as a contaminant of the other. However, adsorption efficiency for Cr (II) and Cd (II) showed to be significantly affected by the presence of Cu (II). This is inverted by the percentage bargain on removal efficiency of Cr (II) and Cd (II) in the existence of Cu (II). It was inferred that Cr (II) and Cd (II) had an analogous reduction percentage of 20% in comparison to that of a single metal system and +/- 15% compared to a binary metal system. Subsequently, a reduction of 15% for Cu (II) was observed in the existence of Cr (II) and Cd (II) in comparison to that of single and 12% compared to that of binary metal system. This implies that Cu (II) is better adsorbed than Cr (II) and Cd (II) in a ternary metal system as it showed a higher affinity and a lower reduction percentage compared to the other metal ion. The initial concentration of 50 ppm for these three ternary samples was considered optimal and used in further batch experiments.

4.5.4 The Effect of Adsorbent Dosage

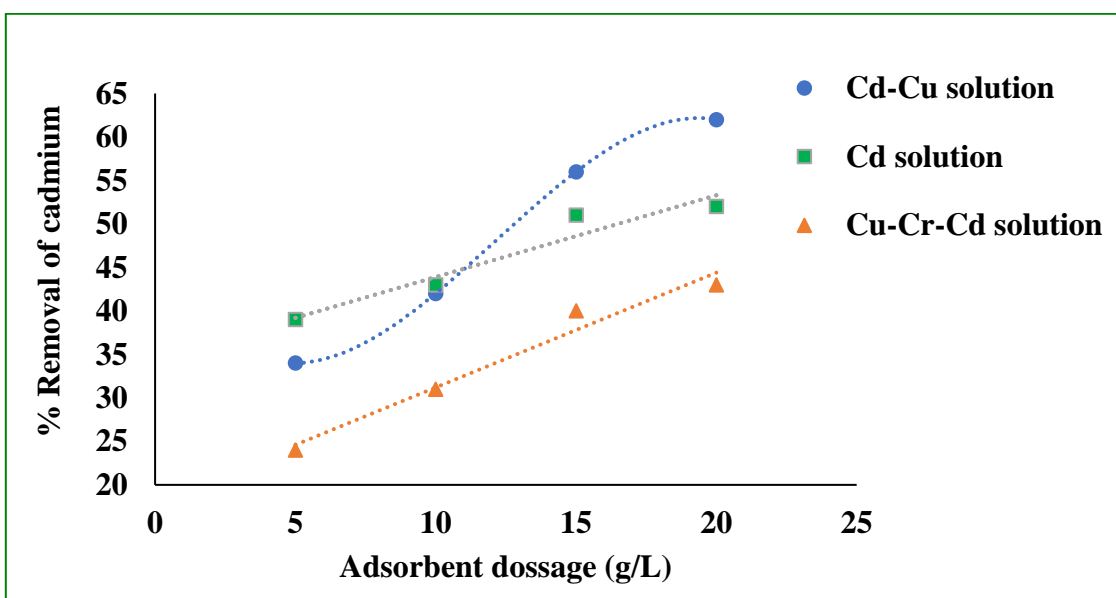
The adsorbent mass is one of the important variables to be investigated as it relates to the number of active sites available and consequently affects the overall efficiency of the water treatment system. Figure 4.18 (a-c) outlines the effects of adsorbent dosage on the removal efficiency of individual metal ions in the presence of two other metal ions. Commonly, the removal efficiency for Cu (II) was higher (59%) for all three ternary solutions but was much expressively inferior associated with both of the single (67%) and binary (78%) metal systems. This designates the decrease metal removal efficiency on sugarcane bagasse in the existence of two other metals due to increased rivalry for adsorption sites. The removal efficiency was seen to increase with an increase in adsorbent dose to a point of equilibrium at which adsorption efficiency alteration was not much substantial. With increasing dosage adsorbents, there is more surface area for copper, chromium, and cadmium adsorption.



(a)



(b)



(c)

Figure 4. 18: Effect of adsorbent dosage on the adsorption for individual metal ions, chromium (a), Copper (b) and cadmium (c) in the ternary component system. [Mixing speed of 150 rpm, contact time of 180 mins, pH of 7, initial concentration of 50 ppm]

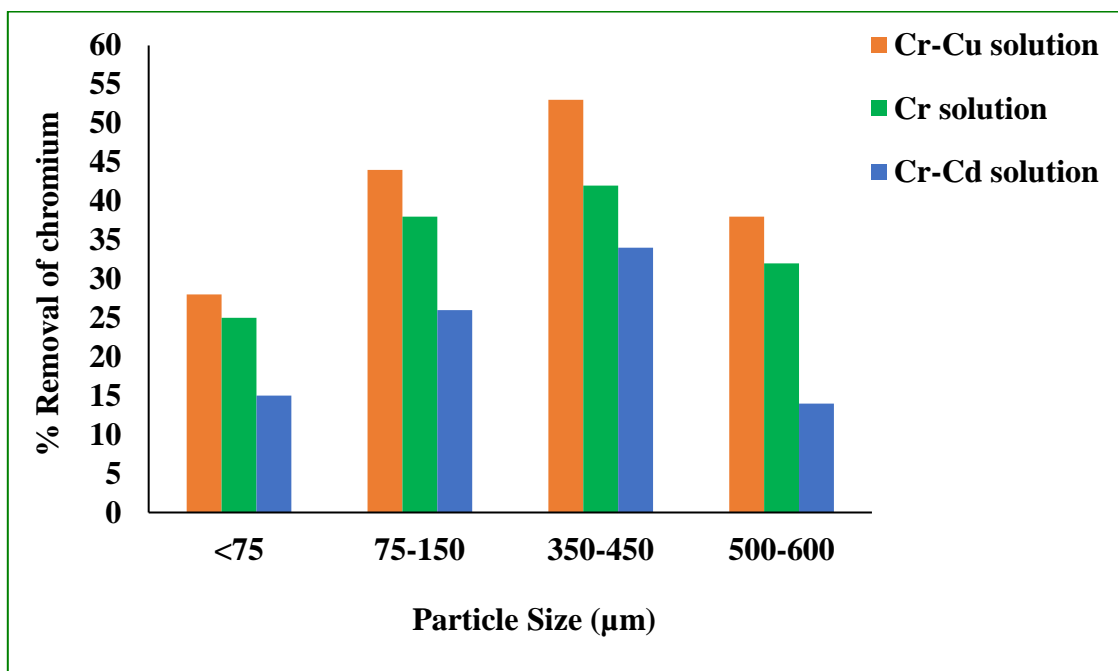
It can be demonstrated from figure 4-18 that at a minimum adsorbent dosage of 5 g/L, the removal efficiency of Cr (II) in a single and ternary system was nearly the same. The reduction was not much noteworthy as it was obtained to be 2%. However, it was established to be 8% compared to that in a binary metal system in the existence of Cd (II).

At an equilibrium dosage of 20 g/L, reduction of 8% and 11% associated with the removal efficiency attained in a single and binary metal system was prominent. This signifies that the presence of other metals at an adsorbent dosage of 20 g/L had a prodigious influence on the removal efficiency as compared to a lower adsorbent dosage (5 g/L). Removal efficiency of Cu (II) at an adsorbent dosage of 10 to 15 g/L exhibited not to be stalled by the presence of Cr (II) as it appeared to have approximately the same adsorption efficiency for the single and binary metal system. This implies that Cu (II) and Cr (II) were adsorbed on the same active sites of the adsorbent. However, the addition of the third metal in the system which was mentioned to be Cd (II) then resulted to a reduction of 2 % and 4% compared to the removal efficiency acquired in a single and binary metal system at an adsorbent dosage of 5 g/L. Subsequently, at an adsorbent dosage of 20 g/L, the adsorption uptake for Cu (II) was prominently influenced by the presence of Cr (II) and Cd (II). The removal efficiency was perceived to decline by 8% and 19% compared to single and binary metal systems.

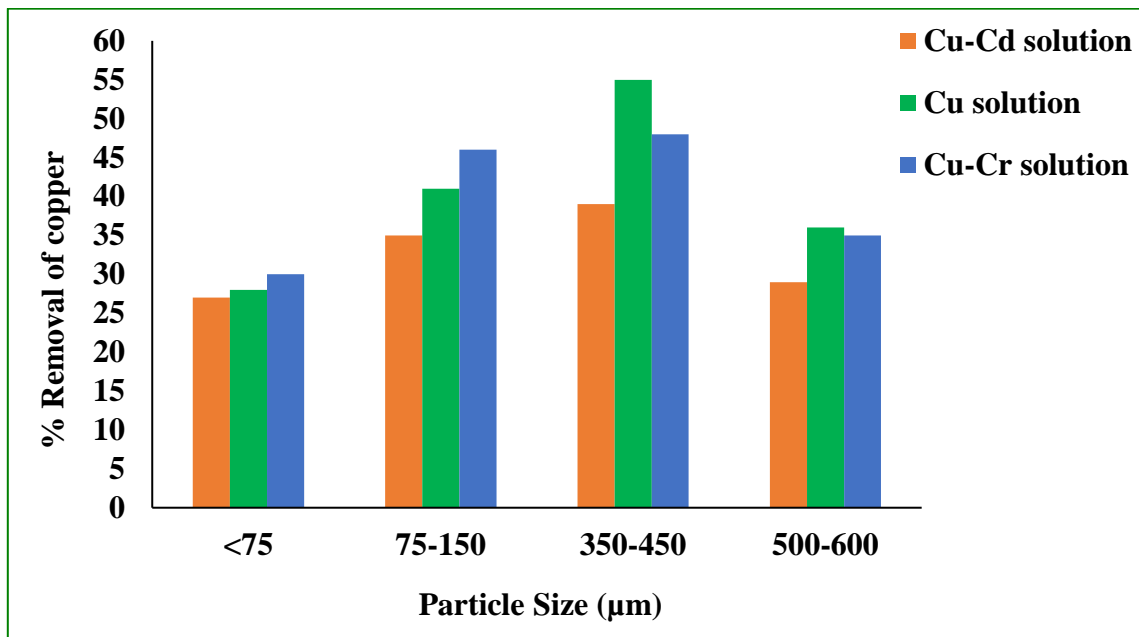
Removal efficiency for cadmium at an adsorbent dosage of 5 g/L was found to be less by 10% and 15% in a ternary metal system as compared to single and binary metal systems. At an adsorbent dosage of 10 g/L, adsorbent uptake for Cd (II) was more or less the equivalent for binary and single metal system but conveyed a reduction of 10% in the presence of an additional metal Cr (II) respectively. At an adsorbent dosage of 20 g/, a reduction of 17% and 7% in the ternary metal system as compared to binary and single metal systems was observed. Among the three heavy metals in the ternary metal ion, Cu (II) was itemized to have the uppermost removal efficiency 59% as compared to Cr (II) and Cd (II) which was enumerated to be 52% and 43%.

4.5. The Effect of Particle Size

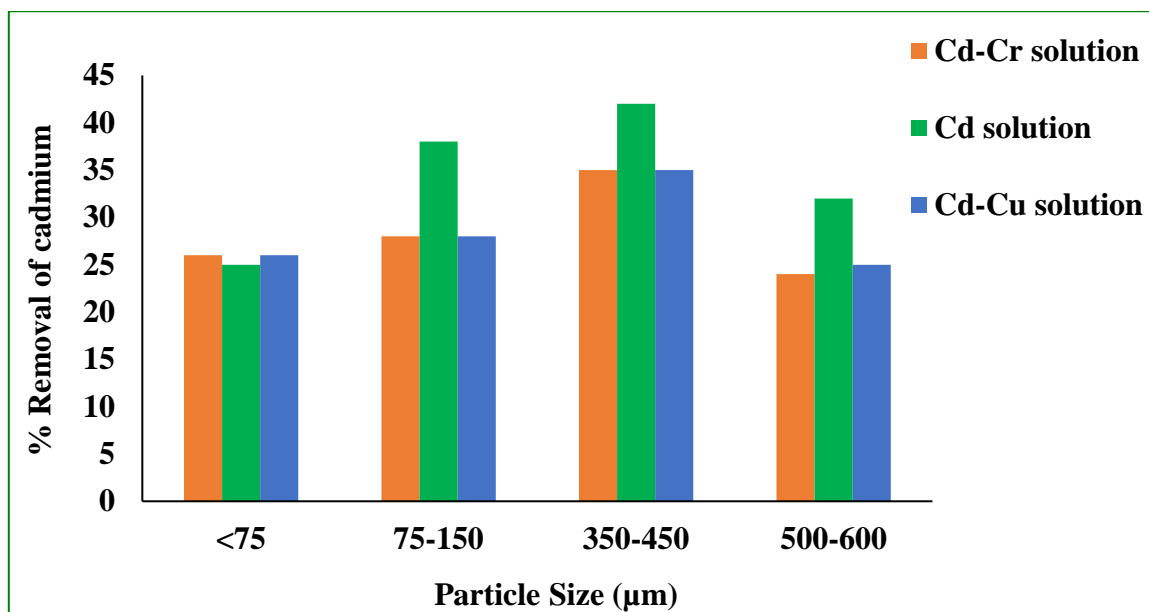
Figure 4.19 (a-c) outlines the effects of particle size on the removal efficiency of individual metal ions in the presence of two other metal ions. Generally, the removal efficiency for Cu (II), Cd (II) and Cr (II) in ternary solutions were much more ominously subsidiary than both of the single and binary component system. The maximum removal efficiency in the ternary metal system was revealed for Cu (II) with a value of 46% as related with 48% in binary system and 55% in single system. The ternary drift is comparable to the trends shown by both the single and the binary system where removal efficiency upsurges with increasing particle size until an equilibrium is reached and then its starts to decrease. This is contrary to what other researchers had reported. It was expected that the small particle size $<75 \mu\text{m}$ will have the greatest removal efficiency as compared to 75-150 and 350-450 μm particle size classes.



(a)



(b)



(c)

Figure 4. 19: Effect of bagasse particle size on the adsorption for individual metal ions, chromium (a), copper (b) and cadmium (c) in the ternary component system. [Mixing speed of 150 rpm, contact time of 180 mins, pH of 7, initial concentration of 50 ppm, adsorbent dosage of 20g/L]

4.6 Adsorption Isotherms

The adsorption isotherms were used to compare the adsorption capacity of an adsorbent for Cu (II), Cr (II) and Cd (II). Adsorption equations were used to analyse the results. Adsorption can take place by physical and chemical adsorption. In case of physical adsorption, the interaction between the adsorbate and the adsorbent are electrostatic as reported by numerous researchers. Chemical adsorption involves specific forces, such as those that are operative in the formation of chemical bonds. Three phenomena may be involved in the physical adsorption: monomolecular and multi-molecular adsorption and condensation in pores or capillaries. The common adsorption isotherms employed to represent the adsorption data are Langmuir and Freundlich isotherms. Adsorption capacity of the adsorbent was determined using the optimal operating parameters that were obtained from the subsequent experiments. Langmuir and Freundlich isotherms were used for the analysis of adsorption data and they represented the equilibrium data for these heavy metal removals.

The isotherm models of Cu (II), Cr (II) and Cd (II) removal were studied by different initial metal concentrations. The isotherm constant K_f and n are Freundlich constants, which represents sorption capacity and sorption intensity, respectively and were evaluated from intercept and slope of the linear plot of $\log q_e$ versus $\log C_e$. While Langmuir constants q and K_L were obtained from the slope of $1/Q_e$ versus $1/C_e$. To analyze the adsorption data, Langmuir and Freundlich isotherm were fitted and the parameters were obtained.

4.6.1 Single Component System

Figures 4.20 and 4.21 shows linearized isothermal Freundlich and Langmuir adsorption of the single component system. Table 4.2 shows the R^2 values obtained from the Langmuir and Freundlich isotherms. R^2 demonstrates the best correlation for the biosorption of Cd ions in sugar cane bagasse within the single component Freundlich model indicating that multiple layers of adsorption occurred.

Table 4. 2: Comparison of the single-component isotherms from Langmuir adsorption isotherms under optimum conditions

Metal Combinations	Langmuir			Freundlich		
	Q_m (mg/g)	K_L (L/mg)	R^2	K_f (L/mg)	n	R^2
<u>Single</u>						
<i>Cd</i>	1.38	0.042	0.953	0.083	1.77	0.998
<i>Cr</i>	4.198	0.021	0.948	0.439	1.836	0.73
<i>Cu</i>	38.41	0.004	0.997	0.312	1.404	0.928

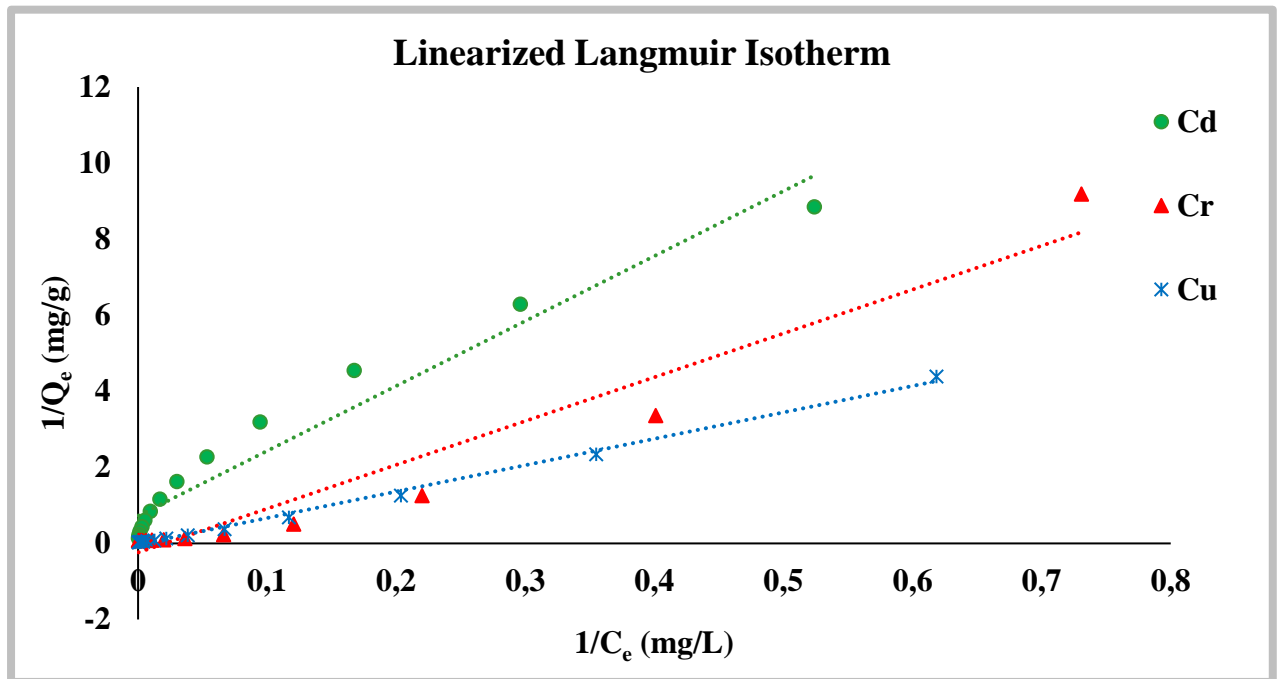


Figure 4. 20: Isotherm plots of single-component Langmuir adsorption of Chromium, Cadmium and Copper at optimum conditions.

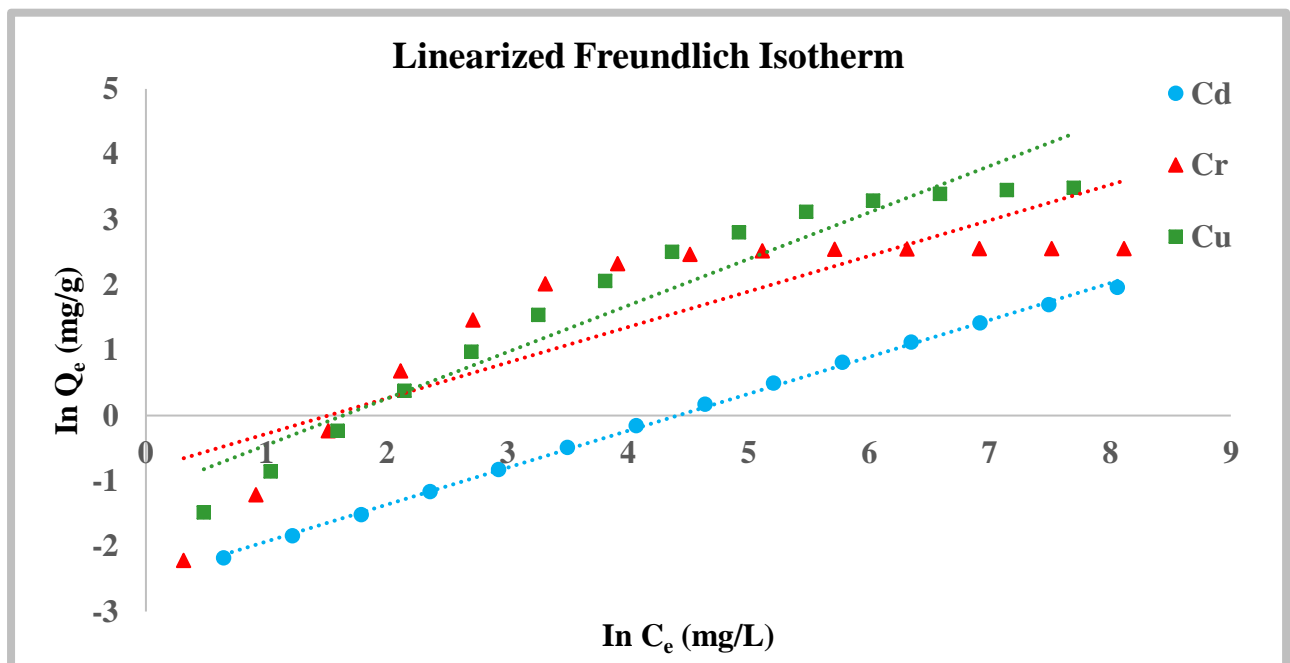


Figure 4. 21: Isotherm plots of single-component Freundlich adsorption of Chromium, Cadmium and Copper at optimum conditions

The best correlation for Cu and Cr was obtained through the use of the single component Langmuir model showing higher monolayer adsorption. Langmuir linearization confirmed that Cu had the highest adsorption capacity (Q_m) which was recorded to be 38.41 mg/g in comparison to Cd (1.38 mg/g) and Cr (4.198 mg/g), however, Cd had the highest binding energy denoted to be 0.042 compared to Cr (II) which was found to be 0.021 Cu (II) which registered to be 0.004 in parameter K_L . The values of the Langmuir isothermal maximum adsorption capacity Q_m show that the adsorption of the metal ions studied followed the order $Cu > Cr > Cd$.

For Cd, Cu and Cr on the adsorbent, the values of Freundlich constant K_f ranged from 0.083 to 0.439 (mg/g), following the order: $Cr > Cu > Cd$. This adsorption sequence can be related to the properties of each metal and the way the adsorbent is interacted. Although the value of K_f (adsorption capacity) for Cu (0.312 L/mg) was higher than that of Cd (0.083 L/mg), this element has lower reactivity (n), and n parameter indicates the reactivity by Freundlich of the adsorbent's active sites. Based on the Freundlich model, Cr had the highest K_f found to be 0.439 L/mg and n values (high reactivity) shown to be 1.836 even though it had the lowest correlation of 0.73. The specific uptakes found in this study of Cr, Cd and Cu were comparable with literature values.

4.6.2 Binary Component System

Figures 4.22 and 4.23 shows linearized isothermal Freundlich and Langmuir adsorption of the binary component system. Table 4.3 shows the R^2 values obtained from the Langmuir and Freundlich isotherms. R^2 demonstrates the best correlation for the biosorption of Cr-Cd ions in sugar cane bagasse within the binary component Freundlich model, while the best correlation for Cu-Cd and Cu-Cr was obtained through the use of the binary component Langmuir model.

Table 4. 3: Comparison of the binary-component isotherms from Langmuir and Freundlich adsorption isotherms under optimum conditions

Metal Combinations	Langmuir			Freundlich		
	Q_m (mg/g)	K_L (L/mg)	R^2	K_f (L/mg)	n	R^2
<u>Binary</u>						
<i>Cu-Cd</i>	3.529	0.036	0.864	0.616	1.997	0.70
<i>Cu-Cr</i>	21.459	0.010	0.987	0.459	1.51	0.923
<i>Cr-Cd</i>	1.45	0.127	0.877	0.114	1.883	0.996

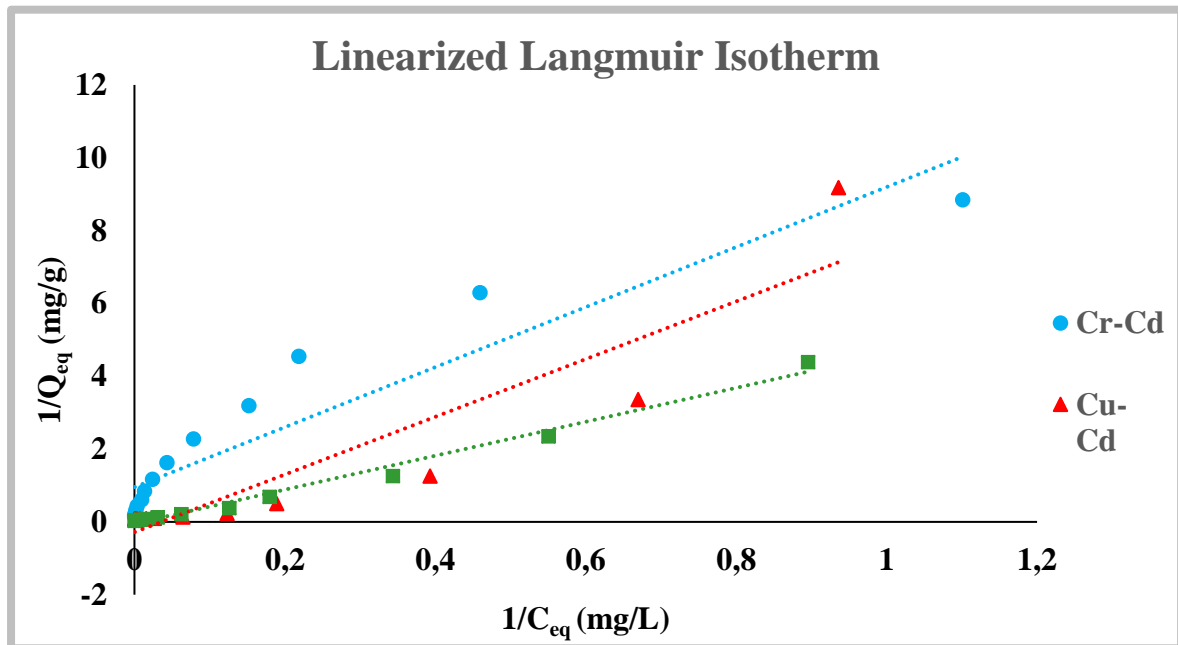


Figure 4. 22: Isotherm plots of binary-component Langmuir adsorption of Copper-Chromium, Copper-Cadmium and Chromium-Cadmium at optimum conditions

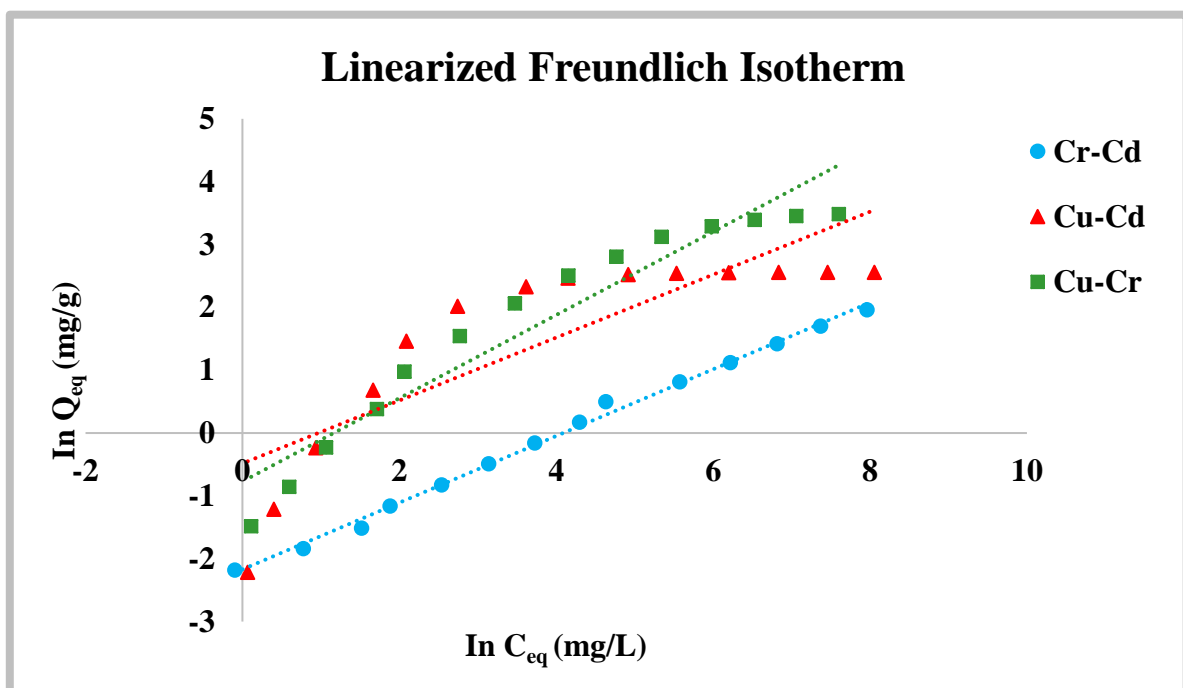


Figure 4. 23: Isotherm plots of binary-component Freundlich adsorption of Copper-Chromium, Copper-Cadmium and Chromium-Cadmium at optimum conditions

The values of the Langmuir isothermal maximum adsorption capacity Q_m , show that the adsorption of the metal ions studied followed the order Cu-Cr > Cu-Cd > Cr-Cd. Generally, the results show that the co-adsorption reduced the adsorption capacity. This reduction can be caused by fewer active sites, i.e. competitively binding sites are divided between metals in the solution (Horsfall and Spiff, 2005).

Langmuir linearization confirmed that Cu-Cr had a highest adsorption capacity (Q_m) noted to be 21.459 mg/g in comparison to Cu-Cd and Cr-Cd which was signified to be 3.529 and 1.45 mg/g, however, Cr-Cd had the highest binding energy which was established to be 0.127 L/mg compared to that of Cu-Cd and Cu-Cr enumerated to be 0.036 and 0.010 L/mg in parameter K_L . The values of the Langmuir isothermal maximum adsorption capacity Q_m show that the adsorption of the metal ions studied followed the order Cu-Cr > Cu-Cd > Cr-Cd. For Cu-Cd, Cu-Cr and Cr-Cd on the adsorbent, the values of Freundlich constant K_f (adsorption capacity) ranged from 0.114 to 0.616 (mg/g), following the order: Cu-Cd > Cu-Cr > Cr-Cd.

These adsorption sequences can be related to the properties of each metal and the way the adsorbent is interacted. Based on the Freundlich model, Cu-Cd had the highest K_f and n values (high reactivity) which were itemized to be 0.616 L/mg and 1.997 even though it had the lowest (0.70) correlation.

4.6.3 Ternary Component System

Figures 4.24 and 4.25 shows linearized isothermal Freundlich and Langmuir adsorption of the binary component system. Table 4.4 shows the R^2 values obtained from the Langmuir and Freundlich isotherms. R^2 demonstrates the best correlation for the biosorption of metal ions solution in sugar cane bagasse within the ternary component Freundlich model. The adsorption capacity of the ternary component system was lesser compared to the binary and the mono component system.

Table 4. 4: Comparison of the ternary-component isotherms from Langmuir and Freundlich adsorption isotherms under optimum conditions

Metal Combinations	Langmuir			Freundlich		
	Q_m (mg/g)	K_L (L/mg)	R^2	K_f (L/mg)	N	R^2
<u>Ternary</u>						
<i>Cu-Cr-Cd</i>	1.237	0.104	0.939	0.125	1.887	0.993

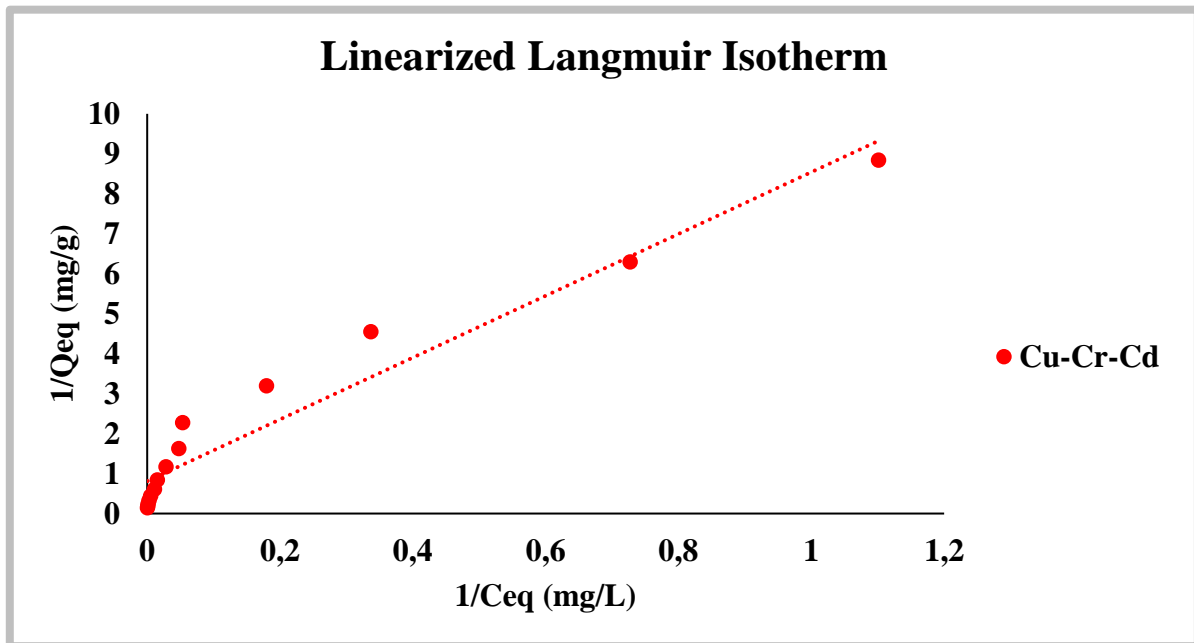


Figure 4. 24: Isotherm plots of ternary-component Langmuir adsorption of Copper-Cadmium-Chromium at optimum conditions

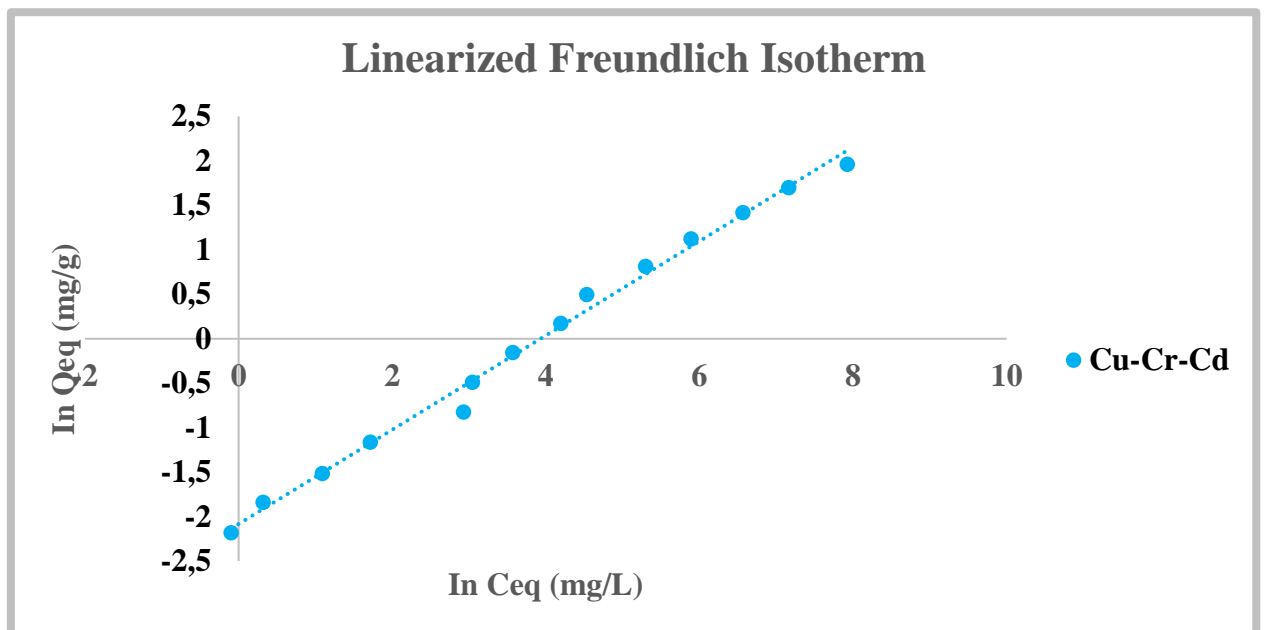


Figure 4. 25: Isotherm plots of ternary-component Freundlich adsorption of Copper-Cadmium-Chromium at optimum condition

4.6.4 Summary

The results show that, due to the existence of other metallic ions in the system, the adsorption capacity was reduced from single to binary and from binary to ternary system. The highest Langmuir capacity for single component systems was found to be 38.41 mg/g. For the binary system, adsorption ranged between 1.45 and 21.459 mg / g and for the tertiary system it was 1.237 mg / g. In order of maximum adsorption capacity, it was found to be single component > binary component > ternary component.

These phenomena were attributed to the dependence of the co-metal ion in each component system. It was also shown that co-cations competed for adsorption sites in the system (Horsfall and Spiff, 2005). The competition between different metal ions for available binding sites on the adsorbents may lead to relatively less adsorption capacity in the binary component. The adsorption capacity reduction in the presence of co-ions could have been shown to be due to progressive ion interference due to overlapping at higher-concentration sorption sites. The adsorption preference of the metals adsorbent in a multi-metal system is affected by physicochemical properties, such as pH, temperature, adsorbent surface properties, and metal characteristics such as electron-configuration, electronegativity and ionic radius(Jain et al., 2016)

CHAPTER FIVE: CONCLUSION AND RECOMMENDATIONS

This chapter summarizes the significant findings from the research and gives a recommendation for further research and decision-making. The adsorbent was characterized using FTIR, XRD and SEM methods. The optimization of the operating parameters was done by OFAT and Regression data-driven approach on the batch using synthetic wastewater and locally sourced sugarcane bagasse as the adsorbent.

The main aim of the study was to evaluate the performance of sugarcane bagasse in the removal of more than one heavy metal from wastewater. The specific objectives were to 1) Preparation and characterization of the adsorbent, 2) determine the optimum process parameters, 3) determine the process adsorption isotherms and 4) evaluate the adsorption capacity and equilibrium isotherms in the removal of heavy metal ions in wastewater.

5.1 Conclusion

A number of heavy metal technologies have been developed to date; however, some are reported to suffer from a number of drawbacks that includes high operational costs, generation of secondary waste, user unfriendliness and efficiency challenges. Having perused all the existing and proposed technologies, adsorption technology emerged as the most suitable heavy metal treatment technology in this case owing to its simplicity, economically viable and cost effectiveness amongst other factors.

In this study sugarcane bagasse was utilized as an adsorbent. The adsorption media was characterized using FTIR, XRD and SEM among other techniques to help establish the adsorbent structure, porosity, and functional groups responsible for the adsorption of heavy metals. From the FTIR results, it was found sugarcane bagasse contained hydroxyl, carbonyl and aromatic rings which are said to be responsible for the adsorption.

These include C-O stretching of cellulose, hemicellulose and lignin, C-O aromatic rings and glycosidic bonds in cellulose. The XRD results indicated that sugarcane bagasse is mainly amorphous in nature as it contained broad peaks or humps and lower intensity for particle size class of 75-150 μm , 350-450 μm and 500-600 μm . Particle size class of <75 μm showed a mixture of crystallinity and amorphous contained in it. SEM results revealed that the adsorbent with a particle size of 350-450 μm had more pores compared to other particle size class.

The following findings were drawn from the study, based on the observation from the experimental results.

- Sugarcane bagasse is an efficient adsorbent of chromium, copper, and cadmium heavy metal ions removal in wastewater. The results showed that the initial concentration, adsorbent dose, pH, contact time, particle size and temperature had a great effect on heavy metal ions removal efficiency. The optimum adsorption conditions were found to be an initial metal concentration of 50 mg/L, pH of 7, contact time of 180 mins, adsorbent dosage of 20g and particle size of 340-450 μm .
- In the single-component system, the maximum adsorption capacities of Cu, Cr and Cd were of 38.41 mg / g, 4.198 mg / g and 1.38 mg / g respectively at optimum conditions. This indicates that the capacity for metal adsorption was in the order Cu > Cr > Cd. However, in the binary-component system, there was a significant decrease in the maximum adsorption capacities of Cu-Cr, Cu-Cd and Cr-Cd which were found to be of 21.459 mg / g, 3.529 mg / g and 1.05 mg / g respectively. This indicates that the capacity for metal adsorption was in the order Cu-Cr > Cu-Cd > Cr-Cd. The ternary-component system had the lowest recorded adsorption capacity of 1.237 mg/g. Therefore, the presence of other heavy metal ions in binary and ternary solutions did interfere with the adsorption process.

- The best correlation of experimental data for the single, binary, and ternary component systems were given by both Langmuir and Freundlich isotherms. In the single component system, Cu and Cr ions adsorption was best described by the Langmuir model whereas for Cd ions it was best described by the Freundlich model. As for the binary component system, adsorption of Cu-Cd and Cu-Cr metal combinations were best described by the Langmuir and Cr-Cd metal ion combination was best described by Freundlich model. The ternary component system was best described by the Freundlich model.

Summary of the main conclusions of this study or review.

- ▶ Optimum adsorption conditions: initial concentration of 50 ppm, pH of 7, contact time of 180 min, adsorbent dosage of 20 g/L and particle size of 340-350 μm
- ▶ The most sensitive parameter for copper removal is adsorbent dose which gave a maximum of 67% in a single metal system, 78% in a binary metal system and 59% in the ternary metal system at an optimum adsorbent dosage of 20g/L.
- ▶ The most sensitive parameter for chromium removal is pH which gave a maximum of 56% in a single metal system, 44% in a binary metal system and 50% in the ternary metal system at an optimum adsorbent dosage of 20g/L.
- ▶ Best parameter for Cadmium is contact time: maximum adsorption of 58,8% single but deviated on binary and ternary system.
- ▶ In single metal system, capacity for metal adsorption was in the order $\text{Cu} > \text{Cr} > \text{Cd}$.
- ▶ In binary metal system, capacity for metal adsorption was in the order $\text{Cu-Cr} > \text{Cu-Cd} > \text{Cr-Cd}$.

- ▶ Ternary metal system had the lowest recorded adsorption capacity of 1,237 mg/g.
- ▶ In single system, adsorption of Cu and Cr ions was best described by Langmuir isotherm whereas Cd ions was best described by Freundlich model
- ▶ In binary system, adsorption of Cu-Cd and Cu-Cr metal combinations were best described by Langmuir isotherm and Cr-Cd metal ion combination was best described by Freundlich isotherm.
- ▶ Ternary system was best described by Freundlich isotherm.
- ▶ Competitive adsorption by other metals affect the performance of sugarcane bagasse in metal removal, hence the focus of this study was on consideration of metal removal competition when applied to real water treatment.

The present study concludes that employing sugarcane bagasse as an adsorbent for the removal of heavy metal ions present in wastewater is economically viable.

5.2 Summary of the results obtained for heavy metal efficiencies at optimum adsorption conditions for all system.

Table 5.1: Shows the removal efficiencies of heavy metals at optimum operating conditions

Parameters	Heavy metals	Optimum Conditions	Metal removal Efficiency (%)		
			single	binary	Ternary
pH	Cu	7	58.8	58	54
	Cr		56	44	50
	Cd		45	37	35
Contact Time	Cu	180 min	56.3	38.6	45
	Cr		54	40	45
	Cd		58.8	35	32
Initial metal concentration	Cu	50 mg/L	60	57	45
	Cr		55	52	34
	Cd		51	46	30
Adsorbent dosage	Cu	20g/L	75	78	59
	Cr		72	63	52
	Cd		59	62	43
Particle size	Cu	350-450 μm	46	48	46
	Cr		42	53	46
	Cd		38	35	39

5.3 Recommendations

- The stability of the adsorbent over a long period should be considered.
- Sugarcane bagasse needs to be treated to change the structure of the bagasse for better removal efficiency.
- Characterization of sugarcane bagasse needs to be conducted after the adsorption of heavy metals to see if there was any change in the surface structure of sugarcane bagasse confirming that adsorption occurred.
- Further study needs to be conducted on the adsorption kinetic models to describe the adsorption rate.
- Variation of heavy metal ratios for binary and ternary systems needs to be further studied.

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APPENDIX

A. Calculations of the Langmuir and Freundlich Constants

SINGLE METAL SYSTEM

Langmuir Constants Q_m and K_L

Cadmium

$$\frac{1}{Q_m} = 0.7246 \quad : \text{Therefore } Q_m = \mathbf{1.38}$$

$$\frac{1}{K_L \times Q_m} = 17.08$$

$$K_L = \frac{0.725}{17.08} = 0.042 \quad : \text{Therefore } K_L = \mathbf{0.042}$$

Chromium

$$\frac{1}{Q_m} = 0.238 \quad : \text{Therefore } Q_m = \mathbf{4.20}$$

$$\frac{1}{K_L \times Q_m} = 11.52$$

$$K_L = \frac{0.238}{11.52} = 0.021 \quad : \text{Therefore } K_L = \mathbf{0.021}$$

Copper

$$\frac{1}{Q_m} = 0.026 \quad : \text{Therefore } Q_m = \mathbf{38.911}$$

$$\frac{1}{K_l \times Q_m} = 6.941$$

$$K_l = \frac{0.026}{6.913} = 0.004 \quad : \text{Therefore } K_l = \mathbf{0.004}$$

Freundlich Constants K_f and n Cadmium

$$\ln K_f = -2.493 \quad : \text{Therefore } K_f = \mathbf{0.083}$$

$$\frac{1}{n} = 0.565 \quad : \text{Therefore } K_f = \mathbf{1.77}$$

Chromium

$$\ln K_f = -0.824 \quad : \text{Therefore } K_f = \mathbf{0.439}$$

$$\frac{1}{n} = 0.545 \quad : \text{Therefore } K_f = \mathbf{1.836}$$

Copper

$$\ln K_f = -1.164 \quad : \text{Therefore } K_f = \mathbf{0.312}$$

$$\frac{1}{n} = 0.712 \quad : \text{Therefore } K_f = \mathbf{1.404}$$

BINARY METAL SYSTEM*Langmuir Constants Q_m and K_L* Cadmium and Chromium

$$\frac{1}{Q_m} = 0.952 \quad : \text{Therefore } \mathbf{Q_m = 1.050}$$

$$\frac{1}{K_L \times Q_m} = 8.243$$

$$K_L = \frac{1.05}{8.243} = 0.127 \quad : \text{Therefore } \mathbf{K_L = 0.127}$$

Copper and Cadmium

$$\frac{1}{Q_m} = 0.283 \quad : \text{Therefore } \mathbf{Q_m = 3.569}$$

$$\frac{1}{K_L \times Q_m} = 7.922$$

$$K_L = \frac{0.238}{7.922} = 0.436 \quad : \text{Therefore } \mathbf{K_L = 0.436}$$

Copper and chromium

$$\frac{1}{Q_m} = 0.047 \quad : \text{Therefore } Q_m = 21.459$$

$$\frac{1}{K_l \times Q_m} = 4.659$$

$$K_l = \frac{0.047}{4.659} = 0.010 \quad : \text{Therefore } K_l = 0.010$$

Freundlich Constants K_f and n Cadmium and Chromium

$$\ln K_f = -2.170 \quad : \text{Therefore } K_f = 0.114$$

$$\frac{1}{n} = 0.531 \quad : \text{Therefore } K_f = 1.883$$

Copper and Cadmium

$$\ln K_f = -0.438 \quad : \text{Therefore } K_f = 0.616$$

$$\frac{1}{n} = 0.500 \quad : \text{Therefore } K_f = 1.997$$

Copper and Chromium

$$\ln K_f = -0.771 \quad : \text{Therefore } K_f = 0.459$$

$$\frac{1}{n} = 0.662 \quad : \text{Therefore } K_f = 1.510$$

TERNARY METAL SYSTEM***Langmuir Constants Q_m and K_L*** **Copper, Chromium and Cadmium**

$$\frac{1}{Q_m} = 0.808 \quad : \text{Therefore } \mathbf{Q_m = 1.237}$$

$$\frac{1}{K_L \times Q_m} = 7.733$$

$$K_L = \frac{0.808}{7.733} = 0.104 \quad : \text{Therefore } \mathbf{K_L = 0.104}$$

Freundlich Constants K_f and n **Copper, Chromium and Cadmium**

$$\ln K_f = -2.083 \quad : \text{Therefore } K_f = 0.125$$

$$\frac{1}{n} = 0.53 \quad : \text{Therefore } K_f = 1.887$$

B. Experimental Data of the operating parameters

Single Metal System

Table B. 1: Effect of contact time in single metal system

Contact Time (mins)	%Removal		
	Cr	Cu	Cd
30	34	39	45.6
60	39	43	50.3
90	42	48	53.4
120	46	51	54.1
150	52	53	56.1
180	54	56.3	58.8
210	54.9	57.5	58.4
240	54.5	57.8	58.4

Table B. 2: Effect of pH in single metal system

PH	% Removal		
	Cr	Cu	Cd
3	16	19.8	10
5	50	54.6	41
7	56	58.8	45
9	53	55.3	38

Table B. 3: Effect of initial metal concentration in single metal system

Initial metal Concentration (mg/L)	% Removal		
	Cr	Cu	Cd
50	55	60	51
250	51	54	42
500	24	26	23

Table B. 4: Effect of adsorbent dosage in single metal system

Dosage (g)	% Removal		
	Cr	Cu	Cd
5	40	44	39
10	51	57	43
15	59	66	51
20	72	75	59

Table B. 5: Effect of particle size in single metal system

Particle Size (μm)	% Removal		
	Cr	Cu	Cd
< 75	25	28	24
75-150	38	41	29
350-450	42	46	38
500-600	32	36	31

Binary metal System**Table B. 6:** Effect of contact time in binary metal solution

Contact Time (mins)	% Removal for Cu		% Removal for Cr		% Removal for Cd	
	Cu-Cr	Cu-Cd	Cr-Cd	Cr-Cu	Cd-Cu	Cd-Cr
30	28	22	20	18	15	8
60	32	24	22	28	21	15
90	33	29	31	35	25	19
120	36	31	33	37	29	29
150	38	31,4	35	39	33	28,9
180	38,6	32	37	40	35	29
210	39	31,6	36	40	34	29,5

Table B. 7: Effect of pH in binary metal solution

pH	% Removal for Cu		% Removal for Cr		% Removal for Cd	
	Cu-Cr	Cu-Cd	Cr-Cd	Cr-Cu	Cd-Cu	Cd-Cr
3	21	23	8	12	10	5
5	55	47	28	35	19	18
7	58	54	33	44	37	25
9	52	50	38	40	41	28

Table B. 8: Effect of initial metal concentration in binary metal system

Initial metal conc (mg/L)	% Removal for Cu		% Removal for Cr		% Removal for Cd	
	Cu-Cr	Cu-Cd	Cr-Cd	Cr-Cu	Cd-Cu	Cd-Cr
50	57	48	52	35	46	35
250	48	35	46	29	35	29
500	26	15	18	14	10	14

Table B. 9: Effect of adsorbent dosage in binary metal system

Dosage (g/L)	% Removal for Cu		% Removal for Cr		% Removal for Cd	
	Cu-Cr	Cu-Cd	Cr-Cd	Cr-Cu	Cd-Cu	Cd-Cr
5	47	54	38	46	34	26
10	56	50	41	45	42	32
15	64	55	48	53	56	39
20	78	70	60	63	62	55

Table B. 10: Effect of particle size in binary metal system

Particle Size (μm)	% removal for Cu		% removal for Cr		% removal for Cd	
	Cu-Cr	Cu-Cd	Cr-Cd	Cr-Cu	Cd-Cu	Cd-Cr
<75	30	27	15	28	26	18
75-150	46	35	26	44	28	25
350-450	48	39	34	53	35	28
500-600	35	29	14	38	25	24

Ternary metal System**Table B. 11:** Effect of contact time in ternary metal solution

Contact time (mins)	% Removal for Cu	% Removal for Cr	% Removal for Cd
	Cu-Cd-Cr	Cu-Cd-Cr	Cu-Cd-Cr
30	30	26	9
60	37	29	15
90	39	38	19
120	43	39	25
150	47	41	31
180	45	45	32
210	44	43	31

Table B. 12: Effect of pH in ternary metal solution

pH	% Removal for Cu	% Removal for Cr	% Removal for Cd
	Cu-Cd-Cr	Cu-Cd-Cr	Cu-Cd-Cr
3	12	16	8
5	50	42	28
7	54	50	35
9	48	45	20

Table B. 13: Effect of initial metal concentration in ternary metal system

Initial metal conc (mg/L)	% Removal for Cu	% Removal for Cr	% Removal for Cd
	Cu-Cd-Cr	Cu-Cd-Cr	Cu-Cd-Cr
50	45	34	30
250	38	30	24
500	25	14	6

Table B. 14: Effect of adsorbent dosage in ternary metal system

Adsorbent dosage (g/L)	% Removal for Cu	% Removal for Cr	% Removal for Cd
	Cu-Cd-Cr	Cu-Cd-Cr	Cu-Cd-Cr
5	40	38	24
10	48	36	31
15	51	45	40
20	59	52	43

Table B. 15: Effect of particle size in ternary metal system

Particle Size (μm)	% Removal for Cu	% Removal for Cr	% Removal for Cd
	Cu-Cd-Cr	Cu-Cd-Cr	Cu-Cd-Cr
<75	29	20	14
75-150	45	45	26
350-450	46	46	39
500-600	28	10	23

C. Experimental Data for C_e and Q_e to Plot the Isotherms

Single Metal System

Cd					
Ce	Qe	1/Ce	1/Qe	lnCe	lnQe
1.908	0.1131	0.524109	8.841733	0.646056	-2.17948
3.375	0.1589	0.296296	6.293266	1.216395	-1.83948
5.972	0.22	0.167448	4.545455	1.787082	-1.51413
10.5669	0.31334	0.094635	3.191421	2.357726	-1.16047
18.68	0.439	0.053533	2.277904	2.927453	-0.82326
33.044	0.61413	0.030263	1.62832	3.49784	-0.48755
58.4523	0.8567	0.017108	1.16727	4.068211	-0.15467
103.396	1.19	0.009672	0.840336	4.638566	0.173953
182.8979	1.6463	0.005468	0.607423	5.208928	0.49853
323.5281	2.26095	0.003091	0.442292	5.779286	0.815785
572.2889	3.07677	0.001747	0.325016	6.349644	1.12388
1012.321	4.1368	0.000988	0.241733	6.920001	1.419923
1790.695	5.477	0.000558	0.182582	7.490359	1.700558
3167.562	7.11	0.000316	0.140647	8.060717	1.961502

Cr

Ce	Qe	1/Ce	1/Qe	lnCe	lnQe
1.368	0.1089	0.730994	9.182736	0.31335	-2.21733
2.493	0.2978	0.401123	3.357958	0.913487	-1.21133
4.544	0.7937	0.22007	1.259922	1.513808	-0.23105
8.2821	1.985	0.120742	0.503778	2.114097	0.685619
15.0942	4.326	0.066251	0.23116	2.714311	1.464643
27.509	7.524	0.036352	0.132908	3.314513	2.018098
50.1355	10.2584	0.019946	0.097481	3.914729	2.328097
91.372	11.804	0.010944	0.084717	4.514939	2.468438
166.525	12.4823	0.006005	0.080113	5.115145	2.524312
303.4926	12.74627	0.003295	0.078454	5.715357	2.545239
553.1154	12.84416	0.001808	0.077856	6.315567	2.552889
1008.052	12.87982	0.000992	0.077641	6.915775	2.555662
1837.176	12.89277	0.000544	0.077563	7.515985	2.556667
3348.253	12.89757	0.000299	0.077534	8.116194	2.557039

Cu

Ce	Qe	1/Ce	1/Qe	lnCe	lnQe
1.61647	0.22772	0.618632	4.391358	0.480245	-1.47964
2.81654	0.42632	0.355046	2.345656	1.035509	-0.85257
4.90754	0.79408	0.203768	1.259319	1.590773	-0.23057
8.5509	1.46523	0.116947	0.682487	2.146037	0.382012
14.89909	2.6582	0.067118	0.376194	2.7013	0.977649
25.96017	4.68273	0.038521	0.213551	3.256563	1.543881
45.233	7.86232	0.022108	0.127189	3.811827	2.062082
78.81397	12.29543	0.012688	0.081331	4.36709	2.509228
137.3255	16.563	0.007282	0.060376	4.922354	2.807171
239.276	22.701	0.004179	0.044051	5.477618	3.122409
416.914	26.89255	0.002399	0.037185	6.03288	3.291849
726.431	29.81574	0.001377	0.033539	6.588144	3.395036
1265.734	31.64208	0.00079	0.031603	7.143407	3.454488
2205.415	32.70586	0.000453	0.030576	7.698671	3.487554
