# OPTMISATION AND APPLICATION OF PLANT-BASED WASTE MATERIALS FOR THE REMEDIATION OF SELECTED TRACE METALS (Cd, Pb and Mn) AND OXYHALIDES ($BrO_3^-$, $ClO_3^-$ and $IO_3^-$) IN AQUEOUS SYSTEM

**By**

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## DECLARATION

I Mohammed Abdulkadir Ibrahim sincerely and solemnly declare that the research conducted in fulfillment of the requirement of the degree of Master of Science entitled “Optimization and application of plant-based waste materials for the remediation of selected trace metals (Cd, Pb and Mn) and oxyhalides ($BrO_3^-$, $ClO_3^-$ and $IO_3^-$) in aqueous system” is my own work and that all sources that I have used or quoted have been indicated and acknowledged by means of references.

Signature and date: ____________________________________________

Student

Signature and date: ____________________________________________

Supervisor

## DEDICATION

This research dissertation is dedicated to the mercy of Almighty Allah in my life. My late Dad, Alhaji Ibrahim Mazankwarai Mohammed and my late grandmother Alhaja Al Janat Mohammed (May Almighty Allah reward them with Al- Janat Firdous) amen. My loving mum, Mrs. Ayishat Mohammed. My lovely sweetheart, Mrs. R.O Mohammed (my merciful angel), in you my prayer to God was answered and you are my jewel of unquantifiable value. My beautiful daughters (queens) Al Janat Firdous and Ayishat Mohammed and my little king, Sheik Ibrahim Mohammed. Daddy loves you all, and in you guys I see my prayers and dreams come true. Mr. O.C. Cocodia and family of the Ministry of Foreign Affairs, Nigeria for all the advice and encouragement.

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## LIST OF ACRONYMS

| | |
|---|---|
| ASCE | American Society of Civil Engineers. |
| BOD | Biological Oxygen Demand |
| CCM E | Canadian Council of Ministers of the Environment. |
| CDC | Centre for Disease Control and Prevention |
| EPA | Environmental Protection Agency |
| GEMS | Global Environmental Monitoring System |
| IAF | Innovative and Alternative Fund. |
| LIE | Liquid ion exchange |
| MHRP | Manganese Health Research Program |
| MSM | Metrohm suppressor module |
| ATSDR | Agency for Toxic Substances and Disease Registry Division of Toxicology and Environmental Medicine |

## ABSTRACT

The research work is directed towards the investigation, optimization and application of some plant-based waste materials for the removal of some toxic trace metals (Cd, Pb and Mn) as well as selected oxyhalides ($ClO_3^-$,$IO_3^-$ and $BrO_3^-$) in aqueous system. Waste materials from three plants; Athrixia philicoide, an indigenous bush tea; the outer covering peels of butternut Squash (*Cucurbita Moschata*) and pineapple (*Ananas comosus*) were evaluated for their sorption efficiency of the selected metals. Batch and continuous experimental processes as well as conditions that might influence the sorption of the metals were investigated. These conditions include effects of pH, sorption time, amount of adsorbent, volume of the aqueous medium, amount of metals etc. Qualitative and quantitative analysis of metal ions in solution was carried out using the ion chromatograph (IC) while the functional group identification present in waste materials was established using the Fourier Transform infra-red spectroscopy (FTIR). Quantitative biosorption equilibrium of 96.99 % was reached within 6h at pH 6 and 100 ppm concentration of Pb metal with Athrixia philicoide under 30 min contact time. Cd and Mn adsorption by the same adsorbent under similar condition were less than 50 % for individual metal evaluation experiment. However, > 99 % adsorption was achieved with Cd in a mixture of the three (3) evaluated metals. Highest adsorption of 93 % of Pb was achieved with the Butternut Squash peel (*Cucurbita moschata*) at the optimal sorption pH of 6 followed by quantitative sorption of 99.2 % of Mn while Cd recorded a sorption level of 45 % all at 6 pH. The sorption efficiency of Pb, Cd and Mn using pineapple peels (Ananas comosus) also at the optimal sorption conditions of (pH 6, 30 min contact time and 100 ppm metal concentration) ranged from 98.7 %, 100 % and 99.90 % respectively. Applicability of the sorption process was tested on wastewater. Results revealed that > 99.93 %; 84.5 % and 64.3 % sorption efficiency was obtained for Mn, Cd and Pb respectively at pH 7 using Ananas Comosus adsorbent. For Athrixia philicoide, sorption efficiency from spiked wastewater ranged from 99.98 % for Cd; 99.96 % for Mn and 82.5 % adsorption for Pb at pH 7. For Juglans Cinerea, wastewater sorption efficiency varied between 78.76 %, 94.50 % and 96.50 % for Cd, Mn and Pb respectively at pH6. Results from the optimized method revealed the applicability of the method to environmental water samples. Possible large scale and industrial/commercial application of developed materials and methods would be explored.

**Keywords:** Waste materials, remediation, trace metals, optimization, oxyhalides, aqueous system

# CHAPTER 1: INTRODUCTION

## 1.1 Background information

Technological and industrial advancement over the past centuries has led to a record level of pollution that now poses a serious threat to man and the environment. The generation and disposal of waste materials from several activities such as mining, chemical production, pharmaceuticals, agricultural practices, petrochemicals etc have therefore continued to challenge the intellectual capacity of man. This is important due to the degradation and decadence of the environment that the improper and inappropriate disposal of these wastes would cause. Some wastes are released into aquatic bodies which ultimately find their way into other ecosystems and eventually man. For example, the improper or inadequate treatment of sewage effluent that is released into aquatic media will negatively impact on users and aquatic organisms.

South Africa is regarded as a semi arid country and the use and conservation of water is very paramount to the government. This is the main reason why research work into the country's water quality and aquatic health are supported by the South African Government. Hence, environmental scientists and other experts on water health studies are constantly looking for effective, simple, applicable and cheap methods for the removal of toxic elemental and organic contaminants in environmental waters. Heavy metals are common metals with a specific gravity of more than 5g/dm$^2$, (Spore tech mold investigations, LLC). The presence of toxic metals in the environment continues to generate lots of concern to environmental scientists, government agencies and health practitioners. This is due to the health implications of their presence since they are non-essential metals that are not required for any function either by plants or animals. The discharge of toxic heavy metals into the environment is a serious pollution problem affecting water quality. Major sources of water pollution with heavy metals are the electroplating plants, mining, metal finishing, welding, and alloys manufacturing (Dabrowski et al., 2004). The Growing concern for the presence and contamination of heavy metals in our water supplies has steadily increased over the last few years. Elements such as mercury and cadmium exhibit human toxicity at extremely low concentrations. Silver, chromium, lead, copper, and zinc also exhibit toxic properties to humans although the concentrations are in orders of magnitude higher than that required for cadmium or mercury toxicity (Murugesan et. al., 2006).

The removal and remediation of toxic metals from aqueous media is imperative especially in countries where portable water is in short supply like South Africa. The presence of toxic metals such as Cd, Pb and Mn in the environment is of great concern due to their health implications. Over the years, anthropogenic activities have greatly increased the level of these toxic metals, especially in aqueous systems therefore, efficient and cost effective methods are being sought for their removal. Conventional physical and chemical methods of metal removal from aqueous streams that have been applied include chemical precipitation, ion exchange, adsorption and electrochemical techniques, (Reed and Nonavinakere, 1992; Atwood et al., 2002).

These methods, which are plagued with incomplete removal, involve the use of large volume of chemicals, high cost especially when contaminant concentrations are within the ranges of 10-100mgl$^{-1}$. They are laborious and generate other wastes that require further disposal (Rostami and Joodaki, 2002). Advances towards effective treatment methods for the removal of heavy metals in aqueous media involve the use of micro-organisms (Viraraghavan and Yan, 2003; Ma et. al., 2004) have been reported. Attention was also focused on the application of fungal species for metal removal from aqueous media using either the batch or continuous modes (Awofolu et al., 2006).

Lately, the use of waste materials from plant origin and other agro wastes as sorbents of toxic metals from aqueous medium is gaining attention due to their ability to adsorb toxic metals from aqueous systems. This is also because agro-wastes are readily available, cheap, biodegradable, sludge free and involve small initial cost and land investment (Uppendra 2006; Horsfall, et. al., 2006). Researches into their applications are becoming popular instead of physical and chemical methods, which are plagued, with several problems and disadvantages as mentioned above. Several plant based materials have been explored and reported in this regard. Cassava tuber back wastes (CTBW) was investigated (Horsfall et. al., 2006). *Alfalfa, Medicago saliva* (Gardea-Torresdey, et al., 1996) and *Moringa oleifera* seeds (Srivastava, et. al., 2007).

The use of wastes from indigenous plants in the country for the remediation of toxic metals from aqueous systems, including municipal and industrial effluent has however not been explored. This research work would therefore investigate the potential application and utilization of plant-based products like waste tea, pineapple peel and butternut squash for the remediation/sorption of toxic trace metals from aqueous systems. Large amounts of used waste tea are being discarded as Tonnes of these are produced annually which are subsequently disposed in landfills and waste disposal sites. In addition, recent advances in researches, application and the use of alternative fuel such as ethanol have generated huge interest all over the world. Alternative fuel is environmental friendly and reduces reliance on fossil fuel based energy. However, the use of the primary raw materials required for the production of these fuels such as maize, sugar cane, etc, usually result in the generation of large volume of wastes in form of the sugar cane fibre, maize tassels etc. The advantages that accrue with the introduction of new technology sometimes result in the production of other wastes that might themselves constitute environmental menace. The aim of this research work is to evaluate the potential re-use of some waste materials; waste Bush tea (*Athrixia philicoide*), pineapple (*Ananas Comosus*) and butternut Squash (*Cucurbita Moschata)* peels for the removal of toxic metals and oxyhalide compounds from aqueous systems. The toxicity and health effects of the selected toxic metals under investigation are discussed below.

## 1.2 Cadmium and its' health effects

Cadmium is a lustrous, silver-white, ductile and very malleable metal and its surface has a bluish tinge. This metal is soft so that it cut could be with a knife and it tarnishes in the air. Cadmium is soluble in acids but not in alkalis. It is similar in many respects to Zinc but forms more complex compounds. It is basically used in Ni-Cd batteries; most of the remaining one–fourth is used mainly for pigments, coatings, and plating, and as stabilizers for plastics. Cadmium has been used particularly to electroplate steel where a film of cadmium only 0.05 mm thick will provide complete protection against the sea (Khan, 2008). Cadmium has the ability to absorb neutrons, so it is as a barrier to nuclear fission. Cadmium can mainly be found in the earth's crust occurring in combination with zinc. It is an inevitable by-product of zinc, Lead and copper extraction in industries. Naturally a very small amount of cadmium is released into the environment; about 25,000 tons a year and almost half of this quantity is released into rivers through weathering of rocks; some of it is released into air through forest fires and volcanoes. The rest is released through human activities, such as manufacturing (Lenntech, 2008). The diseases associated with high dose of Cadmium in the body include diarrhea, stomach pains and severe vomiting, bone fracture, reproductive failure and possibly infertility and damage to the central nervous system (Lenntech, 2008).

Drinking water that contains greater than 0.05 mg/L of cadmium is very dangerous and will be carried in the blood to the liver on consumption. There, it bonds to proteins to form complexes that are transported to the kidneys. It accumulates in kidneys where it damages filtering mechanisms. This causes the excretion of essential protein and sugars from the body and further kidney damage. It takes a very long time before accumulated cadmium in kidney is excreted from a human body (Lenntech, 2008). It has also been well established that excess cadmium exposure produces adverse health effects on human beings. For virtually all chemicals, adverse health effects are noted at sufficiently high total exposures. For certain elements such as copper and zinc which are essential to human life, a deficiency as well as an excess can cause adverse health effects.

Cadmium is not regarded as essential to human life. The relevant questions with regard to cadmium exposure are the total exposure levels and the principal factors which determine the levels of cadmium exposure and the adsorption rate of the ingested/inhaled cadmium by the individual, in other words, the pathways by which cadmium enters the food chain, the principal pathway of cadmium exposure for most human beings. Humans normally absorb cadmium into the body either by ingestion or inhalation. Dermal exposure (uptake through the skin) is generally not regarded to be of significance (Lauwerys, 1984). It is widely accepted (WHO, 1992; ATSDR, 1997) that approximately 2 to 6% of the cadmium ingested is actually taken up into the body. Factors influencing cadmium absorption are the form in which cadmium is present in the food, and the iron status of the exposed individual.

In contrast, 30 to 64 % of inhaled cadmium is absorbed by the body, with some variation as a function of chemical form, solubility and particle size of the material inhaled. Thus, a greater proportion of inhaled cadmium is retained by the body than when cadmium is taken in by ingestion. For the non-occupationally exposed individual, inhalation exposure to cadmium does not usually contribute significantly to overall body burden. The exception to this generalization is the cigarette smoker. One model for human cadmium intake (van Assche, 1998) has estimated that ingestion accounts for 95% of total cadmium intake in a non-smoker. For a smoker, this model estimates that roughly 50% of their cadmium intake arises from cigarettes with the balance due to ingestion and the low levels of cadmium naturally present in ambient air. In the past, occupational exposure was also a significant contributor to total cadmium intake, but with very stringent occupational standards in place today, occupational cadmium intake is much less of a consideration than it was 20 years ago. Thus, the principal determinants of human cadmium exposure today are smoking habits, diet, and, to a certain extent, occupational exposure (Lenntech, 2008).

## 1.3 Lead and its' health effects

Lead is the most abundant toxic heavy metal. World production of lead exceeds 3.5 million tons per year. It is naturally distributed in small amounts on the surface of the earth. Our body has no biological need for lead. However, lead acts like calcium in the body and is stored mostly in the bones. Lead exposure is still among the most important environmental health problems for young children in the U.S. and worldwide. Lead can affect many body systems in both Children and adults (Wisconsin, 2007). The health effects of lead depend upon the amount of exposure, which is determined by three factors: intensity, duration, and timing. Short-term exposure to high levels of lead can cause vomiting, diarrhea, convulsions, coma or even death (Macche, 2003) severe cases of lead poisoning are rare in Canada. However, even small amounts of lead can be harmful, especially to infants, young children and pregnant women. Symptoms of long-term exposure to lower lead levels may be less noticeable but are still serious. Anemia is common and damage to the nervous system may cause impaired mental function. Other symptoms are appetite loss, abdominal pain, constipation, fatigue, sleeplessness, irritability and headache. Continued excessive exposure, as in an industrial setting, can affect the kidneys.

Lead poisoning is the most prevalent environmental disease in the U.S along with mercury toxicity. According to an EPA survey, over 10% of all Americans and over 20% of all black children under two years carry unsafe levels of lead in their bodies which is > 10 mcg/dl (Chou, 2003). In an urban east coast area, almost half of children tested in 1998 had lead levels exceeding the federal blood levels guideline (Bogden, et. al., 1999). Lead (Pb) is a leading cause of birth defects, cardiovascular disease, hypertension, neurological disease, kidney disease, learning disability, retardation, tooth cavities, etc. The presence of about 5 µg/L of lead in the blood corresponds to an increase in depression of 80% (Moss, 1999). Lead also has been shown to depress the immune system and increase cancer rates. Federal studies indicate that exposure to lead in the environment reduces the IQ of hundreds of thousands of U.S. children each year and causes pregnancy complications to over 500,000 U.S. women each year. Children aged 7 to 11 with high levels of lead in their bones were found to exhibit much higher levels of attention problems, aggressive/violent behavior, and delinquency than those with lower levels. Drinking water is a major source of lead in humans according to EPA. Other major sources are lead in old paint, lead solder in cans, and lead in soils from previous gasoline exhaust, lead emissions from incinerators, and lead in waste and solid oil incineration, iron and steel production, in lead smelting, battery and lead alkyl manufacturing (ASSR, 2007).

Everyone is exposed to trace amounts of lead through air, soil, household dust, food, drinking water and various consumer products. The amount of lead in the environment increased during the industrial revolution, and again significantly in the 1920s with the introduction of leaded gasoline. However since the early 1970s, lead exposure in Canada has decreased substantially, mainly because leaded gasoline and lead paint were phased out and the use of lead solder in food cans was virtually eliminated. Within the body, lead is found in circulating red blood cells, soft tissues (liver and kidney), and bone (where lead is accumulated). Blood lead concentrations are the most reliable indicator of recent lead exposure known health effects of lead poisoning include:

1. Anemia
2. Brain and nervous system damage, which can include permanent mental & motor retardation & in extreme cases, death.
3. Severe kidney injury or failure
4. Injury to the gastro intestinal system and the heart.
5. Damage to the reproductive system, (Wisconsin, 2007).

Lead exposure is most serious for young children because they absorb lead more easily than adults and are more susceptible to its harmful effects. Even low level exposure may harm the intellectual development, behavior, size and hearing of infants. During pregnancy, especially in the last trimester, lead can cross the placenta and affect the unborn child. Female workers exposed to high levels of lead have more miscarriages and stillbirths. In most of Canada, the amount of lead in natural water supplies is very low (Health Canada, 2008). However, lead can enter the water supply from lead solder in plumbing, lead service connections or lead pipes in your home. Homes built before 1950 often have leaded distribution lines and service connections. In newer homes, lead may leach from solder for several years until the pipes form a protective oxide layer.

Lead is more likely to be found in soft or very acidic water and in very old or very new homes. The National Plumbing Code of Canada does not permit the use of lead solder in new drinking water plumbing or repairs to drinking water supplies. Several provinces also limit the amount of lead solder in drinking water supply lines. Lead levels in tap water increase as water stands in pipes. Drinking fountains may have higher levels of lead than water from nearby taps, because the water usually sits for a longer time. They may also have more soldered joints. Workers are monitored for blood lead levels. Lead can enter food, especially acidic food such as fruit juice, from lead-based glazes on glassware and ceramics. Canadian regulations limit lead content in glazes on glassware and ceramics used in preparing, serving, or storing food. However, pottery or glassware from abroad may contain enough lead to be a hazard to your health. Leaded crystal is widely used for serving beverages.

When the crystal comes in contact with beverages, especially acidic beverages such as port, wine, fruit juices and soft drinks, some lead dissolves into the liquid. The amount of lead that dissolves depends on the lead content of the crystal, the type of beverage and the length of time they are in contact with each other (Health Canada, 2008). Pregnant women or children should not drink in crystal glasses. Lead fumes or particles can be released when waste oil, colored newsprint, battery casings or lead-painted wood is burned. Candles that contain lead in their wicks may also release harmful levels of lead when burned. Using lead solder in a hobby, such as in making stained glass, lead shot or lead fishing weights, may expose you or your family to harmful lead vapors (Health Canada, 2008).

Lead is readily absorbed by the body via the primary routes of entry, inhalation and ingestion (Karen, 2003). Studies indicate that 10% to 20% of inhaled lead enters the blood stream. In children, approximately 50% of ingested lead is absorbed as compared to 8% to 10% for adults (Wisconsin, 2007). This is especially significant since much of children's lead exposure is caused by their normal habits of mouthing dirty hands, objects, and materials (Wisconsin, 2007). A growing body of research suggested there may be no safe level of lead ingestion (Wisconsin, 2007). Long-term, low level lead exposure causes learning deficits and behavioral problems in children. At presents, children with blood lead levels over 10 micro grams per deciliter (Goldman and Saunders, 2000) is considered lead-poisoned.

Lead poisoning is the most prevalent environmental disease in the U.S, along with mercury toxicity (Science news, 1986). According to EPA (1978) survey, over 10 % of all Americans & over 20% of all black children under 2years carry unsafe levels of lead in their bodies (over 10 mcg / dc) (science news, 1986). Lead is a leading cause of birth defects, cardiovascular disease, hypertension, neurological disease, kidney disease, learning disability, retardation, tooth cavities etc (Nriagu, 1990).

Drinking water is a major source of lead in humans according to EPA. Other major sources are lead in old paint, lead solder in cans, lead in soils from previous gasoline exhaust, lead emissions from incinerators, and lead in food chains (USEPA, 1998). EPA studies show that hundreds of thousands of school children are being exposed to dangerous levels of lead in drinking from fountains at U.S schools (Washington Post, 1986).

### 1.4 Manganese and its' health effects

Manganese is a pinkish-gray, chemically active element. It is a hard metal and is very brittle. It is hardly melt, but easily oxidized. Manganese is reactive when pure, and as a powder it will burn in oxygen, it reacts with water (it rust like iron) and dissolves in dilute acid (Holding, 2008). Manganese comprises approximately 0.085% to 0.095% of the earth's crust and is a component of many rock types, particularly those of metamorphic and sedimentary origin (CCME, 1987). It is associated with iron ores of sub marginal concentration; the Predominant ores of manganese include pyrolusite ($MnO_2$), manganite $Mn_2O_3{\cdot}H_2O$), hausmannite

($Mn_3O_4$), psilomelane and rhodochrosite ($MnCO_3$) (Moore, 1991). Ferromanganese minerals such as biotite mica and amphiboles contain large amounts of manganese and manganese-rich nodules have been identified on the sea floor in conjunction with cobalt, nickel and copper (Moore, 1991). Important natural sources of manganese include soils, sediments and metamorphic and sedimentary rocks:

The aesthetic objective for manganese in drinking water is $\leq$ 0.05 mg/L i.e. $\leq$50 µg/L (Health Canada, 1987). The presence of manganese in drinking water supplies may be objectionable for a number of reasons. At concentrations above 0.15 mg/L, manganese stains plumbing fixtures and laundry and produces undesirable tastes in beverages. As with iron, the presence of manganese in water may lead to the accumulation of microbial growths in the distribution system. Even at concentrations below 0.05 mg/L, manganese may form coatings on water distribution pipes that may slough off as black precipitates. A deficiency in manganese intake can retard growth, cause seizure activity, lead to poor bone formation, impair fertility, and cause birth defects in humans.

At the other spectrum, excessive exposure to manganese is associated with an irreversible brain disease with prominent psychological and neurological disturbances known as manganism. Individuals with manganism resemble patients with Parkinson's disease; however, these syndromes can be distinguished clinically (Calne et. al., 1994). Unlike Parkinsonism, manganism also produces dystonia; a neurological sign associated with damage to the globus pallidus (Calne et. al., 1994). A comprehensive survey of patients afflicted by Parkinson's disease or manganism concludes that although similar in many respects, there are distinct differences between the two neurological disorders. Similarities between

Parkinson's disease and manganism include the presence of generalized bradykinesia and widespread rigidity. Dissimilarities between Parkinson's disease and manganism were also recognized, notably the following in manganism: (a) a less frequent resting tremor, (b) more frequent dystonia, (c) a particular propensity to fall backward, (d) failure to achieve a sustained therapeutic response to levodopa, and (e) failure to detect a reduction in fluorodopa uptake by positron emission tomography (Calne et. al., 1994). Given these differences, it has been proposed that manganese intoxication is associated with preservation of the nigrostriatal dopaminergic pathway, and that chronic manganese intoxication causes parkinsonism-like effects by damaging output pathways downstream of the nigrostriatal dopaminergic pathway (Calne et. al., 1994).

Nevertheless, in a recent small study, Parkinsonism in welders was recently distinguished clinically only by age at onset, suggesting that welding fumes, and potentially manganese, may be a risk factor for Parkinson's disease (Racette et. al., 2001). These uncertainties, along with a limited understanding of transport mechanisms of manganese into the brain, and lack of standardized exposure assessments and reconstruction methodologies, have led to the development of the Manganese Health Research Program (MHRP). Manganese neurotoxicity has been attributed to symptoms in a few workers that have been chronically exposed to aerosols or dusts that contain high levels (> 5 mg Mn/m$^3$) of manganese (ATSDR, 2000; Mergler et. al., 1994). Manganese-induced neurotoxicity may also occur following ingestion. Kondakis et al. (1989) documented outbreaks of manganese toxicity in Japan and Greece due to the consumption of water from wells contaminated with extremely high levels of manganese (1.8 to 14 mg Mg/L). More recently, Woolf et al. (2002) reported that a 10-year old boy with abnormal verbal and visual memory function had elevated serum (0.90 µg/dL vs. normal value of < 0.265 µg/dL), whole blood, urine, and hair manganese concentrations following chronic ingestion of well water containing moderately elevated levels (~1.2ppm) of manganese. Typical manganese water levels in the US are < 0.05 ppm.

Three different types of waste materials are used in this research; two of them are indigenous materials while the remaining one is a worldwide fruit generating waste. The three waste materials are:

1. Bush Tea (*Athrixia philicoide*).
2. Butternut Squash peels (*Cucurbita Moschata*)
3. Pineapple peels (*Ananas Comosus*)

## 1.5 Plant-based waste materials

### 1.5.1 Bush tea (*Athrixia philicoide*)

Bush tea (*Athrixia philicoide*) is indigenous to South Africa where it is commonly known as bushman's tea in English (Mudau et. al., 2007). It is a beautiful shrub used by both individual and institutions to decorate their frontage. The flowering period in the coastal areas occurs between May and June and inland flowers appear between mid-summers (Roberts, 1990). Flowers vary from pink to all shades of pink and attractive purple colour, depending on soil factors and geographical areas (van Wyk and Gericke, 2000). The traditional people of South Africa have been using the bush tea for many years as medicinal tea for cleansing or purifying the blood, treating boils, headaches, infested wounds, cuts and the solution may also be used as foam bath (Mabogo, 1990). The foam bath brew can also be used as lotion dabbed on to the boil, eruption or cut. Propagation is commonly by ripening seeds, which are mostly collected at the end of summer (Roberts, 1990).

The tea adapts well in open grassland and in thick forest margins of South Africa, especially in Limpopo province, Free State province, KwaZulu-Natal and some parts of the Eastern Cape Province, and in neighboring Swaziland. The plants need well-drained soil with full sunlight and enough space for spreading their branches (Roberts, 1990). Series of experiments have been performed on the usage of the bush tea. Moller et al. (2006) and Mudau et al. (2006) investigated the main component of this tea and it was reported that the bush tea does not contain caffeine as is very common among some other forms of tea. The intention of this research work is to utilize the wastes generated from powdered tea to remove selected toxic trace metals from aqueous system.

### 1.5.2 Pineapple (*Ananas Comosus*)

Next to bananas, pineapple is the second most popular tropical fruit, it is native to South America particularly in Brazil and Paraguay. It is also known as pina, nanas and Ananas. Among the countries of the world highest producers of pineapples are Hawaii, Costa Rica, Mexico, Honduras, South Africa, Taiwan, Dominican Republic, Ivory Coast, Cote d’Ivoire, Guinea, India, El Salvador, Ecuador, Nicaragua, Australia, Thailand, the Philippines and Martinique. With improvement in planting it is a fruit that can be planted throughout the year. It is a fruit that is eating basically for its taste and its mineral composition. Since because of its nutritional value a lot of it is being consumed all over the world and thereby a lot of waste is being generated, it is this waste that will be used in this research for bio-remediative purposes.

### 1.5.3 Butternut (*Cucurbita moschata)*

Butternut is called "white walnut" because of its light-colored wood, which has a natural golden luster that becomes satin-like when polished. The wood is only moderately hard and saws and carves easily. It has been used for furniture, cabinetry, instrument cases, interior woodwork, including hand-carved wall panels and trim, and church decoration and altars. It is stocked in specialty lumberyards because little is cut annually (NRCS, 2003).

**1.5.3.1 Adaptation:** Butternut is found most frequently in rich woods of coves and stream benches and terraces, on slopes, in the talus of rock ledges, and on other sites with good drainage; at elevations of 0-1000 (-1500) meters (Karen, 2003). Young trees may grow in considerable competition, but they are shade-intolerant and mature trees must reach the over story. Flowering occurs from April-June and fruiting from September-October (USDA, 2003).

**1.5.3.2 General:** Seed production begins at about 20 years and is optimum from 30-60 years. Good crops can be expected every 2-3 years, with light crops during intervening years. Premature seed losses may result from consumption by insects, birds, and rodents and a lack of butternut trees in the immediate vicinity may limit pollination and fruit formation. Seeds germinate in the spring after seed fall and a cold period at 20°-30°C for 90-120 days to break dormancy (USDA, 2003). Small to medium-sized native trees with stiff upright branches and a wide-spreading crown, the young twigs, stems, and leaflets have hairs sticky-oily to the touch; terminal buds 12-18 mm long; bark brownish-gray, thick, shallowly divided into smooth or scaly plates. Leaves are pinnately compound, the leaflets 11-17 cm, ovate to lanceolate or oblong-lanceolate, ± symmetric, mostly 5-11cm long, with finely toothed margins, terminal leaflet present, the lower surfaces densely covered with stellate hairs. Flowers are unisexual, female (pistillate) and male (staminate), but on the same tree (the species monoecious), usually not opening simultaneously on any individual tree; male flowers in slender catkins 6-14 cm long, the female flowers in terminal clusters of 6-8 flowers each. Fruit is an oblong-ovoid nut 4-6 cm long, single or in clusters of 2-5, with a hard, thick, deeply furrowed shell enclosed by a thick husk with a sticky-glandular surface. The nuts usually remain on the tree until after leaf fall. The common name refers to the mature nut kernels, which are sweet and oily, like butter (USDA, 2003).

#### 1.5.3.3 Distribution

Butternut is primarily a species of the northeastern and north-central US and southern Canada from southeastern New Brunswick to Ontario and Quebec; in the US in Minnesota to Missouri and eastward through Tennessee into North Carolina and Virginia, with disjoint out layers in Arkansas, Mississippi, Alabama, South Carolina, and Georgia. It is uncommon throughout most of its range and formally listed as rare in many of the states in which it occurs (Ostry, 2003).

# CHAPTER 2

# LITERATURE REVIEW

## 2.1 Introduction

Water appears on earth in liquid, solid and gaseous phases, which are linked together in a closed cycle, with average annual precipitation equal to annual evaporation from oceans and land. Only 2.5 percent of the total volume of the world's water is fresh (Tolba et al., 1992). Data collected under Global Environmental Monitoring System (GEMS/WATER) project indicate that about 10 percent of all rivers monitored may be described as polluted as they have a Biological Oxygen Demand (BOD) of more than 6.5mg/l (UNEP/WHO, 1998).

Other pollutants of fresh water which are of concern are potentially toxic substances, especially toxic metals and deposited acids. In the last twenty (20) years, Particular effort has been made to reduce the contamination of river draining industrial areas, such as Rhine (Germany). Between 1975 and 1985, there was a steady decline in the level of arsenic, cadmium, chromium, copper and mercury. Lead, nickel and zinc in the Rhine system (Germany) as a whole (van Gunten et. al., 2001).

In countries where potable water is in short supply such as South Africa, the presence of toxic metals such as Pb, As, Mn Hg and Cd in the environment is of great concern due to their health implications (Awofolu et. al., 2005). Consequently, efforts should be made to prevent and continually find ways of removing these toxicants from aqueous media. The application of biosorption in environmental treatment has become a significant research area in this direction. Heavy metal ion is reported as a priority pollutant, due to its mobility in natural water ecosystems and to its toxicity (Volesky and Holan, 1995). Cadmium, Lead and Manganese are regarded as toxic metal contaminants in water because of their damaging effects on the health of human and animals. A proper, efficient and effective method need to be devised for their removal, since their presence in water systems can affect the health of the aquatic ecosystem and indirectly of man (Nicholas, 2005).

Adsorbent materials derived from low cost agricultural wastes can be used for the effective removal and recovery of heavy metal ions from waste water streams. The major advantages of biosorption technology are its effectiveness in reducing the concentration of heavy metal ions to very low levels and the use of inexpensive biosorbents materials (Holan and Volesky, 1995; Kratochvil and Volesky, 1998). Several sorbents have been applied in the removal of trace metals from wastewater. A wide range of commercial sorbents including chelating resins and activated carbon have been applied for metal sorption but are relatively expensive.

In recent years, numerous low cost natural materials have been proposed as potential biosorbents. These include moss peat, algae, leaf mould, sea weeds, coconut husk, sago waste, peanut hull, hazel nut, bagasse, rice hull, sugar beet pulp, plant biomass and bituminous coal, (Lee and Volesky, 1997; Gupta et al., 1998). In this research, waste from Bush tea (Athrixia philicoide), the peels of both butternut and pineapple were processed (dried and pulverized into fine powdery form) were assessed for the removal of cadmium, lead and manganese in aqueous systems. Effects of conditions such as temperature, pH, metal concentrations, effects of other metals, amount of adsorbents were also evaluated on the sorption efficiency of the metals. Wastewater is simply water that has been used. It usually contains various pollutants, depending on what it was used for. It is classified into two major categories

1. Domestic or sanitary wastewater. This comes from residential sources including toilets, sinks, bathing, and laundry. It can contain body wastes containing intestinal disease organisms.
2. Industrial wastewater. This is discharged by manufacturing processes and commercial enterprises. Process wastewater can contain rinse waters including such things as residual acids, plating metals, and toxic metals.

Wastewater is treated to remove pollutants (contaminants). Wastewater treatment is a process to improve and purify the water, removing some or all of the contaminants, making it fit for reuse or discharge back to the environment. Discharge may be to surface water, such as rivers or the ocean, or to groundwater that lies beneath the land surface of the earth. Properly treating wastewater assures that acceptable overall water quality is maintained (EPA, 1993).

Waste water treatment is needed so that we can use our rivers and streams for fishing, swimming and drinking water (USEPA, 2004). Treatment technology includes physical, biological, and chemical methods. Residual substances removed or created by treatment processes must be dealt with and reused or disposed of in a safe way (Karen, 2003). Presence of heavy metals in the aquatic systems has become a serious problem. As a result, there has been a great deal of attention given to new technologies for removal of heavy metal ions from contaminated waters. Biosorption is one such emerging technology which utilized naturally occurring waste materials to sequester heavy metals from industrial wastewater (Suleman et. al., 2007).

The history of on-site programs dates back to the early part of this century. The first publications developed by the American federal government in the 1920's to deal with on-site wastewater management issues addressed the design of septic tanks. In the early to mid 1950's with the housing boom created by returning Second World War veterans, design concerns addressed by the U.S. Public Health Service included improved tank designs and the use of a percolation test to assess the hydraulic capacity of a site. Much of the early work was accomplished by Dr. J. T. Winneberger at the University of California at Berkeley.

In the 1960's the Federal Government passed the first of the Clean Water Acts. This act established the USEPA and on the first of the EPA activities initiated soon after its formation was the development of the construction grant program for the development of wastewater infrastructure. The initial efforts funded by the EPA were sought programs to reduce the cost of public infrastructure. This resulted in passage of P.L. 92-500, The Clean Water Act Amendments of 1972. This federal program established an incentive program whereby communities could qualify for a large federal grant if the wastewater treatment technology proposed for a specific application was deemed an innovative or alternative technology. Onsite wastewater management systems are considered innovative and alternative and would qualify for I and A (Innovative and Alternative) funds except the federal program to provide grants for wastewater management has been discontinued.

Fortunately, the USEPA did recognize the importance of onsite wastewater management systems and did fund a considerable amount of excellent research dealing with onsite wastewater management systems. During the years that the EPA funded the research addressing onsite wastewater management issues, the focus of the onsite system went from a wastewater disposal alternative to a wastewater treatment system. The EPA recognizes that when properly sited, sized, designed, installed, operated and maintained, an onsite wastewater management system is a long term option for managing domestic, commercial, and industrial wastewater (Rubin, 1998). Awofolu et al. (2005) discover that the heavy metal from this wastewater have a lot of effect both on the soil and the produce from it.

The earliest recorded attempts to find or generate pure water date back to 2000 before Christ Early Indian and Indus writings outlined methods for purifying water. These methods ranged from boiling or placing hot metal instruments in water before drinking it to filtering that water through crude sand or charcoal filters (Baker and Tara's, 1981). These writings suggest that the major motive in purifying water was to provide better tasting drinking water. It was assumed that good tasting water was also clean. People did not yet connect impure water with disease nor did they have the technology necessary to recognize tasteless yet harmful organisms and sentiments in water.

Centuries later, Hippocrates, the famed father of medicine, began to conduct his own experiments in water purification. He created the theory of the "four humors," or essential fluids, of the body that related directly to the four temperatures of the seasons. According to Hippocrates, in order to maintain good health, these four humors should be kept in balance. As a part of his theory of the four humors, Hippocrates recognized the healing power of water. For feverish patients, he often recommended a bath in cool water. Such a bath would realign the temperature and harmony of the four humors. Hippocrates acknowledged that the water available in Greek aqueducts was far from pure in its quality.

Like the ancients before him, Hippocrates also believed good taste in water meant cleanliness and purity of that water. Hippocrates designed his own crude water filter to “purify” the water he used for his patients. Later known as the “Hippocratic sleeve,” this filter was a cloth bag through which water could be poured after being boiled (Baker and Tara’s, 1981). Different processes or techniques have been used for the removal of toxic metal from the waste water, and also different types of material have been used, some of these processes will be briefly mentioned below.

## 2.2 Precipitation processes

In industry, by far the most widely used process for removal of heavy metals from solution is that of chemical precipitation; approximately 75% of the electroplating facilities employ precipitation treatment (Patterson and Minear, 1975). Chemical precipitation of heavy metals may be accomplished by either batch or continuous processes. For small flow rates (less than 50,000 gallons per day), simpler and less expensive batch systems are more feasible. A continuous treatment system is applicable when wastewater characteristics are uniform or when flow rates are large (Robert and Young-Ku, 1985). Other types of precipitations are Hydroxide precipitation. Hydroxide precipitation of heavy metals is well suited for automatic pH control and has been shown to be an effective treatment technique in industry. An example of the effective nature of hydroxide precipitation removal efficiencies exceeded 98% for Cadmium, Chromium and Lead ions using spiked well waters (Sorg et. al., 1978). Limitations associated with the use of hydroxide treatment include

- Hydroxide precipitates tend to resolubilize if the solution pH is changed.

- Chromium (VI) is not removed by hydroxide precipitation.
- Removal of metals hydroxide precipitation of mixed metal wastes may not be effective because the minimum solubility for different metals occur at different pH conditions.
- The presence of complexing agents may have an adverse effect on metal removal.
- Cyanide interferes with Heavy metal removal by Hydroxide precipitation.
- Hydroxide sludge quantities can be substantial and are generally difficult to dewater due to the amorphous particle structure. (Peters et al., 1984).

### 2.3 Carbonate precipitation

Peterson et al. (1977) studied the feasibility of carbonate precipitation for heavy metals removal. Carbonate precipitation has several advantages over that of conventional hydroxide precipitation.

- Optimum carbonate precipitation treatment occurs at lower pH conditions than those for optimum hydroxide treatment.
- Metal carbonate precipitates are reported to be denser than the hydroxide precipitate causing improved solids separation.
- Carbonate sludge’s have better filtration characteristics than hydroxide sludge’s.

### 2.4 Sulphide precipitation

Sulfide precipitation has been demonstrated to be an effective alternative to hydroxide precipitation (Bhattacharyya et. al., 1979) for removal of heavy metals from industrial wastewaters. Attractive features of this process include:

- Attainment of a high degree of metal removal even at low pH (pH ~ 2-3).
- Low detention time requirements in the reactor because of the high reactivity of sulfides.
- Feasibility of selective metal removal and recovery.
- Metal sulfide sludge is three times less subject to leaching at pH 5 as compared to metal hydroxide sludge (Whang et al., 1982) making final disposal safer and easier.
- Metal sulfide sludges exhibit better thickening and dewatering characteristics than the corresponding metal hydroxide sludges.

Limitations of the process involve the potential of $H_2S$ gas evolution and the concern for sulfide toxicity. Eliminating sulfide reagent overdose prevents formation of the odour causing $H_2S$. In currently operated soluble sulfide systems which do not match demand, the process tanks must be enclosed and vacuum evacuated to minimize sulfide odour problems.

## 2.5 Co precipitation/Combined Chemical Treatment

McAnnaly et al. (1984) studied the use of soluble sulfide and carbonate for their effectiveness in reducing nickel in a synthetic nickel plating wastewater. Employing jar tests, an optimum pH range for nickel removal from the synthetic wastewater was found to be 10.0 - 11.0. Optimum removal occurred at pH 11 where a residual total nickel concentration of 0.1mg/l was obtained with a sulfide: nickel weight ratio of 2.0 and a carbonate: nickel weight ratio of 20.0. At pH 10, a similar degree of removal (0.2mg/l residual total Ni) was obtained using a $CO_3$: nickel ion ratio of 10.0 and a Sulphur-Nickel ion ratio of 0.5. The authors of this current paper speculate the excellent Ni removals observed are due to co -precipitation phenomena.

## 2.6 Coagulation/flocculation

Coagulation refers to the charge neutralization of the particles. Flocculation involves slow mixing to promote the agglomeration of the destabilized particles. (EPA, 1978) Investigated the use of lime softening and coagulation (using ferric sulfate or alum) for removal of such heavy metals as Pb, Cd, $Cr^{+3}$, $Cr^{+6}$ ions etc. While lime softening achieved removals of greater than 98% in the pH range of 8.5-11.3 for cadmium, cadmium removals by ferric sulfate and alum coagulation were lower than that of lime softening and were shown to depend on pH. Cadmium removals increased with increasing pH. Ferric sulfate coagulation of a river water containing 0.3 mg/l Cd showed the removal to increase from 20 % at pH 7.2 to above 90% at pH >8. Alum coagulation results also increased with increasing pH; however above pH 8, removals may depend on the raw water turbidity. Both ferric sulfate and alum coagulation achieved greater than 97% removal of lead from a river water containing 0.15 mg/l Pb in the pH of 6-10.

## 2.7 Floatation

Foam flotation depends on the use of a surfactant that causes a non surface active material to become surface active, forming a product that is removed by bubbling a gas through the bulk solution to form foam. The use of foam flotation techniques for removal of heavy metals has been well studied (Chavalitnitikul and Bunker, 1981). With dilute wastewaters containing heavy metals in the parts per billion or parts million ranges, foam flotation offers several distinct advantages:

1. Simplicity
2. Flexibility and effectiveness of operation.

3 Limited space requirements due to rapid reactions.

4 Production of small, concentrated volumes of sludge.

5 Moderate costs comparable to that of lime precipitation

6 .Low costs in terms of labor, equipment, energy, and chemicals.

7 Capable of application on small intermediate and large scales.

8 Capability of reducing the contaminant concentrations well below the standards established by regulatory agencies.

### 2.8. Ion exchange

Ion exchange is an effective means of removing heavy metals from wastewaters. It is a reversible chemical reaction, where the removal of heavy metals is accomplished by the exchange of ions on the resin for those in wastewater. When the resins are saturated, they must be regenerated with an acid or alkaline medium to remove the metal ions from the resin bed. The regenerant brine is smaller in volume and higher in concentration than the original wastewater, but these metals must then be adequately treated or recovered (Robert and Young, 1985).

Due to the fact that ion exchange is efficient in removal of dissolved solids from normally dilute spent rinse waters, it is well suited for use in water purification and recycles. Many of the plating chemicals, acids, and bases used in metal finishing are ionized in solution and can be removed by ion exchange. Factors making ion exchange effective for such applications (USEPA, 1981) Include:

1. Ion exchange can economically separate dilute concentrations of ionic species from solutions.

2. The process can consistently provide high purity water over a broad range of conditions.
3. The resins used for separation are durable under severe chemical environments.

## 2.9. Liquid ion exchange/ liquid-liquid extraction

The process basically involves a two phase system (composed of an organic liquid containing a dissolved, water-insoluble active compound and the heavy metals in the aqueous phase) involving liquid – liquid extraction. The liquid extractant is typically present at a 10 - 40 % active level in a solvent, such as kerosene. The extracting solution is run counter current to an aqueous feed containing one or more types of metal ion, usually at a temperature slightly above ambient to improve the exchange kinetics and to facilitate phase separation. Acid-treating the organic fraction releases the metal in a concentrated water-soluble form (Robert and Young, 1985). Several advantages have been noted with application of liquid ion exchange (LIE) technology (Knocker, et al., 1978).

1. LIE can selectively extract a desired metallic cat ion from a feed solution containing a significant amount of metallic impurities.
2. LIE can concentrate the desired cat ion in final aqueous solution so that it can be treated by methods inappropriate for the initial dilute feed.
3. LIE is well suited for process automation and efficient metal recovery from mixed metal hydroxide slurry. One drawback with liquid- liquid extraction is its limited ability to concentrate the metals during the extraction process; in most cases, extraction produces no more than a tenfold increase in metal concentration.

## 2.10 Cementation

Cementation is a metal- replacement process in which a solution containing the dissolved metallic ion(s) comes in contact with a more active metal such as iron. Cementation is thus the recovery of an ionized metal from solution by spontaneous electrochemical reduction to the elemental metallic state with subsequent oxidation of a sacrificial metal (such as iron). The reaction for copper and iron is:

$Cu^{2+} + Fe \rightarrow Cu + 3Fe^{++}$ equation 2.1

$2Cr^{+6} + 3Fe \rightarrow 2Cr^{+} + 3Fe^{+2}$ equation 2.2

$Cr^{+6} + 3Fe^{+2} \rightarrow Cr^{+3} + 3Fe^{+3}$ equation 2.3

The result is to replace copper with iron in solution; the copper plating onto the solid iron surface. If hexavalent chromium is present in a wastewater, it can react with either elemental or ferrous iron to yield trivalent chromium:

The cementation process can be predicted in terms of electrode potentials. Advantages of the process include:

1. Simple control requirements.
2. Low energy utilization.
3. Recovery of valuable high purity metals, such as copper. (Robert and Young, 1985).

## 2.11 Complexation/sequestration

Complexation involves the formation of a complex compound through a complexing or chelating agent. Sequestration involves the removal of a metal ion from solution by formation of a complex ion that does not have the chemical reactions of the ion that is removed, in other words that metal ion is tied up or complexed. Complex formation alters the chemical characteristics of the metal ions and affects the removal mechanisms involved (Huang and Bowers, 1980).

## 2.12 Electrochemical operations

Electrolytic metal recovery is one of a number of technologies capable of removing metals from process wastewaters. The technology has been used for many years in the mining industry for electro-winning and electro refining of ores, and has been used to recover copper from pickle liquors. During the last 25-30 years, electrolytic metal recovery has been investigated for recovery of metals in drag out from plating tanks. In electrolytic recovery, a direct current is passed through an aqueous solution containing metal ions between cathode plates and insoluble anodes. The positive charged metallic ions adhere to the negatively charged cathodes leaving a metal deposit that can be stripped off and recovered (Robert and Young, 1985).

## 2.13. Biological treatment

Reid et al. (1968) studied the effects of metallic ions on biological waste treatment processes. Activated sludge treatment processes can tolerate up to 10mg/l of heavy metals ($Cr^{+6}$ , Cu, Ni, and / or Zn) either singly or in combination with only a 5 % reduction in efficiency. These same four heavy metals may be present either singly or in combination, up to concentrations of 10mg/l without any adverse effect on anaerobic sludge digestion. Biological treatment of domestic sewage will not be adversely effected if the concentration of $Cr^{+6}$ does not exceed 2mg/l. Biomass concentration strongly affected the amount of copper that could be removed from the solution.

## 2.14 Evaporation/distillation

The primary use of evaporation and distillation treatment has been for product recovery with some limited use to treat final concentrated wastewater to dryness. These techniques are basically end of the line processes (Robert. and Young, 1985). Generally evaporative processes are economical only for concentrated rinses and multistage countercurrent rinsing (Saito, 1977). This technique requires segregation of wastes by compatible types and use of various means for exclusion and /or removal of impurities. Evaporative recovery concentrates the chemical drag out in the rinse water to bath strength returning the concentrated solution to the process tanks. The evaporated water is condensed and returned to the rinsing system, thereby minimizing water consumption.

Two types of evaporative recovery system are commonly used: The vacuum evaporator and the atmospheric evaporator (Patterson and Minear, 1975). The atmospheric evaporator operates at atmospheric pressure and the normal boiling temperature of the solution being treated. A vacuum evaporator operates at sub atmospheric pressures enabling evaporation to occur at temperatures in the range of 130-190$^{o}$F. Both types of evaporator can be operated in either open or closed loop processing cycles. In the closed loop operation, the system is designed to recover 100% of the processing bath chemicals lost in the drag out for re- use in the metal finishing cycle. No external rinse water is added for makeup except that required to replace the loss due to atmospheric evaporation. The only chemical required are those required to replace what has been deposited on parts or due to any spillage and accidental losses. The open loop system is often employed in installations where there are an insufficient number of rinse tanks. It is designed for partial recovery of the processing bath.

## 2.15. Adsorption

Due to the historical development and use of activated carbon in water and wastewater treatment, most of the applications and research effort on activated carbon have been oriented towards organics removal (Huang, 1978). Activated Carbon was reported to be a potential adsorbent for heavy metal removal (Argaman and Weddle, 1973). Salvaged automobile tires are capable of removing trace metal (Al, Hg, Ni, Cd, Cr, Co, Cu, Fe, Pb, Mn, Ag, and Zn) from solution due to various materials present in the tires, such as sulfur, carbon black, fillers synthetic rubber, antioxidants etc. While some people use fungus to remove these toxic metals (Awofolu et al., 2005) while (Horsfall Jnr., 2005) used wild Cocoyam to remove $Pb^{2+}$ and $Cd^{2+}$. Different people have worked on the remediation of wastewater using waste product. Savannah River National Laboratory uses Agricultural oils comprising different types of oils which includes cotton seed oil, rape seed oil, coconut oil, corn oil and others as remediating medium for ground water and waste water . Different types of leaves grounded together have been used by some to remove heavy toxic metals like lead and Chromium from the wastewater (Suleman et. al., 2007). Chitosan Microsphere were also used to remediate coal wastewater containing lead, Fe, Mn, Al, Cu, Cd, Zn and Be).

Marian et al. (2007) used Carbon developed from Walnut hazelnut and that at pH 7 it was able to adsorb all the heavy metal to near neutrality. Benassi et al. (2006) used hapistachio shell and apricot stone to remove Lead, Cadmium, Zinc and Copper from Industrial Wastewater. Awofolu et al. (2005) evaluated Chelest Fiber Iry (Aminopolycarboxylic acid- type cellulose) to remove cadmium ions from aqueous solution. Awofolu et al. (2005) also investigated Aspergillus niger for the sorption of lead from wastewater, while Horsfall Jnr et al. (2004) used Caladium bicolor (Wild Cocoyam) biomass with the effect of the pH to adsorb $Pb^{2+}$ and $Cd^{2+}$ ions from aqueous solution. Rostami and Joodaki (2002) used Aspergillus niger and Penicillium austurianum to adsorb Cadmium from aqueous solution.

# CHAPTER 3: RESEARCH METHODOLOGY

## 3.1 Materials and Method

### 3.1.1 Sample and sample preparation

As mentioned in the introduction, three basic waste materials were evaluated for their sorption efficiencies of the selected toxic metal (Cd, Pb and Mn) in aqueous medium. These include used tea waste (*Athrixia philicoide*) and the outer peel of both pineapple (*Ananas Comosus*) and Butternut Squash (*Cucurbita Moschata*). These waste materials were thoroughly washed in de-ionized water to remove dirty particles contained in them and then air dried at room temperature for three (3) days. The pineapple peel and butternut peel wastes were further dried in the oven at 60°C for 24 hours while the Bush tea was allowed to dry at the same room temperature for 48 hours in order to blend them into a powdery from in a food blender. The powder was then sieved using 0.65μm sieve and kept in an air tight sealed plastic container which was kept in desiccators in order to preserve it from humidity.

### 3.1.2 Instrumentation

#### 3.1.2.1 Fourier Transform Infra-red (FT-IR)

FTIR (Fourier Transform Infra-red) Spectroscopy or simply FTIR analysis is a technique that provides information about the chemical bonding or molecular structure of materials (www.fareast.com 2005). The powdery form of the waste materials, which had been stored in the desiccators, was subjected to FTIR analysis in order to have an idea of the functional groups present on the surface of the waste adsorbents. The functional groups present on the waste adsorbents were identified through the internal library of the instrument as well as the Merck FT-IR ATLAS. The resulting spectral patterns were analyzed, matched and interpreted by comparison with known signatures of identified materials in the FTIR library (FTIR 1998).

#### 3.1.2.2 Ion Chromatograph

Ion Chromatograph was used for the detection of analyzed metals in sample solutions. The Advanced Compact Ion Chromatograph 861 model with 2.861.0020 suppressor module “MSM 11” which is linked to a PC controlled system for ionic analysis was used. The components and conditions of the instrument include:

1. An injector Valve for individual injections was used (due to Non – availability of sample changer.
2. High-pressure Pump- extremely low-pulsation double piston pump with a flow range from 0.2-2.5mL/min and a maximum pressure of 35MPa (350 bar). For cation but for an ion, it is 15 MPa.
3. Pulsation dampener- This protects the column from pressure changes even at low level pressure changes.
4. Peristaltic pump- Integrated two-channel peristaltic pump with a flow rate of 0.4 – 0.5 mL/min for regeneration and rinsing of the suppressor module “MSM II built into the machine.
5. Detector – This is where the measurement of the electrical conductivity of ions in a solution takes place. It is a conductivity detector with outstanding temperature stability whose temperature detectability varies by less than 0.01°C.

6. Column – This is where the stationary and mobile phase competes for the analyte. Chromatography really happens in the column where the analytes form a weak ionic bonding with the stationary phase.

Anion determination works on the principle of suppression developed by Small, Stevens and Baumann (Methrohm 2009). This method is based on the idea to remove the ion background of the eluents by ion exchange after the separation. In anionic analysis, suppressed conductivity was used where the suppression reduces the background conductivity. In anionic chromatography cation exchanger is used where all cations are replaced by the $H^+$ (Methrohm 2009).

Below are the Anionic chromatography /chemical suppression equations between the column and the detector:

$Na^+ + HCO^-_3 \ +H^+ \rightarrow -Na^+ \quad H_2CO_3 \rightarrow H_2O + CO_2$ equation 3.1

$Na^+ + Cl^{-\rightarrow} +H^+ \rightarrow \ -Na^+ \ H^+$

By this reaction, an eluent with high conductivity is converted to water and carbon dioxide ($CO_2$) which is of low conductivity. Cation determination works on the same principle mentioned above where the stationary phase is the resin packed in the column and the eluent is the mobile phase. Stationary phase = Polar (e.g. $R- SO_3$ ) while the mobile phase = polar (e.g. $HNO_3$ aq).

#### 3.1.2.3 Shaking water bath

The shaking water bath model LSB-015S/LSB-030S/LSB-045S supplied by Labotech was used and It was used at the speed of 80stroke/min with a temperature (35 to 45°C) throughout the procedure.

#### 3.1.2.4 pH METER and magnetic stirrer

The pH meter used throughout the analysis was supplied by Mettler Toledo model FE20/FG2. It has a pH range of 0.00 to 14.00. The magnetic stirrer was supplied by Heidolph model MR 3001K and was set at 60 – 70 stroke/min.

#### 3.1.2.5 Sieve and sieve shaker

Electromagnetic sieve shaker EMS-8 can shake the powder between 1mm to 99mm, Electro Pharma was used together with KINGIEST Laboratory Test Sieve throughout the study. Kingiest Laboratory Test Sieve 150µ was also used throughout for sieving samples.

#### 3.1.2.6 Industrial oven

The industrial oven used was supplied by Labcon, and it was used throughout this study for drying of materials between 50-100°C.

#### 3.1.2.7 Weighing balance (mono-blocks)

$+ Cl$ equation 3.2

The weighing balance used in the study was supplied by Mottler Toledo Model 73/23/EEC; it was used for weighing the powder samples as well as the salts to be dissolve. It has a weighing capability of up to 0.0001g.

#### 3.1.2.8 Degasser

The degasser KNF Neuberger type NO22AN.18 supplied by Labotec was used in de-gassing all the eluents used in the Ion Chromatograph Analysis.

### 3.1.3 Chemicals and reagents

All reagents used were of analytical grades. Working solutions were prepared by dilution of the standard solution. Deionized water prepared from Milli-Q instrument (Millipore, Bedford, USA) was used in the preparation of all aqueous solutions.

Mineral acids used were of high purity > 99.5 %. Standards of lead chloride ($PbCl_2$), cadmium nitrate, Cd $(NO_3)_2 . 4H_2O$ and manganese chloride ($MnCl_2$) were employed in the analysis. Calculation of required concentrations was based on the formula:

$C_1V_1 = C_2V_2$……………………………………………………equation 3.3.

$C_1 =$ Concentration of the stock solution.

$C_2$ = Concentration to be made

$V_1$ = Volume to be determined

$V_2$ = Volume to be made up to.

### 3.1.3.1 Chemicals used in the preparation of anionic eluent

The following chemicals were employed in the anionic analyses:

- Sodium Carbonate anhydrous ($Na_2CO_3$) Analytical reagent supplied by BDH chemicals Ltd Poole, England.
- Sodium Hydrogen Carbonate ($NaHCO_3$) supplied by Saarchem (Pty) Ltd.
- Sulphuric Acid (98 % pure) supplied by Rochelle was used together with the eluent diluted to 50 mmol/L (2.5 ml of conc $H_2SO_4$; 98 %).

### 3.1.3.2 Chemicals used in the preparation of cationic eluent

The following chemicals were employed in the cationic analyses:

- Tartaric Acid supplied by Saarchem (from Merck chemicals).
- Dipicolinic acid ($C_7H_5NO_4$) Supplied by (from Aldrich chemical).
- De-ionized water (Millipore Bedford, U.S.A) was used in dilution and solution preparations.

- Acetone ($CH_3COCH_3$) from Merck was used in the cleaning of all glassware as well as in enhancing the capacity of the cationic eluent.

### 3.1.4 Experimental

All glassware were washed with liquid detergent, rinsed with water and then soaked in 10% $HNO_3$ over night ( IPCS, 2000).They were rinsed with water and then rinsed with distilled water before use followed by acetone in order to remove any organic compounds that might adhere to the glassware (Perrin et. al., 1981). Working solutions were prepared from the stock standard solutions (1000 mg/L) of the metals lead, cadmium and manganese while the working solutions of bromate, chlorate and Iodate for the anionic analysis were also prepared from their respective standards. Experimental concentrations of 5, 20, 30, 50, 100 mg/L were prepared from the working solution. pH 2, 4, 6 and 7 were evaluated in relation to adsorption of the metals using 0.5 M HCl to adjust the pH. Three different amounts of adsorbents of each material (0.5, 1, 1.5 gram) were also evaluated with respect to the effect of amount of adsorbent to sorption capacity (Amir, 2005). In this research work, both batch and continuous mode of sorption evaluation were investigated.

#### 3.1.4.1 Batch experiment

From the stock solution of 1000 mg/L, different working solution of 5, 20, 30, 50 and 100mg/L was prepared and adjusted to the required evaluated pH as mentioned above i.e. (pH 2 and 7 which falls within the strength of the column). The grinded adsorbents were then weighed and transferred into the beaker containing the range of the working solution. This was stirred using magnetic stirrer between 60-70 rpm with the evaluating contact time of 2, 4 and 6 hours. After the required evaluation time, the mixture was sieved using 0.45 μm membrane filter. The resulting solution was then analyzed for their metallic content in order to determine the remaining concentration after adsorbent using the ion chromatograph. The Effects of conditions of pH, metal concentration, amount of adsorbent, contact time and temperature were evaluated in this study. The same procedure was repeated for other the anionic analysis.

# CHAPTER 4: RESULTS

## 4.1 Effect of pH on Individual metal adsorption capability of investigated waste materials.

### 4.1.1. Effect of pH on Lead adsorption capability using bush tea, pineapples peel and butternut Squash peel waste.

Result of the effect of pH on the adsorption of lead (Pb) by bush tea is as presented in Figure 4.1 below.

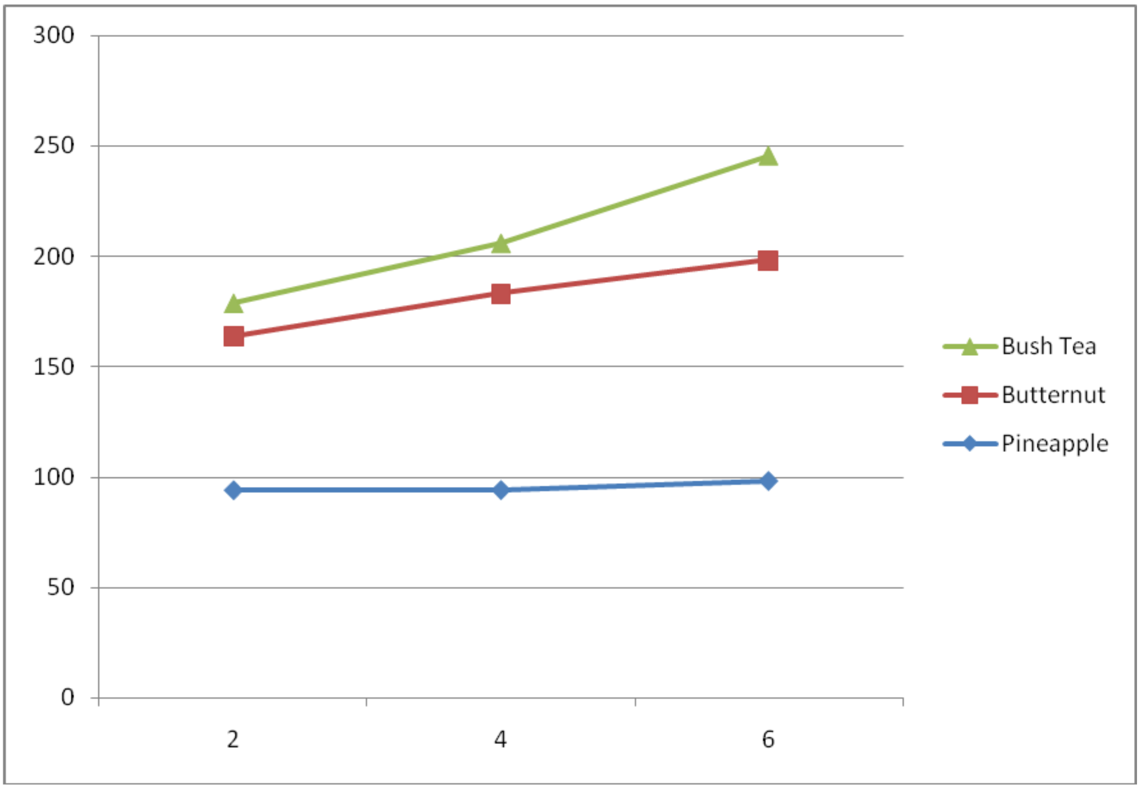


**Figure 4.1: Effect of pH on Lead adsorption capability using bush tea, Butternut peel and Pineapple waste**

From the Figure above, it could be observed that the highest adsorption of lead (Pb) occurred at pH 6 while the lowest adsorption was at pH 2. Hence, adsorption of the metal was in the decreasing order of pH 6 > 4> 2. Therefore, increase in pH favours the adsorption of lead.

**4.2. Effects of pH on cadmium (Cd) adsorption capability using bush tea, Butternut peel and pineapple waste.** Using the waste from Bush tea (*Athrixia philicoide);* pineapple peel (*Ananas comosus*) as well as Butternut Squash peel (*Cucurbita Moschata*).

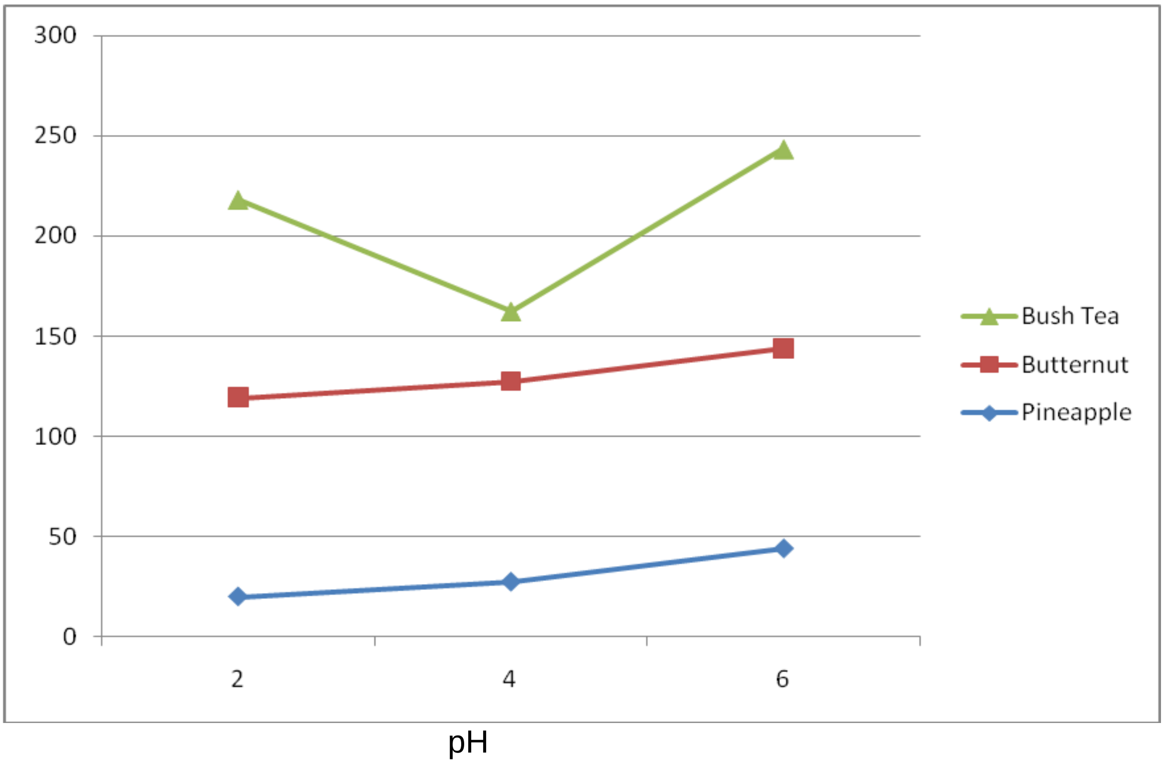
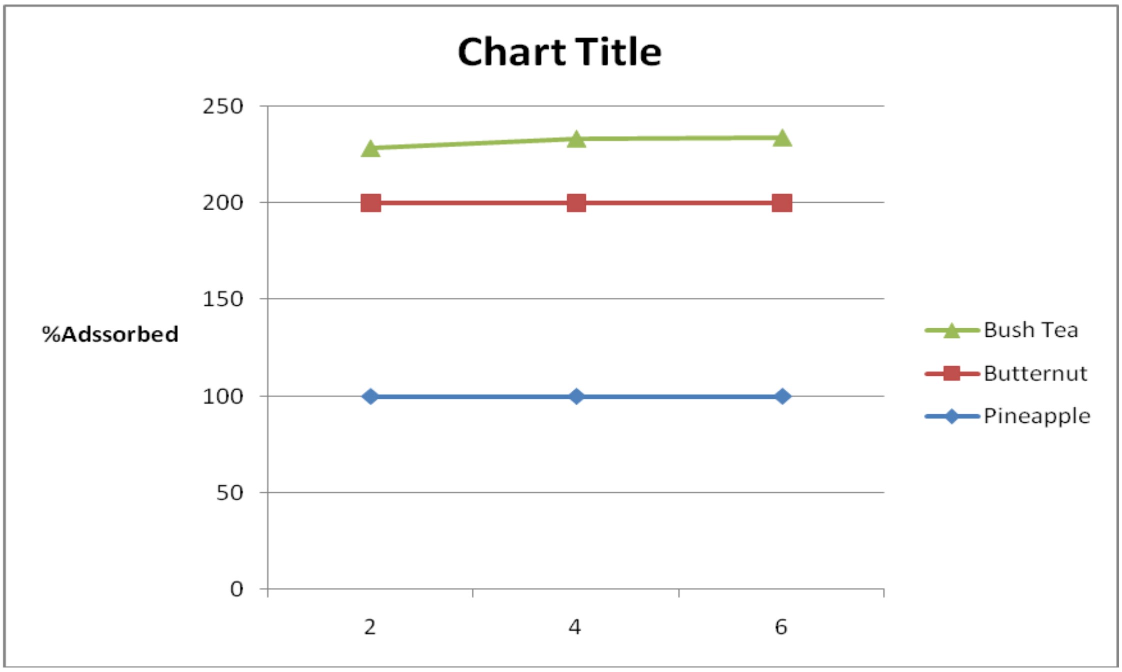


**Fig 4.2. Effect of pH on adsorption of Cadmium adsorption capability using Bush tea, Butternut peel and Pineapple waste**

From Figure 4.2 above, an appreciable or significant adsorption of Cadmium by the bush tea occurred at both pH 2 (99.85 %) as well as pH 6 (100 %). A poor adsorption of this metal was recorded at pH 4. Hence, pattern was in the order of pH 6 > 2 >4. Butternut peel adsorption of Cadmium increased as the pH increased. Though the level of adsorption of Cadmium by Pineapple peel cannot be compared to the other two adsorbents, it presented the same pattern like the other two.

### 4.3. Effect of pH on Manganese (Mn) adsorption capability using Bush Tea, Butternut peel and Pineapple peel:

Using wastes from Bush tea (*Athrixia philicoide*); pineapple peel (*Ananas comosus)* as well as Butternut Squash peel (*Cucurbita Moschata*).



pH

**Fig 4.3: Effect of pH on Manganese adsorption capability using bush tea, Butternut peel and Pineapple peel waste**

Figure 4.3 above, it could be observed that the increase in pressure did not make much difference in the adsorption capacity of these adsorbents on Manganese, and the same applies to the other adsorbents, though they all adsorbed manganese very well above 90 %.

## 4.4 Effects of pH on adsorption of metal mixture

### 4.4.1: Effects of metal mixture on adsorption using wastes from pineapple peel (*Ananas comosus*).

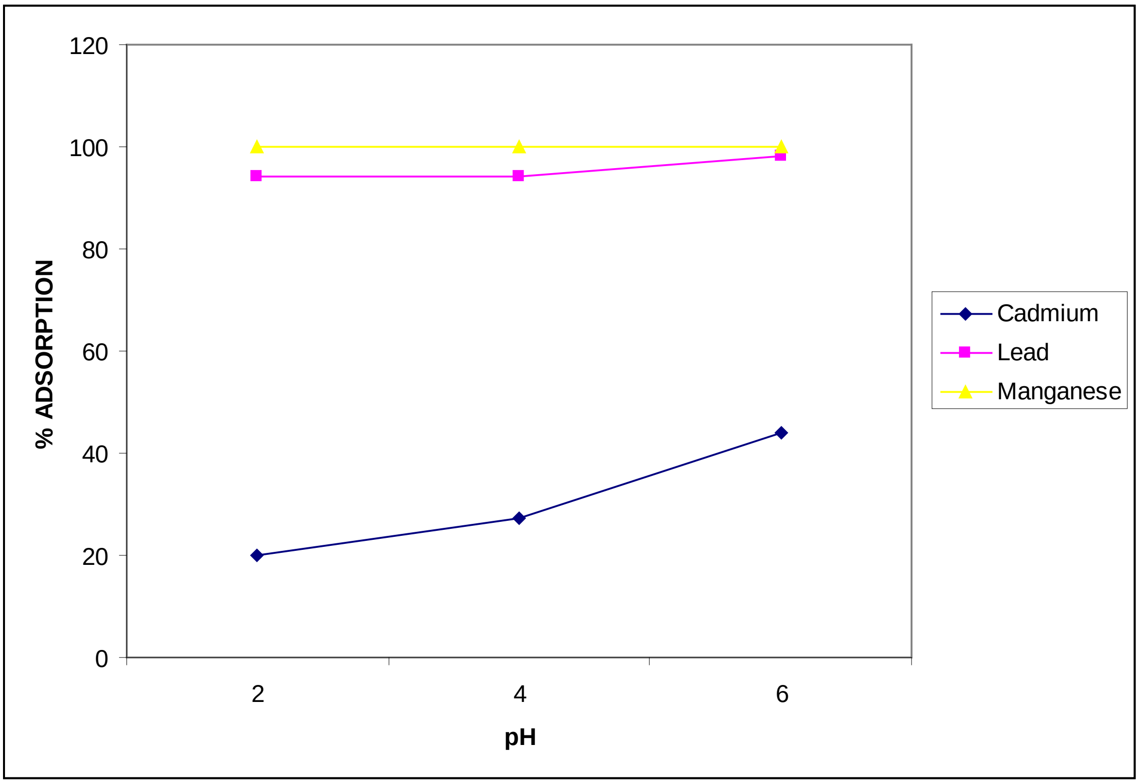


**Fig 4.4: Effect of pH on adsorption of metal mixture (Pb, Cd & Mn) from waste of pineapple peel (*Ananas Comosus*).**

From Fig 4.4 above, it was observed that Mn recorded the highest adsorption of the evaluated metals at all the pH with a 100 % adsorption of all the spiked concentration. The lowest adsorption for this adsorbent was recorded by Cd. Lead (Pb) however, recorded an adsorption of 98 % at pH 6 and 97 % at pH 2.

### 4.4.2. Effects of pH on adsorption of metal mixture from Bush tea (*Athrixia philicoide*)

The result of the effect of pH on adsorption of mixture of metals using Bush tea (*Athrixia philicoide*) is as presented below in Fig 4.5:

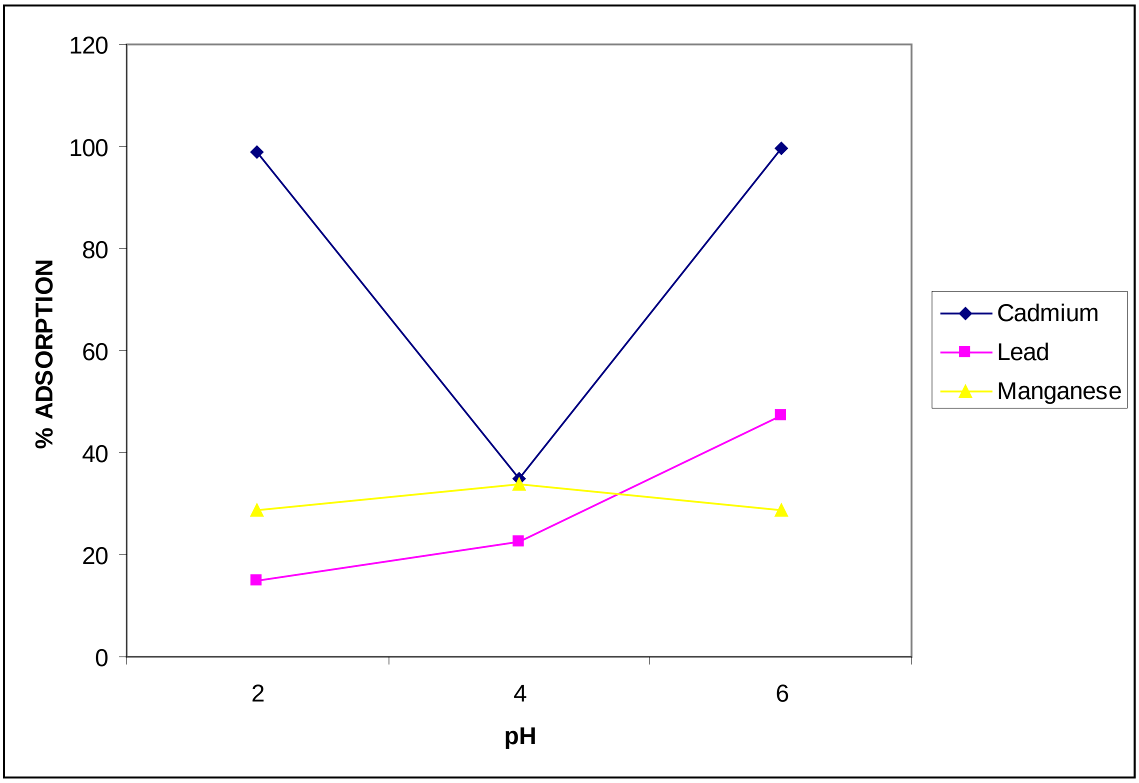


**Fig 4.4: Effect of pH on metal adsorption using Bush tea (*Athrixia philicoide*)**

From Figure 4.3 above, the highest level of adsorption of 100 % was recorded by Cd at a pH 6 and 2 respectively at the spiked concentration of 10ppm. Lead recorded an adsorption of 43, 22 and 18 % at pH 6, 4 and 2 respectively i.e. adsorption decreased as pH also decreased. In other words, the percentage of Pb adsorbed and optimized pHs is proportional. Manganese generally recorded percentage adsorption below 40 % at all evaluated pH.

### 4.4.3 Effects of pH on adsorption of metal mixture on adsorption from Butternut peel (*Curcubita Moschata*)

The result of the effect of pH on adsorption of mixture of metals Butternut peel is as presented below in Fig 4.6:

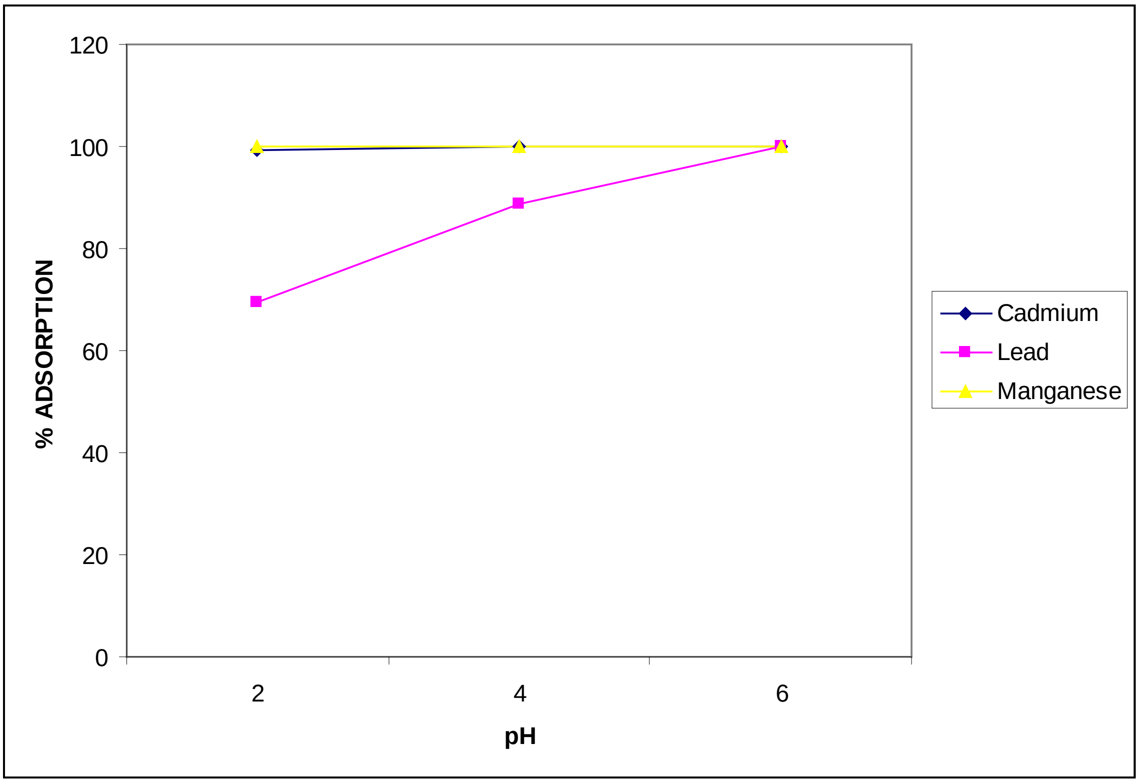


**Fig 4.5: Effect of pH on adsorption of metal mixture from waste Butternut Squash peel (*Cucurbita Moschata)***

Figure 4.5 above, almost a 100 % adsorption of all the analyzed metals (Mn, Cd and Pb) was observed at pH 2, 4 and 6). Lower adsorption of 85 and 64 percentages were recorded by Pb at pH 4 and 2 respectively.

## 4.5 Effects of the amount of adsorbent on % of individual metal adsorbed by evaluated plant-based wastes.

### 4.5.1 Effect on cadmium using the Bush tea (*Athrixia philicoide*) pineapple peel (*Ananas Comosus*) as well as Butternut Squash peel (*Cucurbita Moschata).*

The results of the effect of the amount of adsorbent on % of Cd adsorbed by the adsorbents from the spiked deionized water are as presented in Figure below.

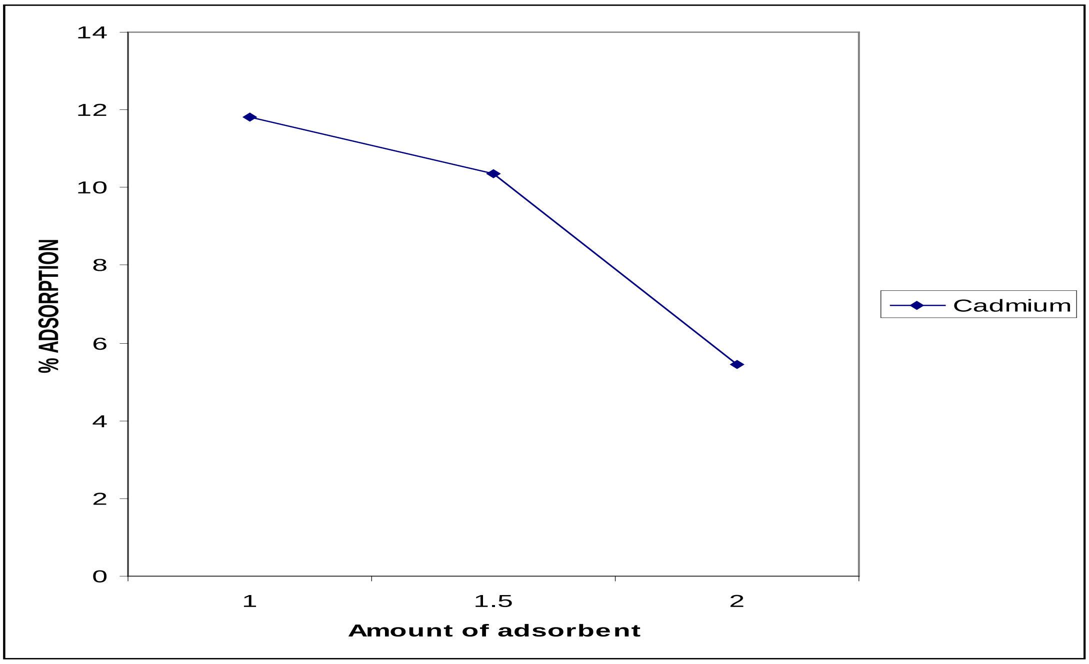


**Fig 4.6: Effect of amount of adsorbent on % adsorption of Cd by waste Bush tea**

From the Figure 4.6 above, the highest adsorption of Cd was achieved at 1.0g of waste Bush tea (adsorbent), while the lowest adsorption of the metal occurred at 2g, this shows that the higher the amount of adsorbent the less the adsorption of the cadmium.

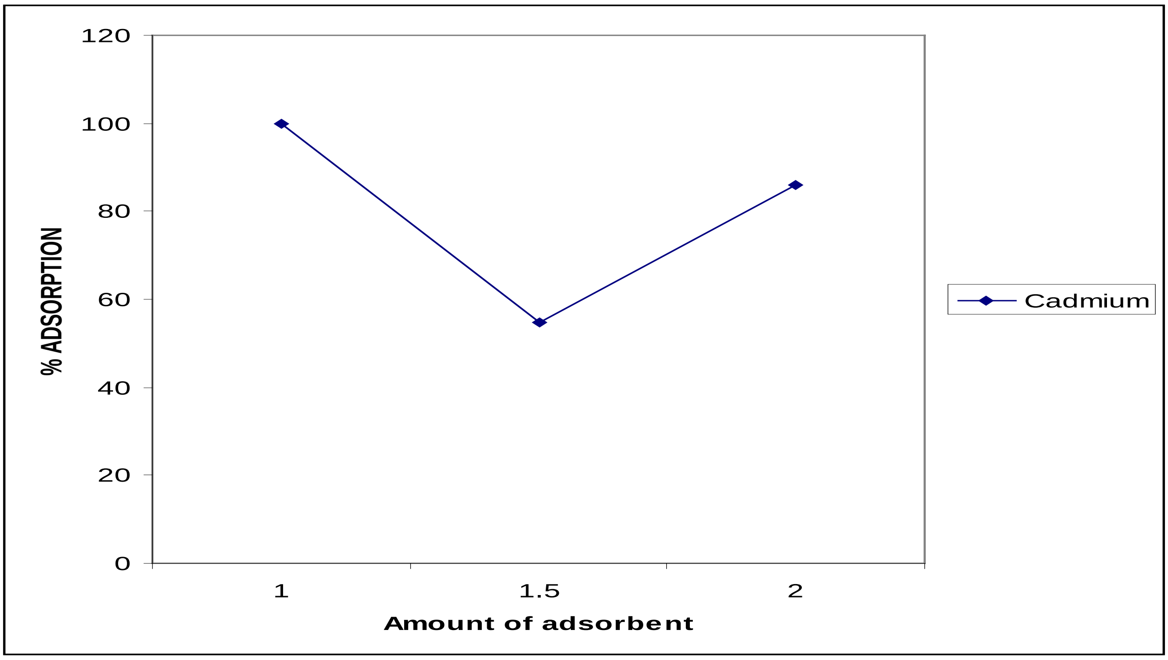


**Fig 4.7: Effect of amount of adsorbent on % adsorption of Cd by waste pineapple peel**

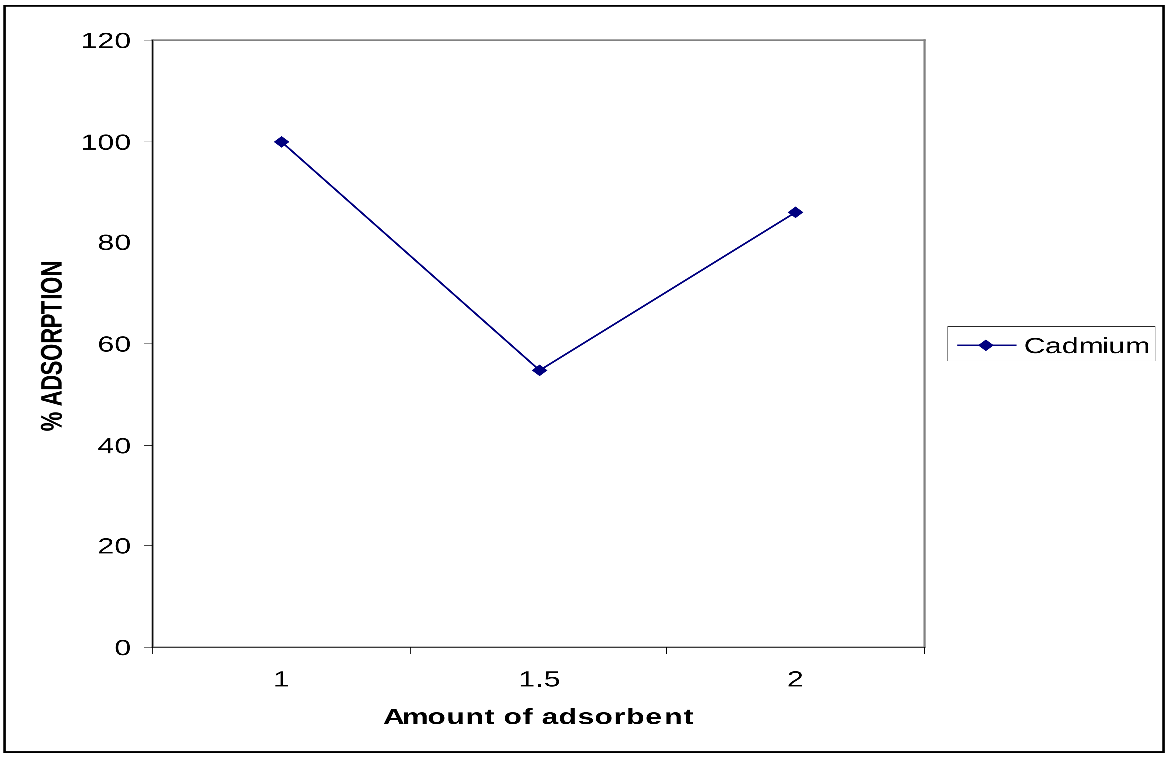


**Fig 4.8: Effect of amount of adsorbent on % adsorption of Cd by waste Butternut peel**

From the Figure 4.8 above, the highest adsorption of Cd was achieved by the butternut peel at 1.5g of waste Butternut peel (adsorbent), while the lowest adsorption of the metal occurred at 2.g. This is contrary to the adsorption result presented in the Bush tea and Pineapple peel.

### 4.5.2 Effect on manganese using the Bush tea (*Athrixia philicoide*) pineapple peel (*Ananas comosus*) as well as Butternut Squash peels (*Cucurbita Moschata).*

The results of the effect of amount of adsorbent on % of Mn adsorbed by the adsorbents from spiked deionized water are as presented in Figures 4.6a, b and c below:

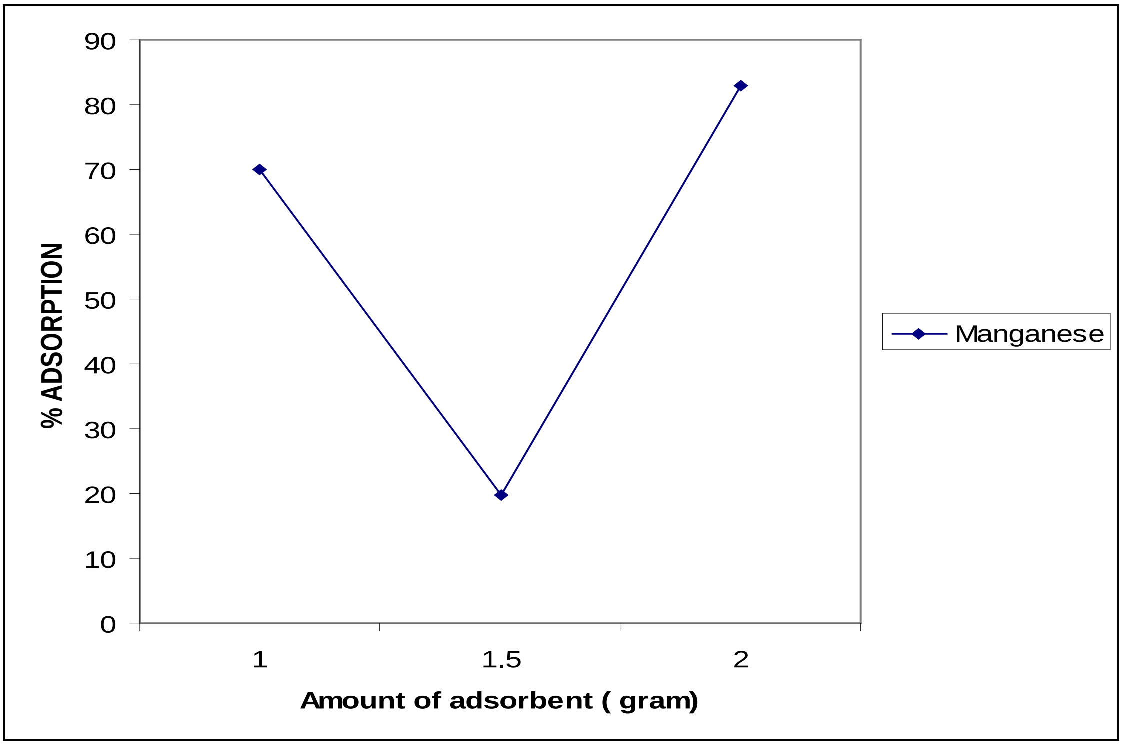
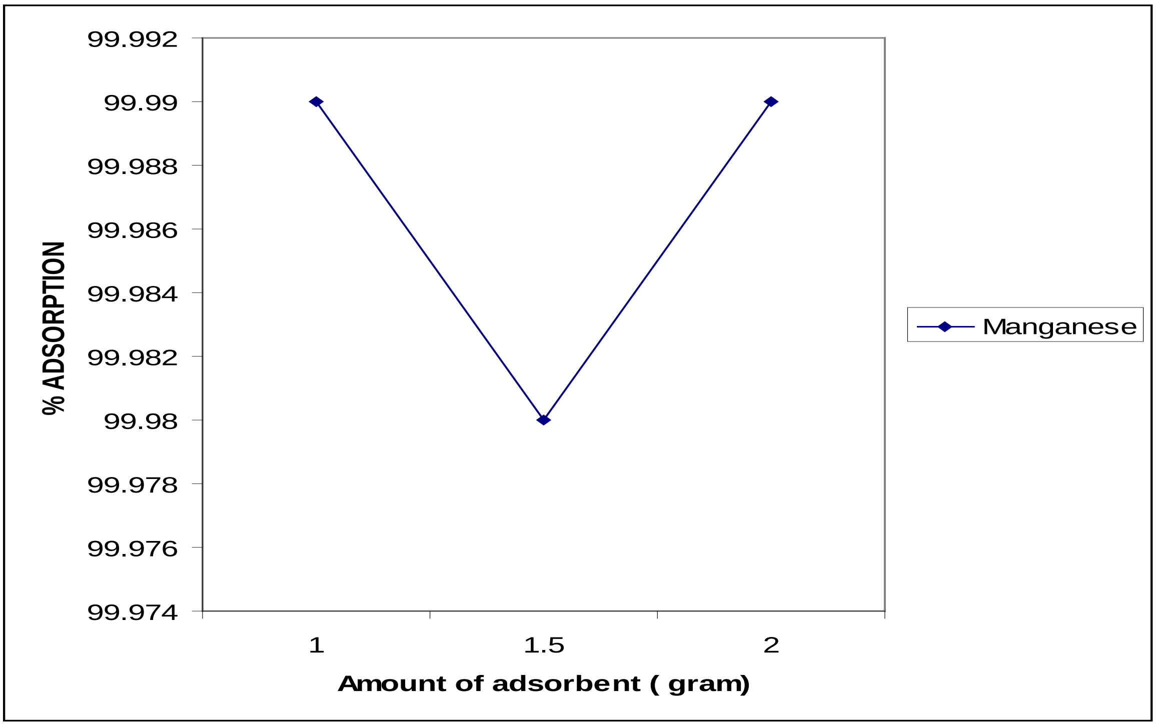


**Fig 4.8: Effect of amount of adsorbent on % adsorption of Mn by waste Bush tea**

Figure 4.8 above showed that the highest adsorption of Mn was achieved by waste bush tea at 2.0 g which represented 89 % of adsorbed metal, while the lowest adsorption occurred at 1.5 g and was adsorbed at 13 % adsorption.



**4.9: Effect of amount of adsorbent on % adsorption of Mn by waste Butternut peel**

From Figure 4.9 above, the highest adsorption of Mn was achieved by the butternut peel at two ends both at 1.0gram and 2.0 g which are both 99.99 % adsorption while the lowest adsorption occurred at 1.5 g of waste Butternut peel waste (adsorbent).

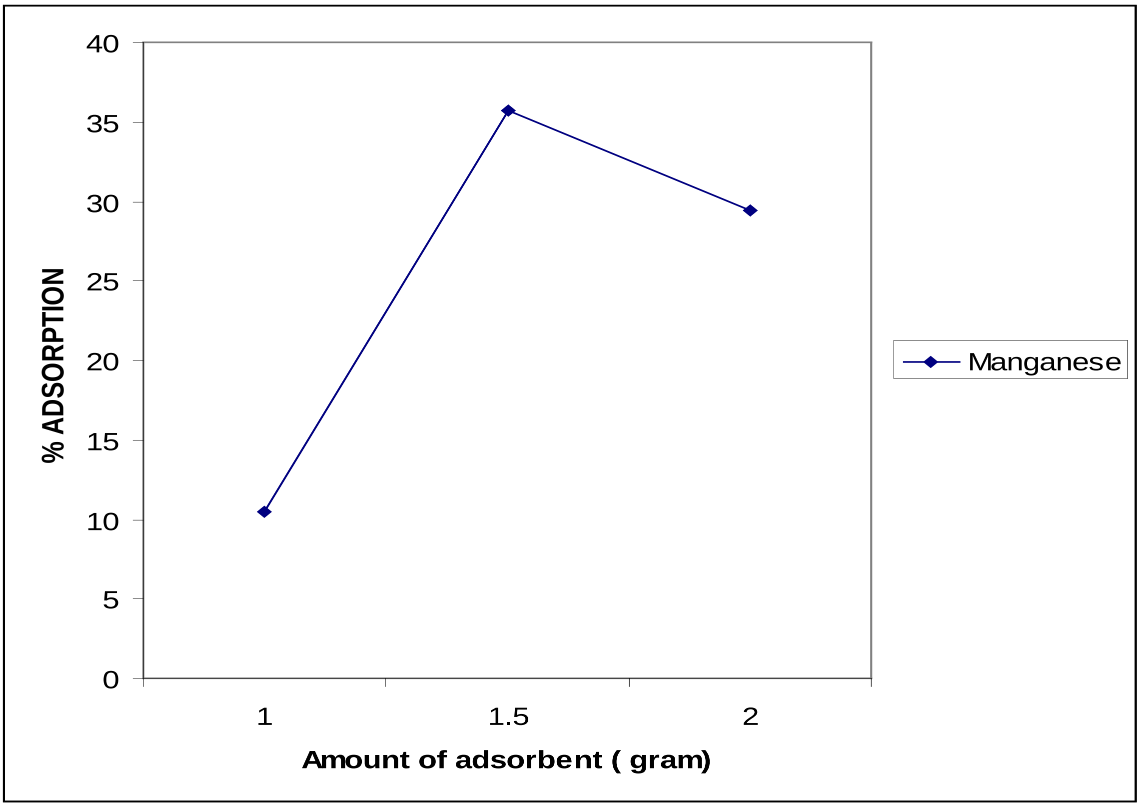


**Fig 4.10: Effect of amount of adsorbent on % adsorption of Mn by waste pineapple peel**

Figure 4.10 shows that the highest adsorption of Mn was achieved with the pineapple peel at 1.5g (adsorbent), while the lowest adsorption of the metal occurred at 1.0g.

### 4.5.3. Effect of amount of adsorbent on % of a mixture of metals (Pb, Cd and Mn) adsorbed using deionised water

#### 4.5.3.1. Effects of amount of adsorbent:

On lead (Pb), Manganese (Mn) and Cadmium (Cd) using waste from bush tea (*Athrixia philicoide*), pineapple peel (*Ananas comosus*) as well as Butternut Squash peel (*Cucurbita Moschata).*

Results of the effect of amount of adsorbent on % of Pb adsorbed by bush tea from the spiked deionized water are as presented in Figures 4.7a, b and c below:

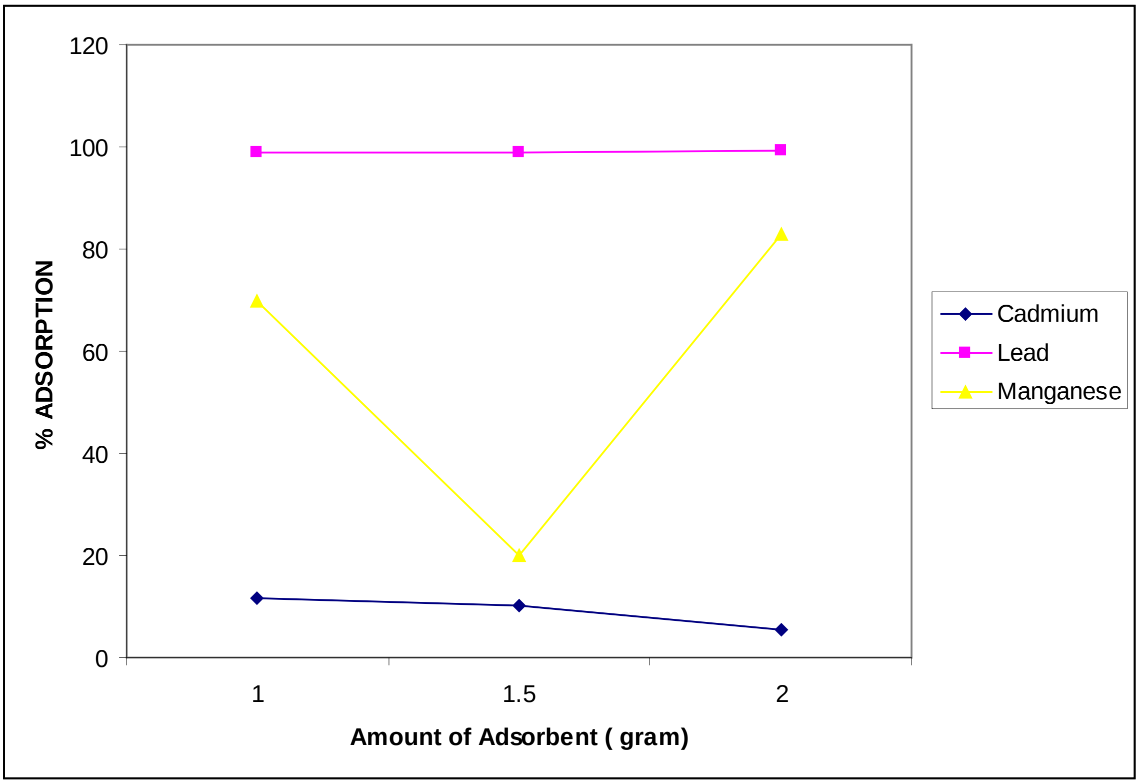


**Fig 4.11: Effect of amount of adsorbent on % adsorption of metals by waste Bush tea**

From the Figure above, irrespective of the mass of the adsorbent, Lead was adsorbed throughout at 100%, While Manganese was highly adsorbed at 82 % when 2g of the waste bush tea was used and the lowest adsorption was got at 1.5g of the adsorbent, Cadmium was not really adsorbed, probably due to the effects of the other metals on its adsorption level.

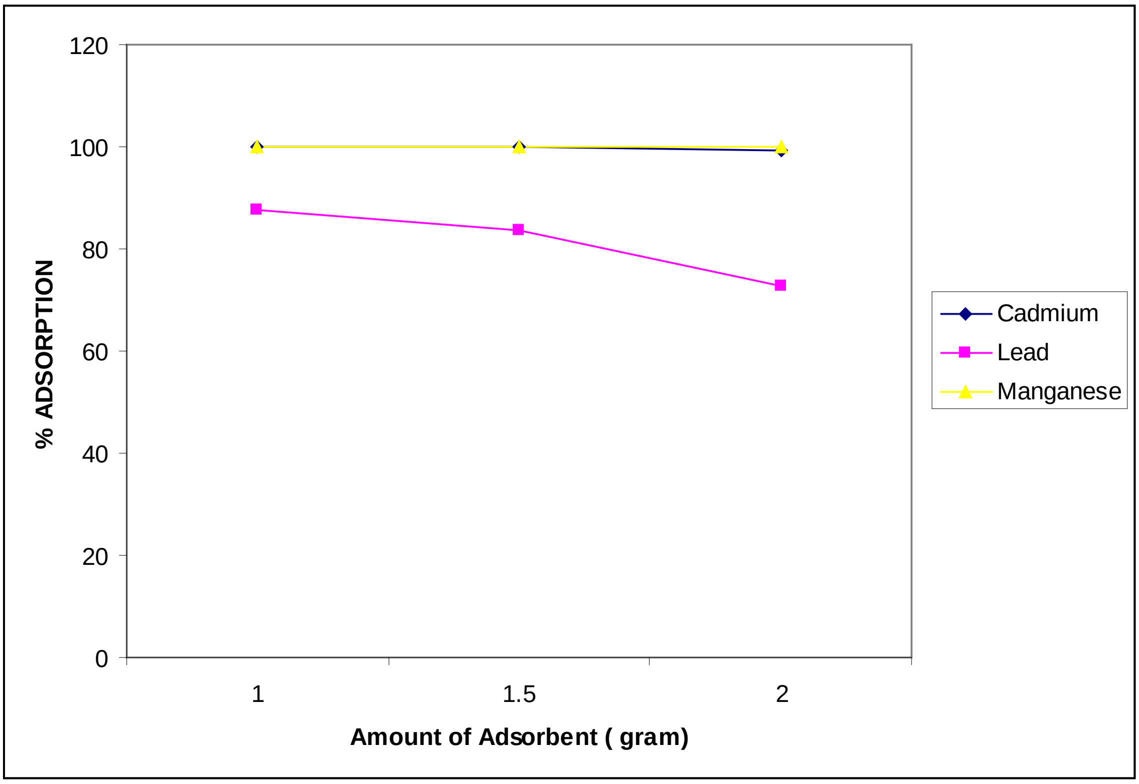


**Fig 4.12: Effect of amount of adsorbent on % adsorption of metals by waste Butternut peel (*Cucurbita Moschata*)**

From the Figure above, the highest level of adsorption occurred for both Cadmium and Manganese. Manganese is on top of Cadmium because both of them were adsorbed at 100 % at 1 and 1.5 g of the butternut peel. However, Cadmium was 99.98 % adsorbed at 2g and Manganese 100 % adsorbed. That is why there is a trace of cadmium under manganese. Lead was well adsorbed but at a lower percentage, it was highly adsorbed at 1g of the adsorbent at 82 % adsorption.

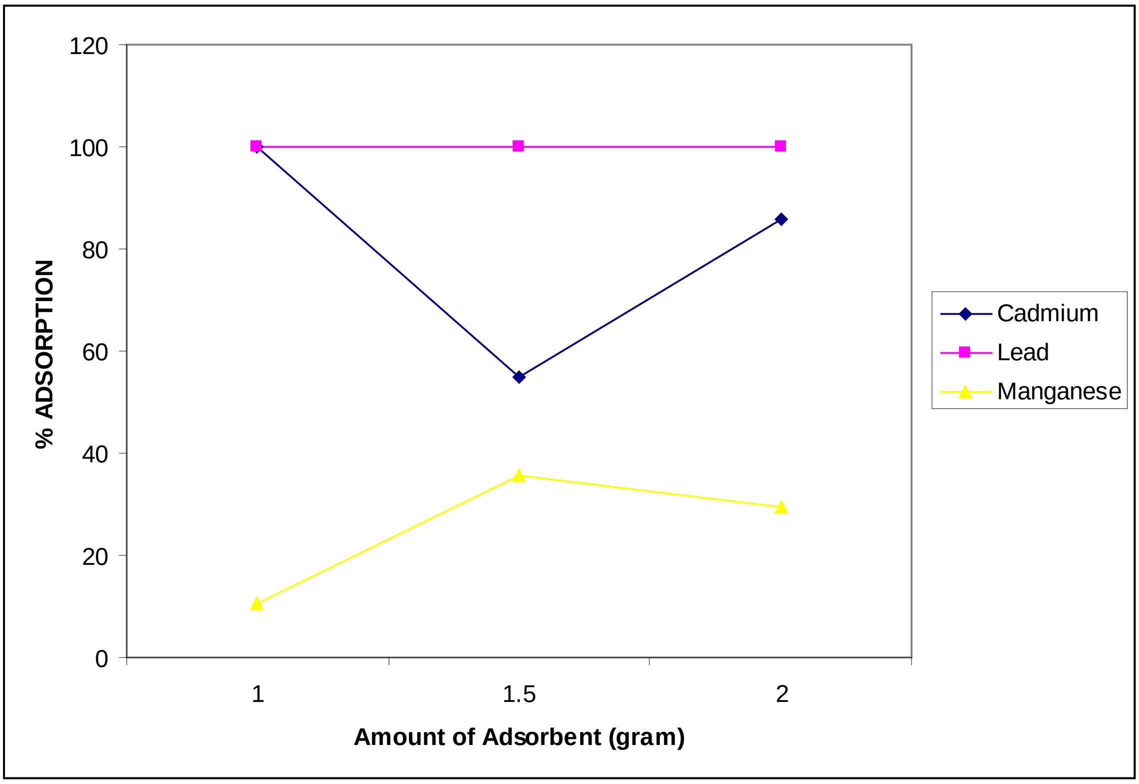


**Fig 4.13: Effect of amount of adsorbent on % adsorption of metals by waste pineapple peel (*Ananas Comosus*)**

From the Figure above, the highest adsorption of Pb was achieved throughout using waste Bush tea (adsorbent), 100% adsorption was got at 1g in the case of Cadmium while its lowest adsorption was recorded at 1.5 g. The lowest adsorption level of Manganese was recorded at 1g which was 5 % adsorption while its highest adsorption was at 1.5 g at 39 % adsorption.

### 4.6 Effect of contact time on % of metals adsorbed using deionised water

4.6.1. Result of the effect of contact time (agitated period) of metal and adsorbent (pineapple peel) on % of metal (Cd, Pb and Mn) adsorbed from spiked deionized water is as shown in Figure 4.14 below.

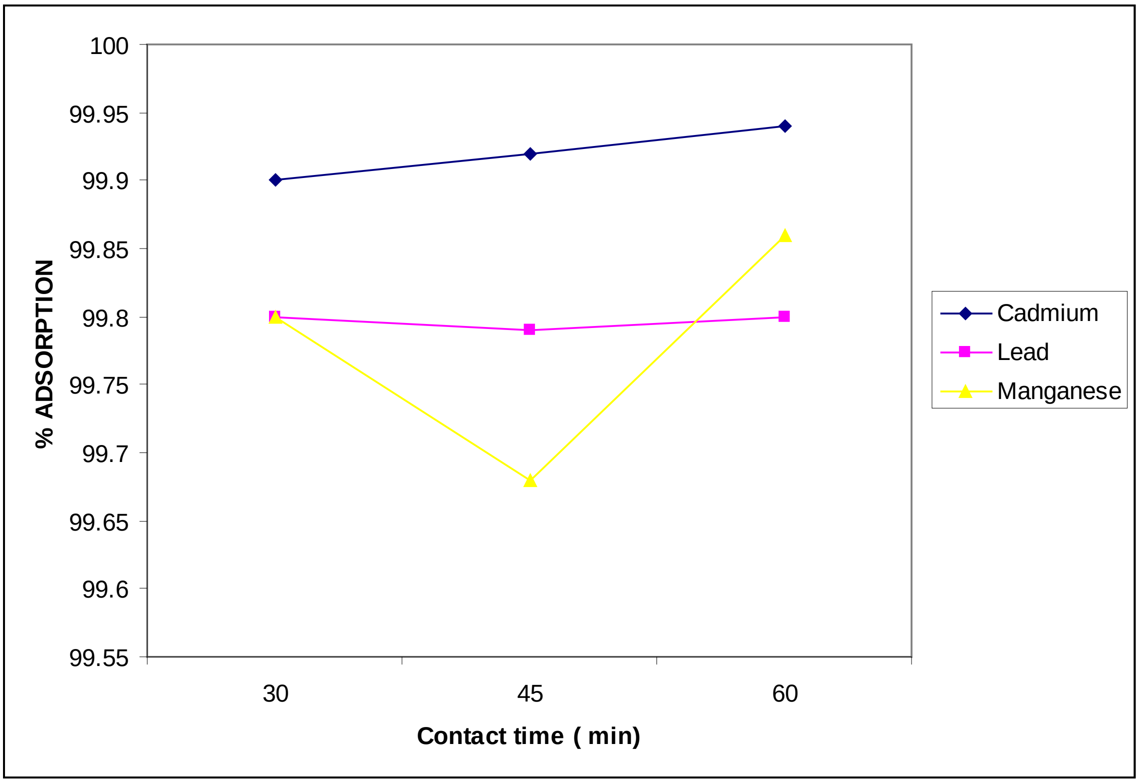


**Fig 4.14: Effect of contact time on adsorption of metal using pineapple peel**

From the Figure 4.14 above, it could be seen that the rate of adsorption of cadmium was very high and the longer the contact time it takes, the more the metal is adsorbed. Lead was adsorbed at the same rate albeit slightly lower at 45 minutes contact time. Manganese was highly adsorbed at 60 minutes and it dips steeply at 45 minutes contact time.

**4.6.1** Result of the effect of contact time (agitated period) of metal and adsorbent (Bush tea; Athrixia philicoide) on % of metal (Cd, Pb and Mn) adsorbed from spiked deionized water is as shown in Figure 4.8b below.

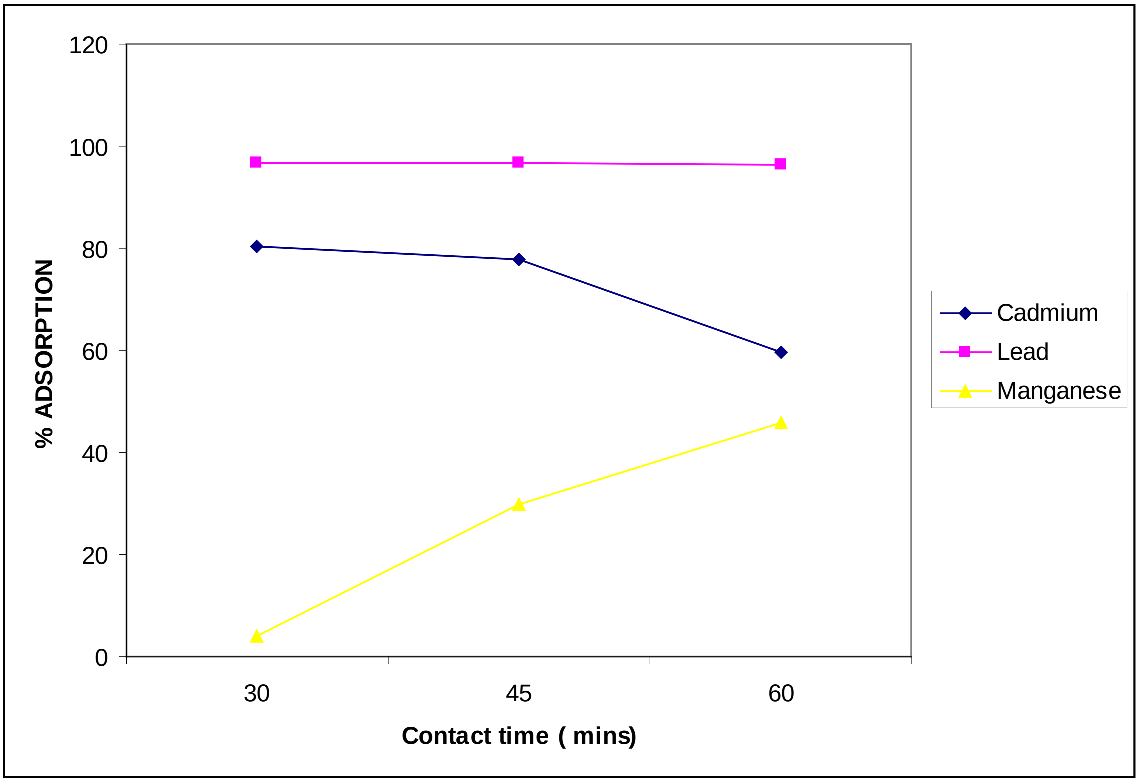


**Fig 4.15: Effect of contact time on adsorption of metal using adsorbent (waste bush tea)**

Highest adsorption of 98 % was achieved for Lead within 60 minutes contact time while 80 % adsorption was achieved for Cadmium under 30 minutes contact time using bush tea as adsorbent. A lower adsorption of 42 % was recorded with Manganese under same sorption conditions.

**4.6.2:** Result of the effect of contact time (agitated period) of metal and adsorbent (using waste butternut peel) on % of metal (Cd, Pb and Mn) adsorbed from spiked deionized water is as shown in Figure 4.16 below:

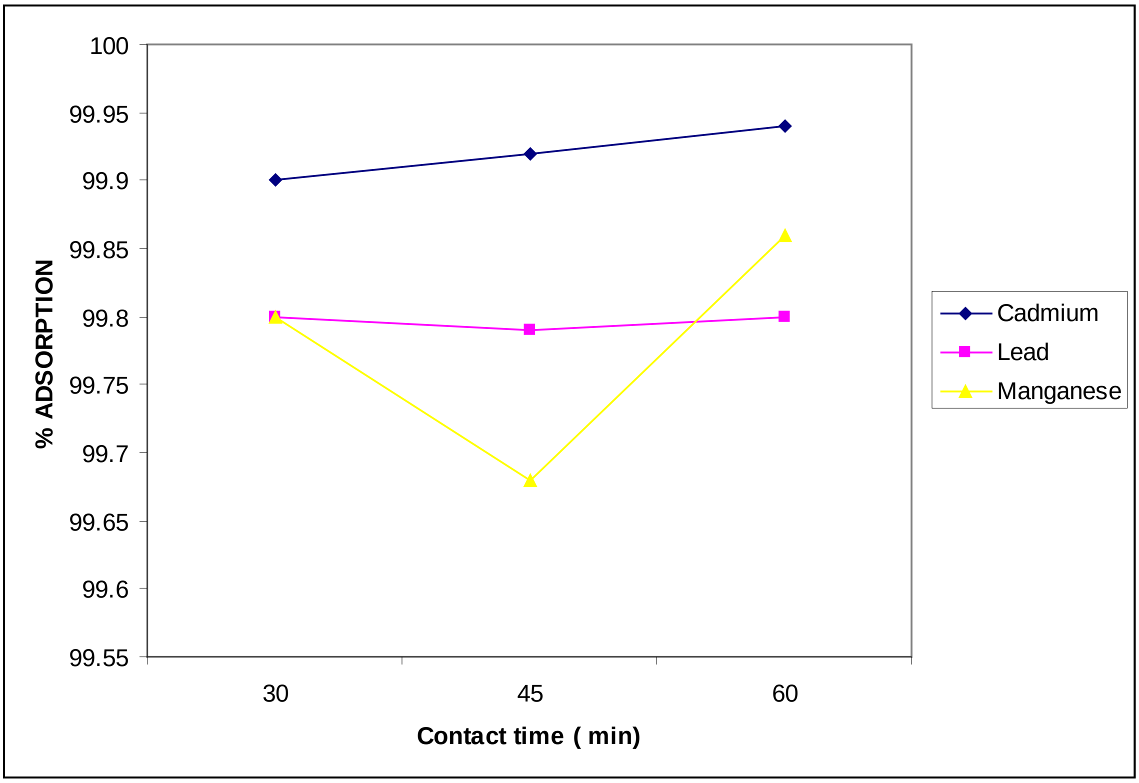


**Fig 4.16: Effect of contact time of metal and adsorbent (butternut peel) on % adsorption**

From Figure 4.16 above, Cadmium recorded the highest adsorption of less 99 % across all the evaluated contact time. Similar good adsorption of (~98 %) of the metal was obtained with Pb across evaluated contact time. A very good adsorption of 99.85 % and 99.8 % was obtained with Mn at the 60 and 30 minutes contact time respectively while 99.6 % adsorption of the metal was obtained at 45 minutes contact time.

## 4.7: RESULT OF THE EFFECT OF METAL CONCENTRATION ON % ADSORPTION

### 4.7.1 Using pineapple peel *(Ananas comosus)*

Result of the effect of metal concentration on % adsorption using waste pineapple peel from spiked deionized water is as shown in Figure 4.17 below:

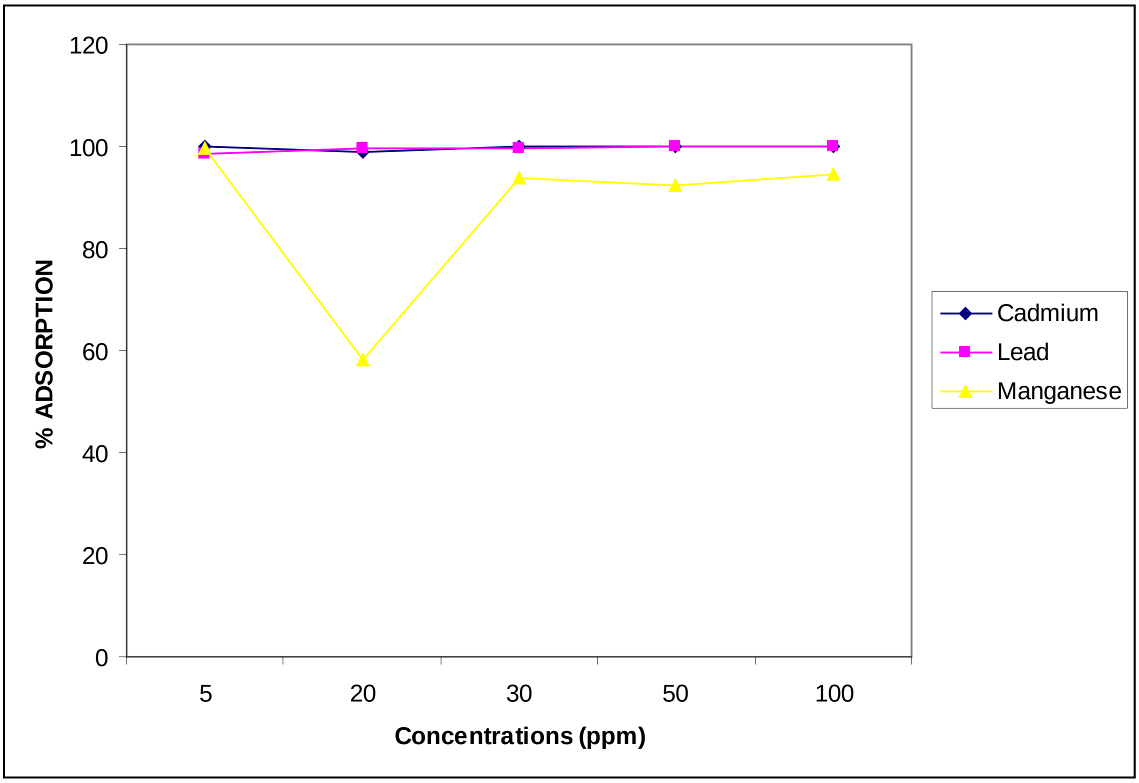


**Fig 4.17: Effect of metal concentration on % adsorption using pineapple peel**

The outcome of the experiment on the effect of metal concentration on % adsorption using 1.5 g of adsorbent at pH 7 for 30 minutes contact time (optimized parameters) from spiked deionised water is as shown in Figure 4.17 above. It could be seen that the concentration increase of (5, 20, 30, 50 and 100 ppm) does not have any effect on the adsorption rate of both Cadmium and Lead. This is because they were 100 % adsorbed across the evaluating metal concentrations. But the same cannot be said of Mn with 49 % adsorption at 20 ppm. The rate of its adsorption picked up again with an increase in concentration.

### 4.7.2 Using waste Bush tea

Result of the effect of metal concentration (Cd, Pb and Mn) on % adsorption using waste Bush tea at the optimal evaluated conditions from spiked deionised water is as shown in Figure 4.18 below:

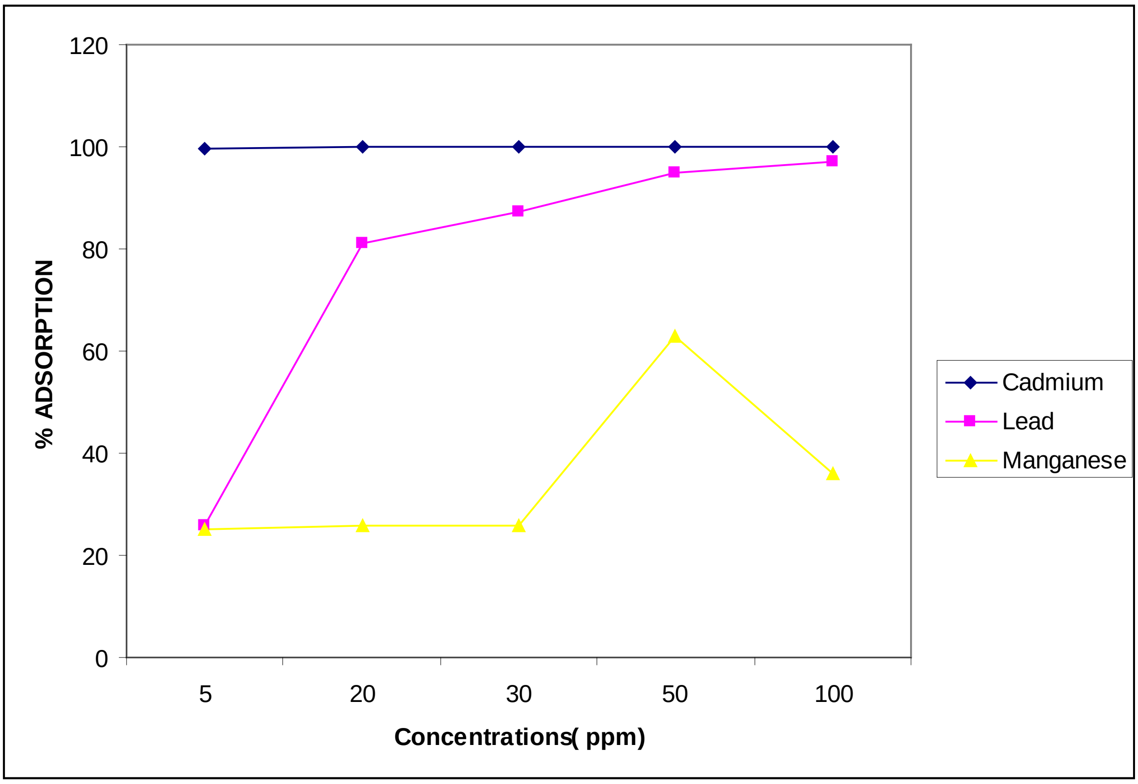


**Fig 4.18: Effect of metal concentration on % adsorption using waste bush tea**

Result of the experiment on the effect of metal concentration on % adsorption using the optimized parameters (1.5 g of adsorbent) at pH 6 and 30 minutes contact time from spiked deionized water is as presented above in Figure 4.18 . Similar to the results obtained for butternut and pineapple peel adsorbents, Cadmium was highly adsorbed at 99.90% % irrespective of an increase in concentration of the metal while Lead follows the same pattern of the other adsorbent and the highest adsorption for manganese was achieved at 50 ppm.

### 4.7.3 Using Butternut peel (*Juglans Cinerea*)

Result of the effect of metal concentration (Cd, Pb and Mn) on % adsorption using waste Butternut peel at the optimal evaluated conditions from spiked deionised water is as shown in Figure 4.19b below:

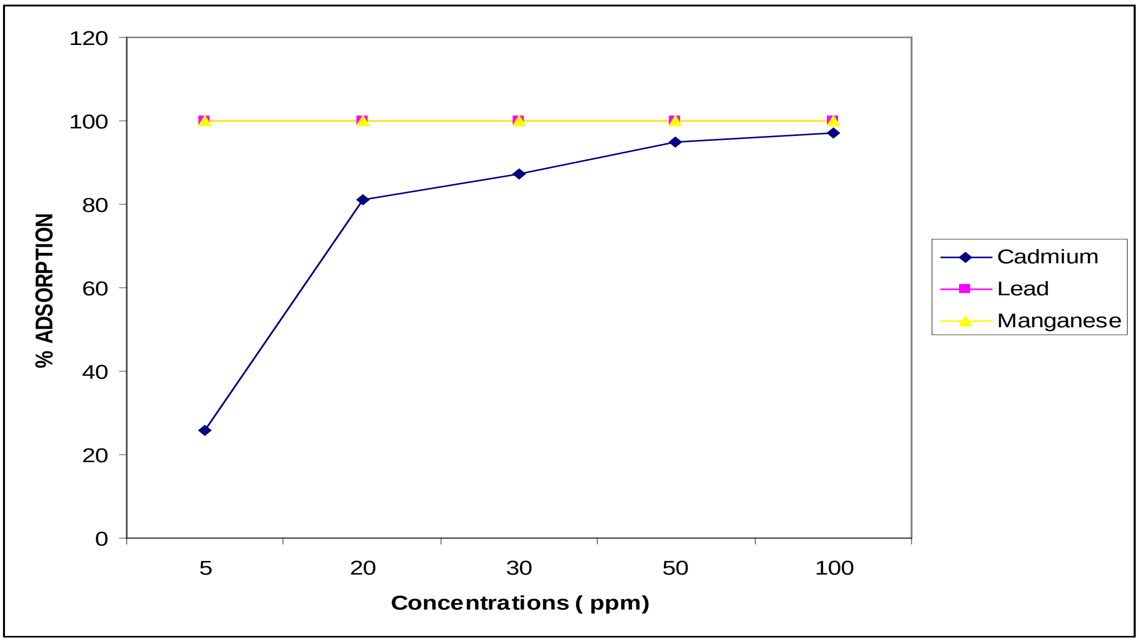


**Fig 4.19: Effect of metal concentration on % adsorption using butternut peel (*Juglans cinerea*)**

Result of the experiment on the effect of metal concentration on % adsorption using the optimized parameters (1.5 g of adsorbent), at pH 6 and 30 minutes contact time from spiked deionized water is as shown in Figure 4.19 above. > 99 % adsorption was recorded at 5 ppm for Mn and Pb but gradually decreases across other evaluated concentrations. The pattern of Cd adsorption in the other hand reduces from 100 ppm to 5 ppm. The effect of this pattern might be due to low the adsorption site on the adsorbent which had been occupied by Mn and Pb.

## 4.8. REGENERATION OF THE USED ADSORBENTS

### 4.8.1 Using Bush tea (*Athrixia Philicoide*)

Regeneration involves the time it takes to remove adsorbed metals from the already used adsorbent. The rationale behind the regenerating ofs the used adsorbent is to ensure a regular availability of sorbent and to reduce the volume of wastes adsorbent that will eventually be disposed.

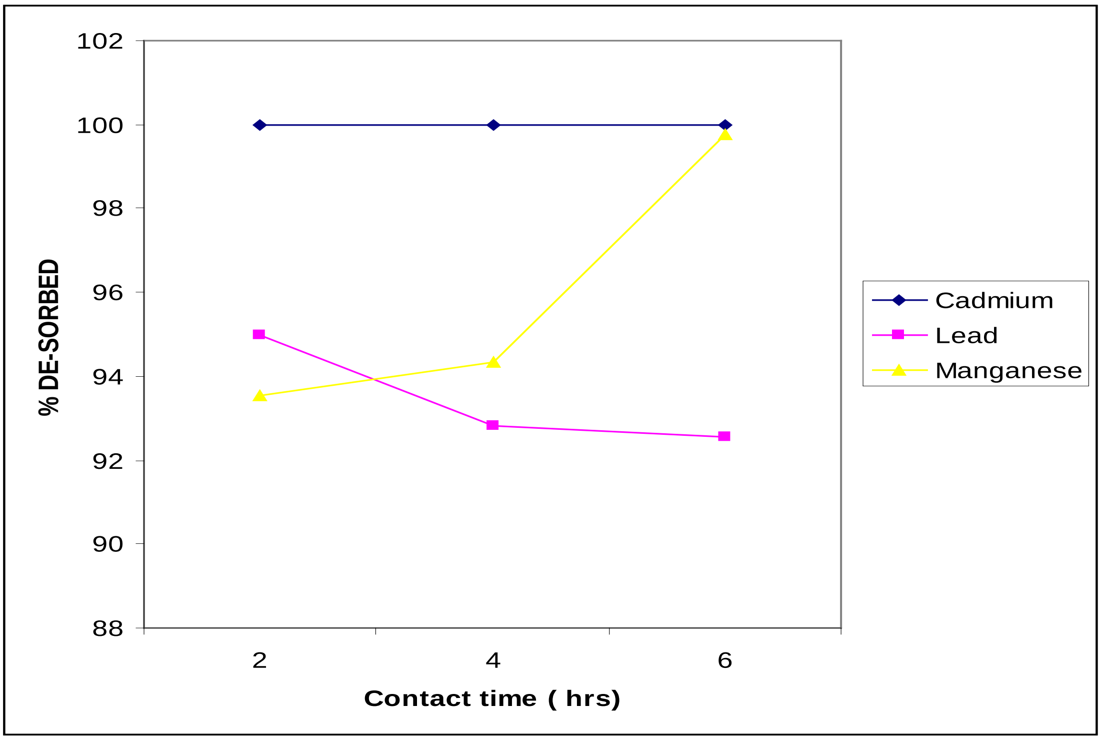


**Fig 4.20: Regeneration of bush tea (*Athrixia philicoide*)**

From the Figure above, it could be seen that the reaction of cadmium to the desorption process was negative while a slow desorption across the contact time was recorded for the three metals.

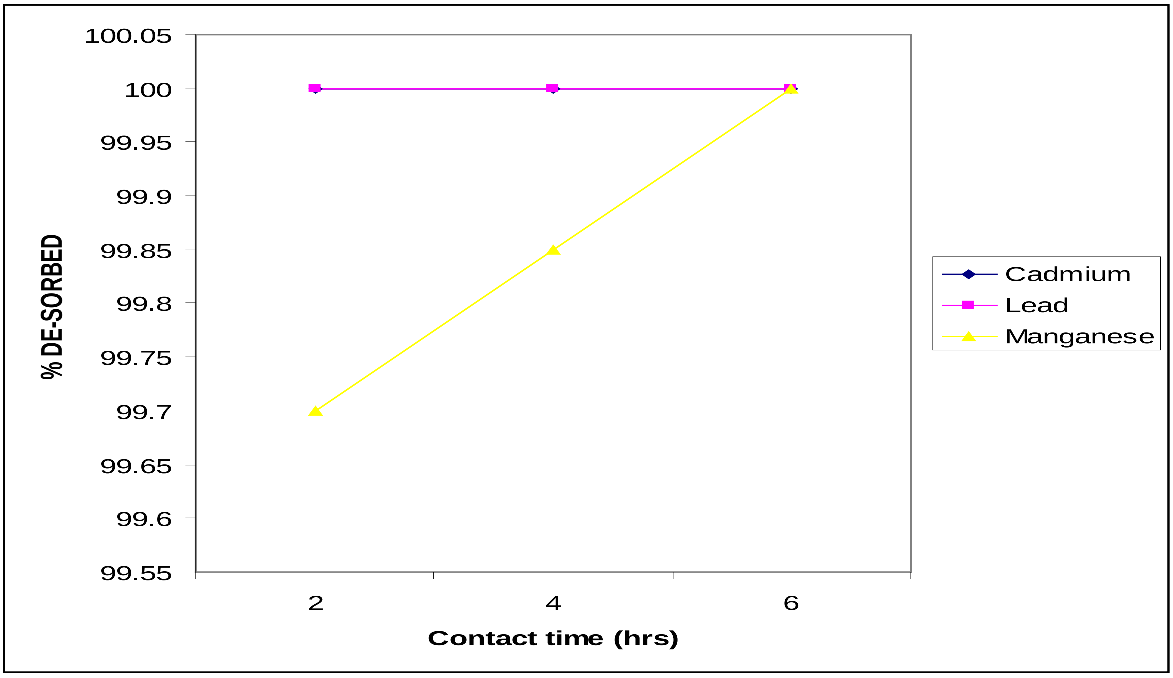


**Fig 4.21: Regeneration of pineapple peels**

From the Figure above, cadmium and Lead were desorbed at the same pace and this account for Pb overlapping with cadmium. The rate of de-sorption for Mn was increased as the contact time between the used adsorbent and the dilute nitric acid was decreased.

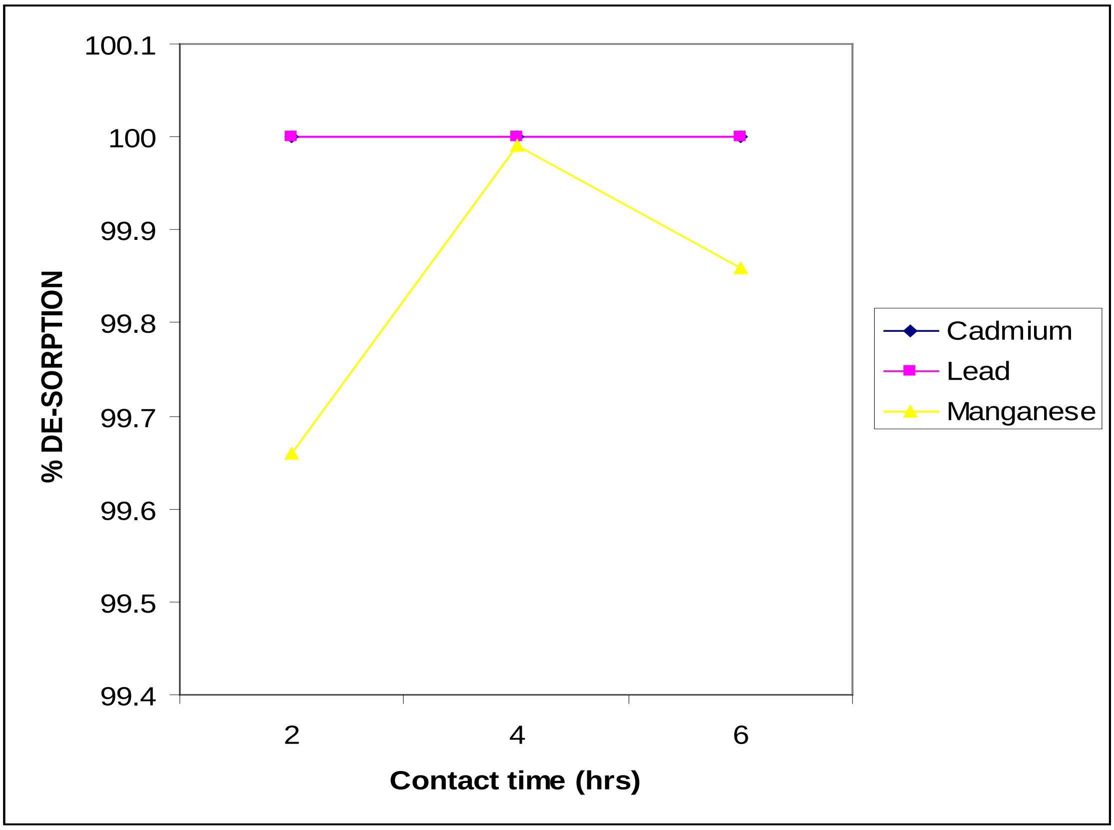


**Fig 4.22: Regeneration of used butternut waste**

From Figure 4.22 above, both Cadmium and Lead recorded similar desorption pattern with an overlap of their desorption line peaks. This is similar with the pattern recoded for the Bush tea and pineapple waste regeneration patterns.

### 4.9. Application of optimized method and adsorbent on raw water (wastewater)

The optimized adsorption conditions were applied to the uptake of the selected metals using raw water samples. The essence of this is to reveal whether the conditions, including the adsorbents are applicable for the removal of the toxic metals from environmental water samples.

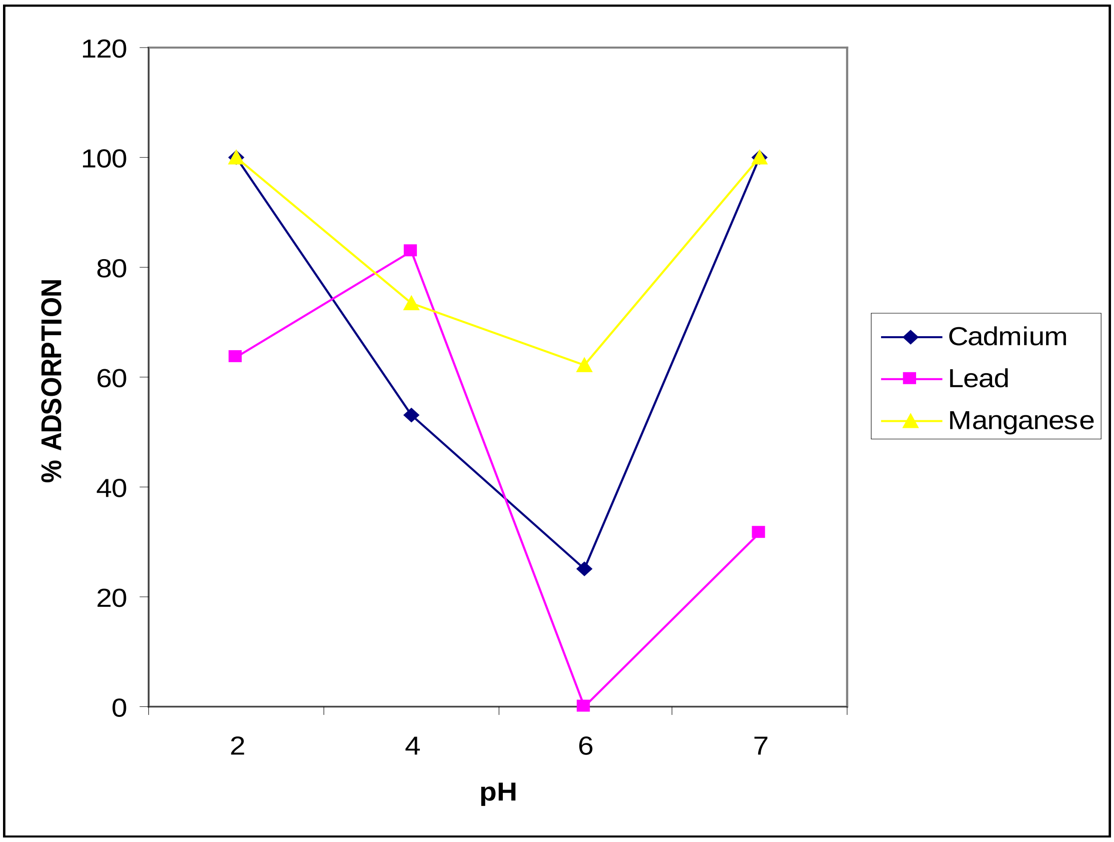


**Fig 4.23: % sorption of metals from wastewater using the bush tea**

Cd and Mn were highly adsorbed at pH 2 and 7 with an average adsorption at pH and 6 for Mn. pH 4 favours the adsorption of Pb from the wastewater with > 80 % adsorption. No adsorption of Pb was however evident at pH 6 with a poor sorption at pH 7 (~ 30 %).

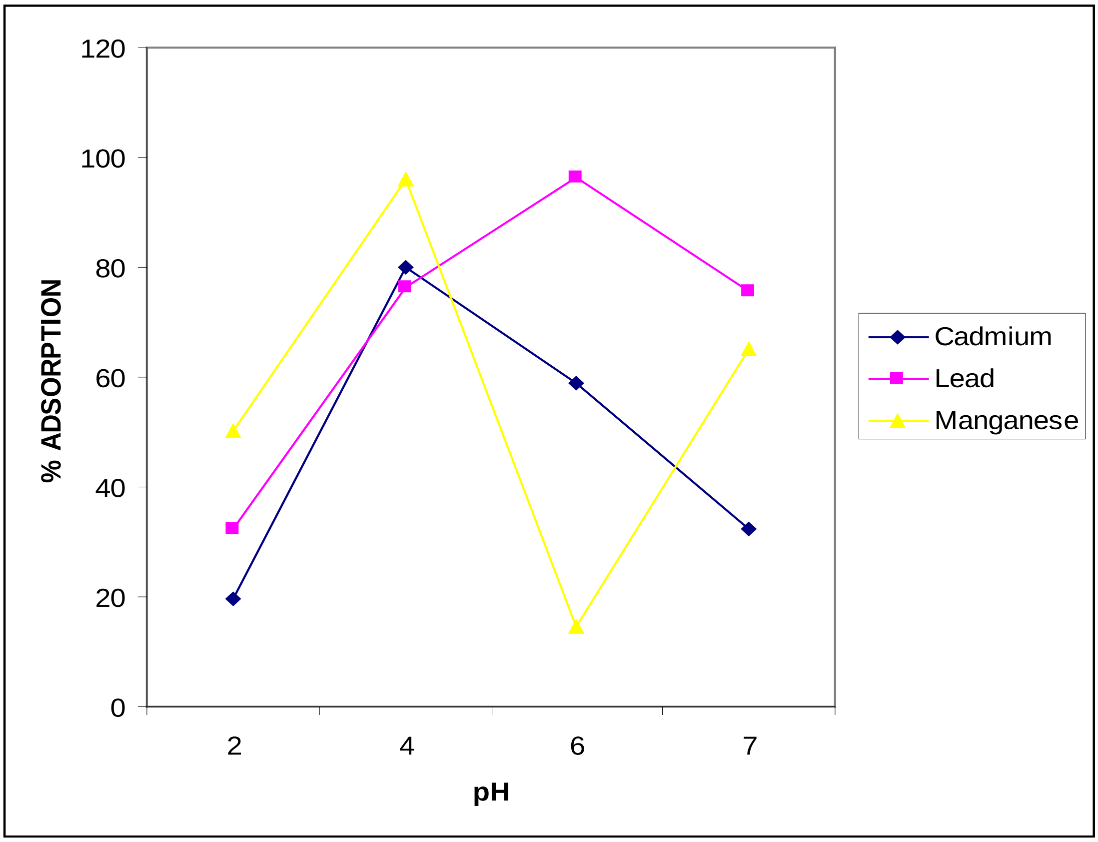


**Fig 4.24: % sorption of metals from wastewater using butternut peel**

The highest sorption of Pb and Mn (~98 %) at pH 4 was obtained with the adsorbent from the butternut peel as presented in Fig 4.24 above. An appreciable sorption was also obtained with Cd and Pb at pH 4 which revealed that this pH favours the uptake of these metals. Poor adsorptions also were recorded with the three metals at pH 2, 6 and 7.

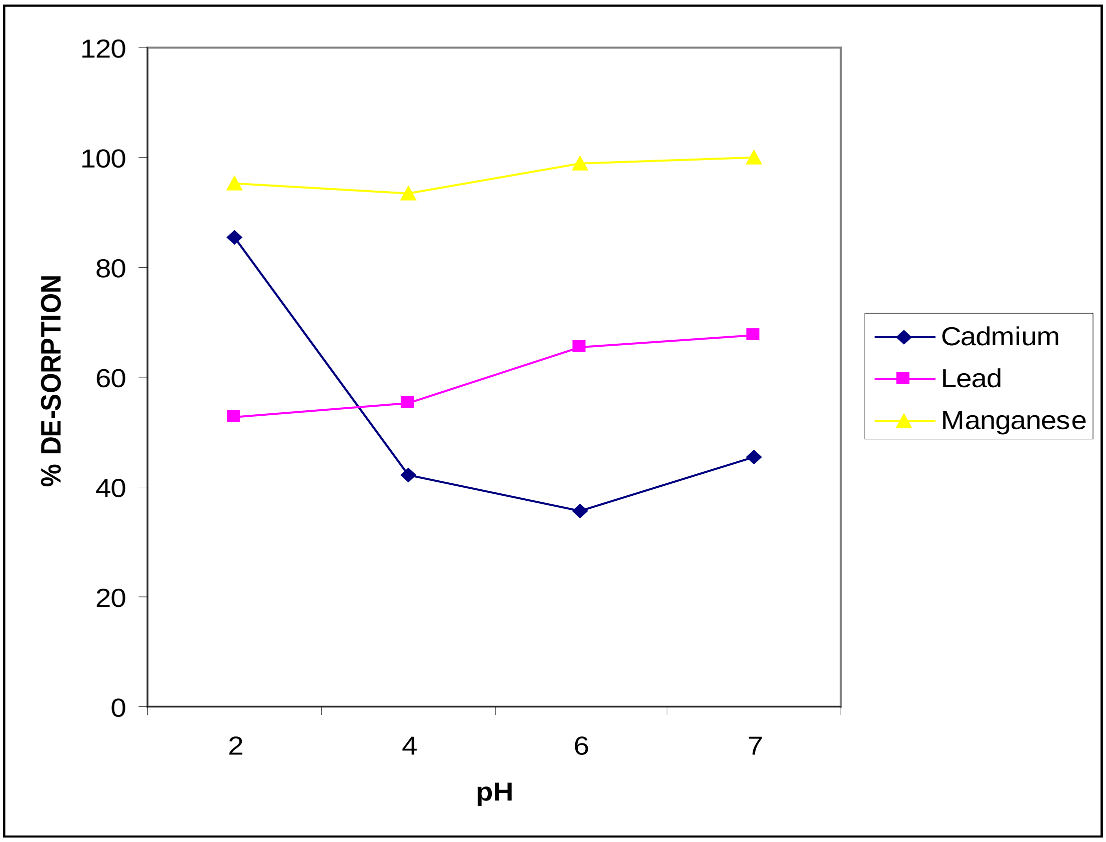


**Fig 4.25: % sorption of metals from wastewater using waste pineapple peel**

From Fig 4.25 above, Mn was highly adsorbed (> 98 %) at all the evaluated pH range. Quantitative adsorption was also recorded by Cd with an adsorption of 85.4 % at pH 2. An average sorption range of 60 – 65 % was recorded by Pb across the evaluated pH range.

## 4.10. Effects of pH on % of oxyhalides adsorbed from spiked de-ionised water

**4.10.1 Effect on Bromate ion ($BrO_3^-$):** Using wastes from Bush Tea (*Athrixia philicoide)*, pineapple peel (*Ananas comosus*) and Butternut peels (*Cucurbita Moschata*).

Result of the effect of pH on the adsorption of Bromate ($BrO_3^-$) by waste from bush tea is presented in Figure 4.26 below:

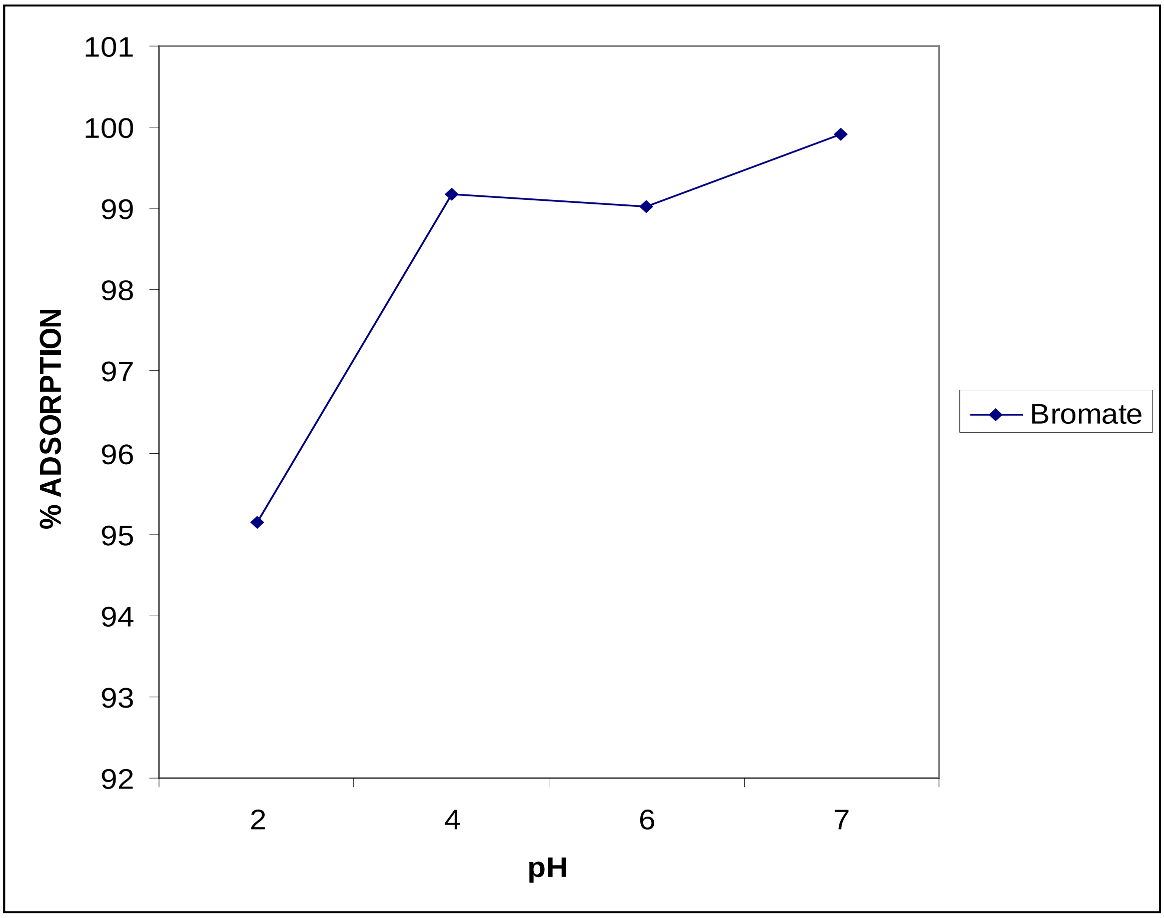


**Fig 4.26: Effects of pH on oxyhalides adsorption from spiked de-ionised water using Bush tea**

Generally, quantitative adsorption of bromated ion by the adsorbent was obtained as presented in Fig 4.26; however, the pH still had an effect on the relative amount of this ion. The % adsorption pattern was 99.5, 99.2, 99.0 and 95 % at pH 7, 4, 6 and 2 respectively. Although quantitative, it could still be seen that a low pH of 2 has an effect on the sorption of the metalloid by the adsorbent.

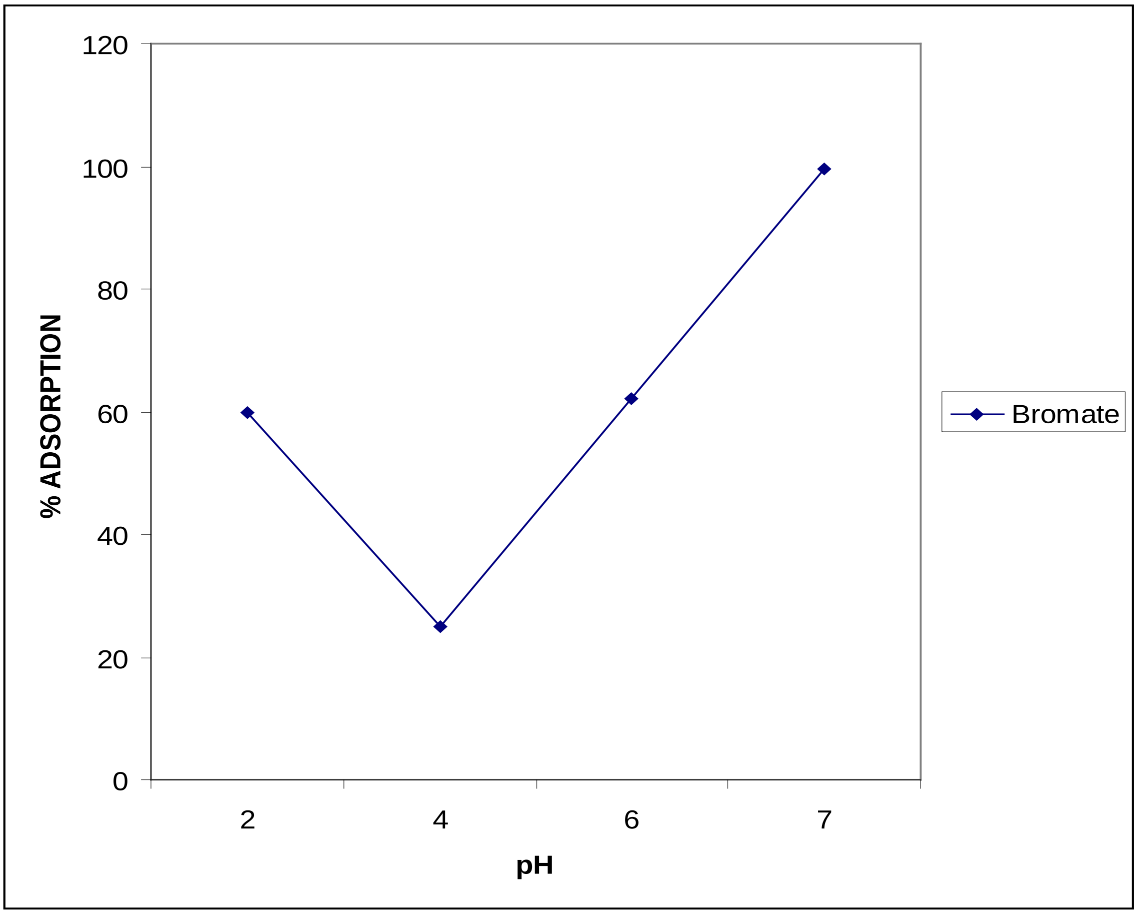


**Fig 4.27: Effects of pH on oxyhalides adsorption from spiked de-ionised water using pineapple peel**

From the Fig 4.27 above, a very good sorption of 98.9 % of the bromated ion was sorbed by the adsorbent (waste pineapple peel) at pH 7. An average adsorption of 65 % and 60 % were obtained at pH 6 and 2 respectively. A poor sorption of the metalloid was however recorded at pH 4. In one word, it could be inferred that this plant-based waste adsorbent is applicable for the removal of the bromated ion from aqueous medium.

In Figure 4.28, the highest adsorption of about 99 % was recorded at pH 2 and 7. This is followed by 83 % adsorption at pH 4 and about 64 % sorption at pH 6.

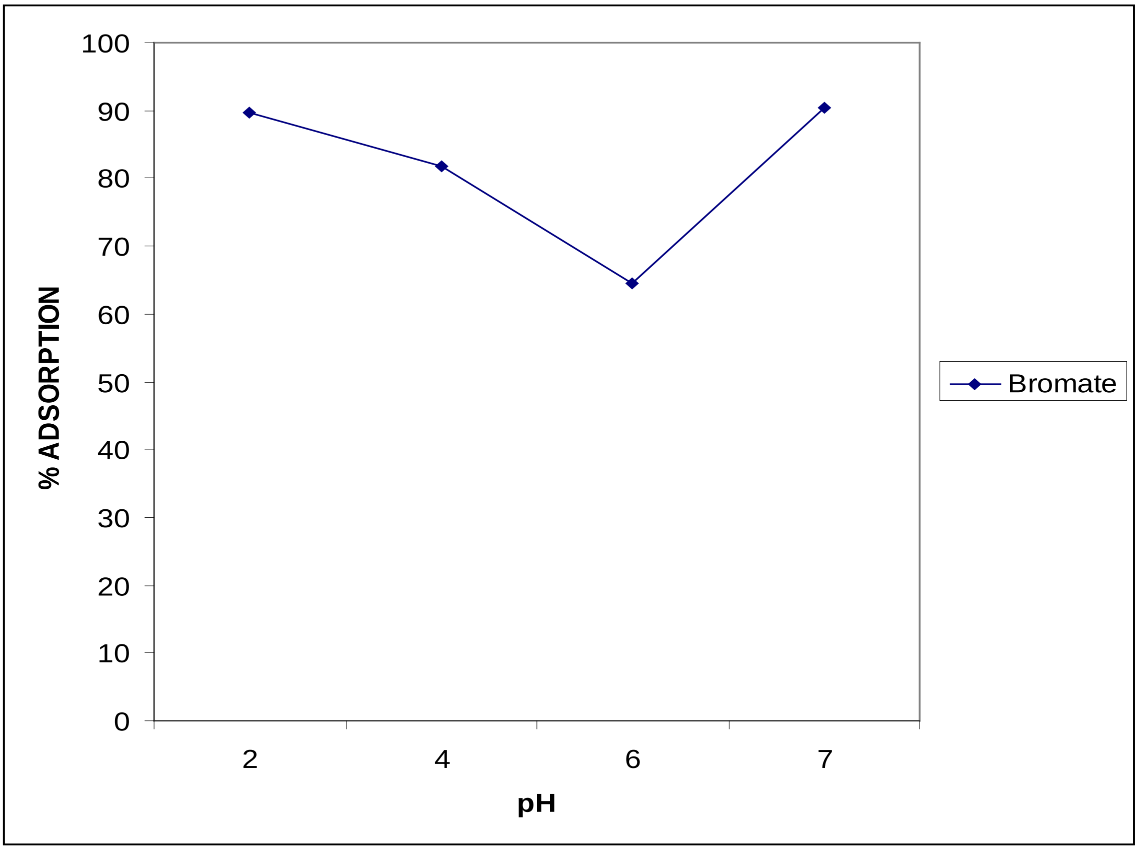


**Fig 4.28: Effects of pH on oxyhalides adsorption from spiked de-ionised water using Butternut peel**

### 4.11: % of adsorption of chlorate ions ($ClO_3^-$) from spiked deionised water using the evaluated plant-based adsorbents.

From the Figure 4.30 below, the highest adsorption of about 99.2 % was achieved at pH 2 using waste from the bush tea, while the lowest adsorption of 2 % was recorded at pH 4. The rate of sorption rose again after pH 4 to an adsorption of 35 and 64 % at pH 6 and 7 respectively. This revealed that the adsorbent could be quantitatively used for the removal of the chlorate ion from aqueous medium.

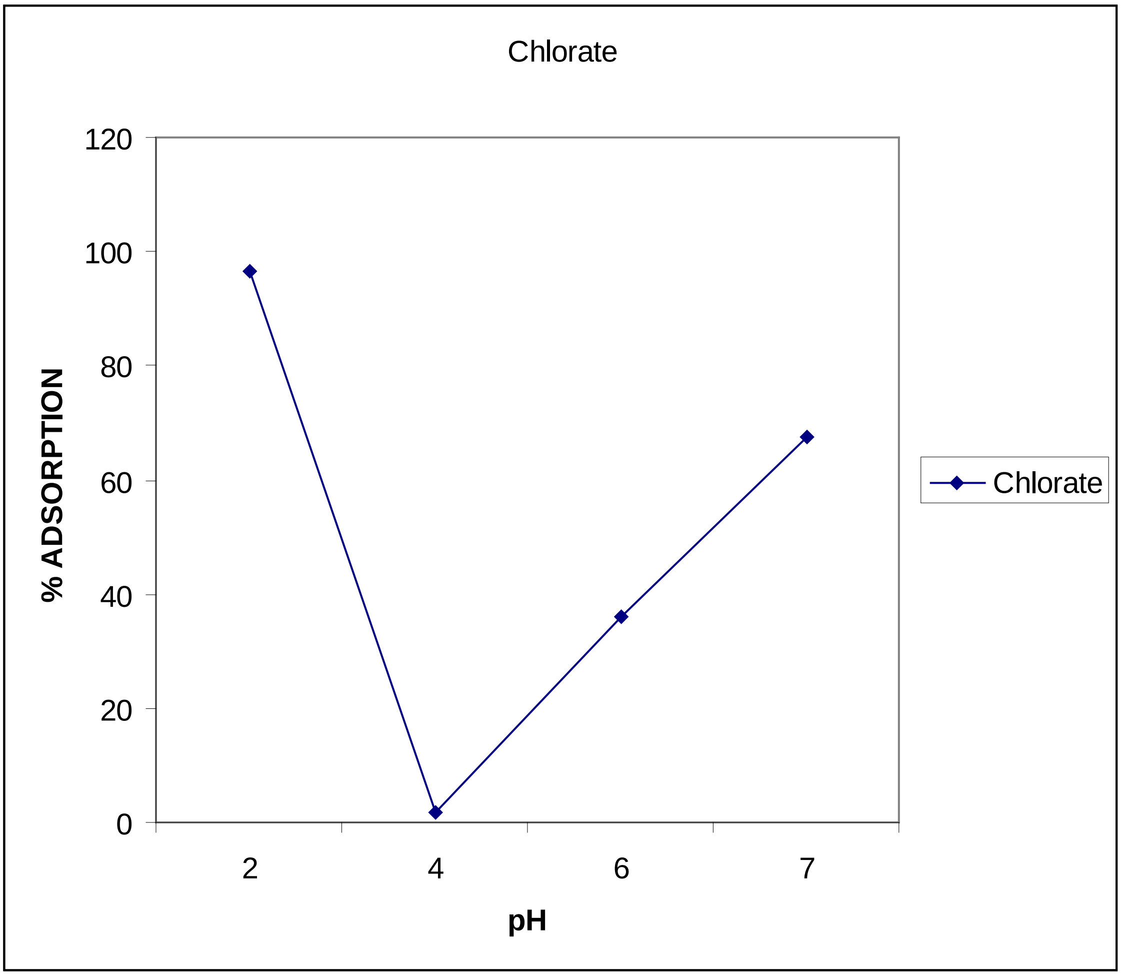


**Fig 4.29: Effects of pH on chlorate adsorption from spiked de-ionised water using Bush tea *(Athrixia Philicoide*)**

Figure 4.30 below shows the highest adsorption of about 89.8 % of the ion at the low pH of 2. However, a poor sorption of the metalloid was obtained at other pHs. This ranged from 5, 12 and 10 % adsorption at pH 4, 6 and 7 respectively.

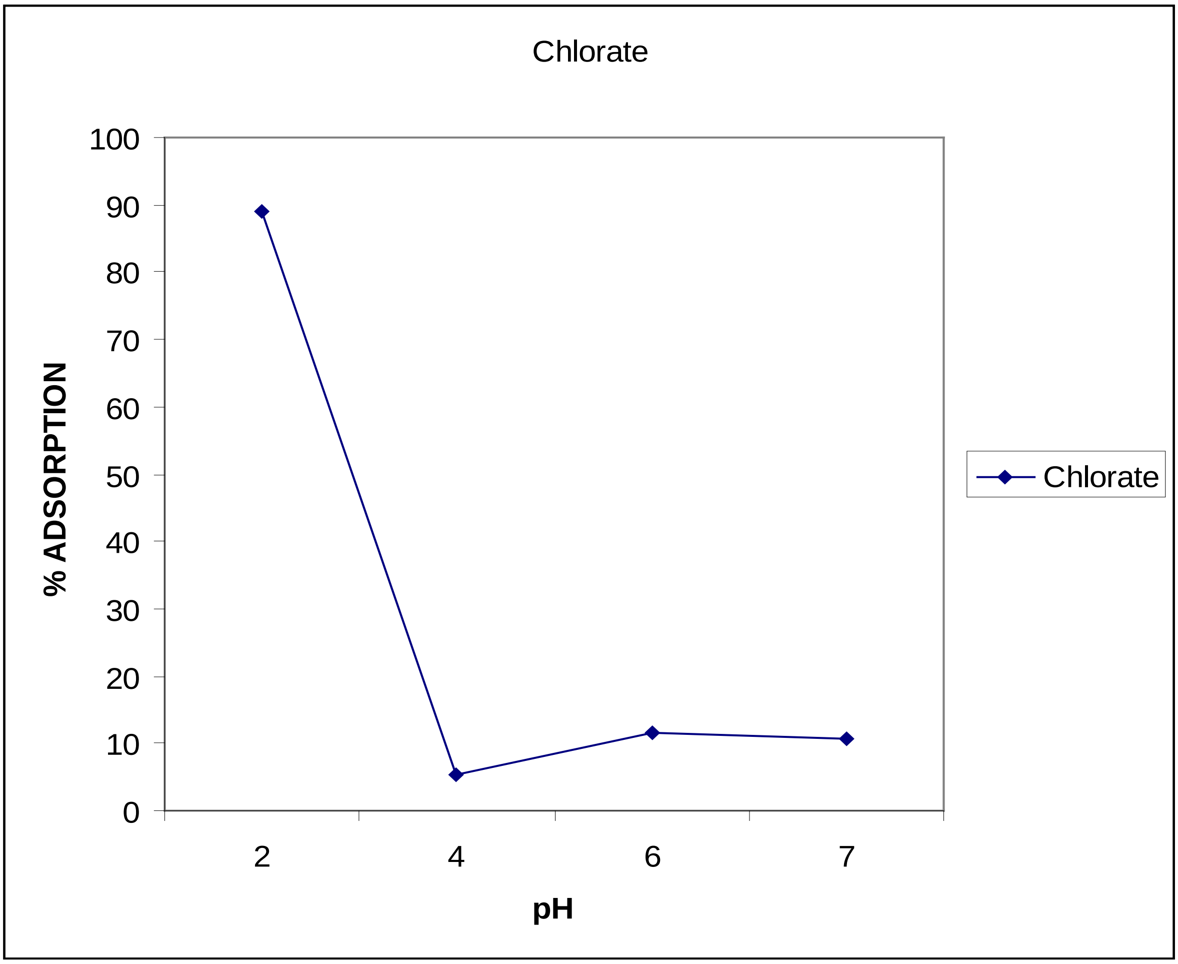


**Fig 4.30: Effects of pH on chlorate adsorption from spiked de-ionised water using pineapple peel (*Ananas Comosus*)**

Figure 4.31 below shows the highest quantitative adsorption of the chlorate ion at 98 % at pH 2 while the lowest was at pH 7 which gave an adsorption of 4.12 %. Similarly, a poor adsorption of about 8 % was recorded at pH 4 for the ion while an average sorption of 55 % was obtained at pH 6. It could then be concluded that the removal of the chlorate ion from aqueous stream is most applicable at pH 2.

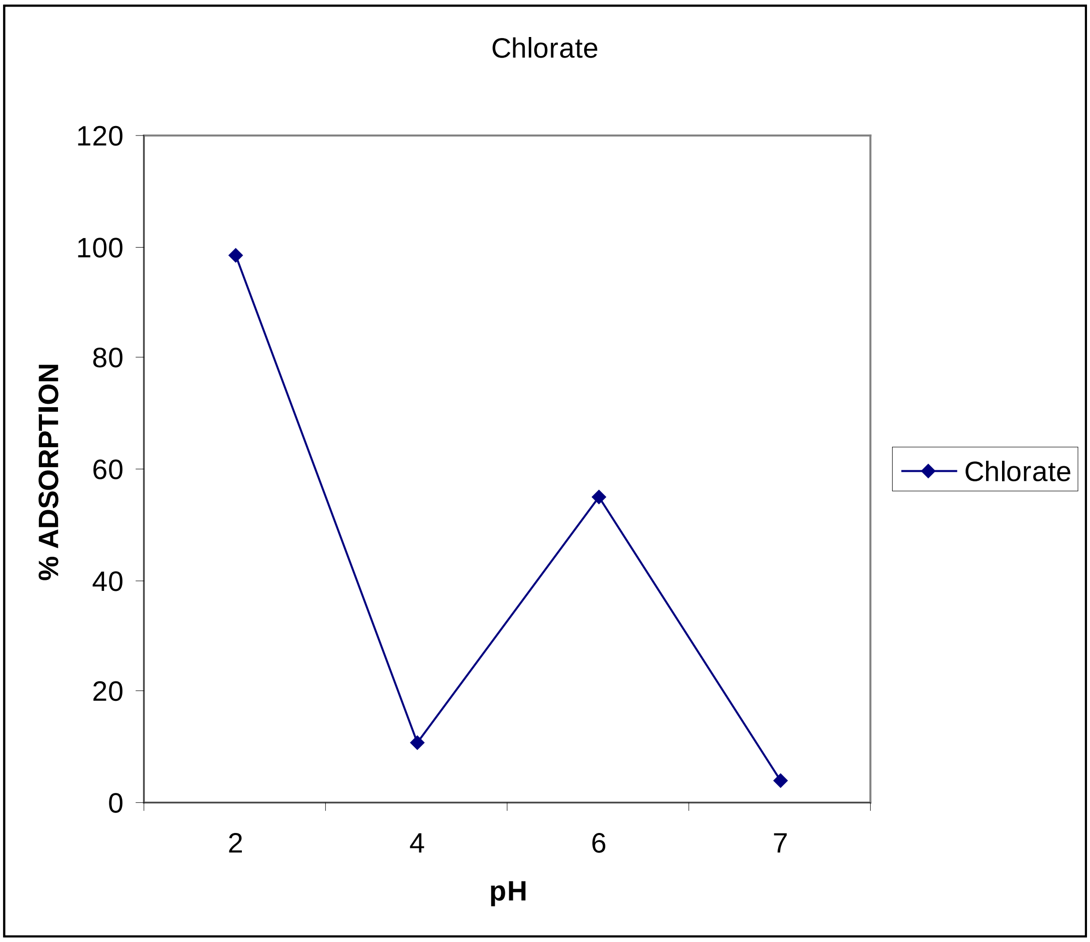


**Fig 4.31: Effects of pH on chlorate adsorption from spiked de-ionised water using butternut peel (*Cucurbita Moschata)*)**

### 4.12: % of adsorption of iodate ions from spiked deionised water using the evaluated plant-based adsorbents.

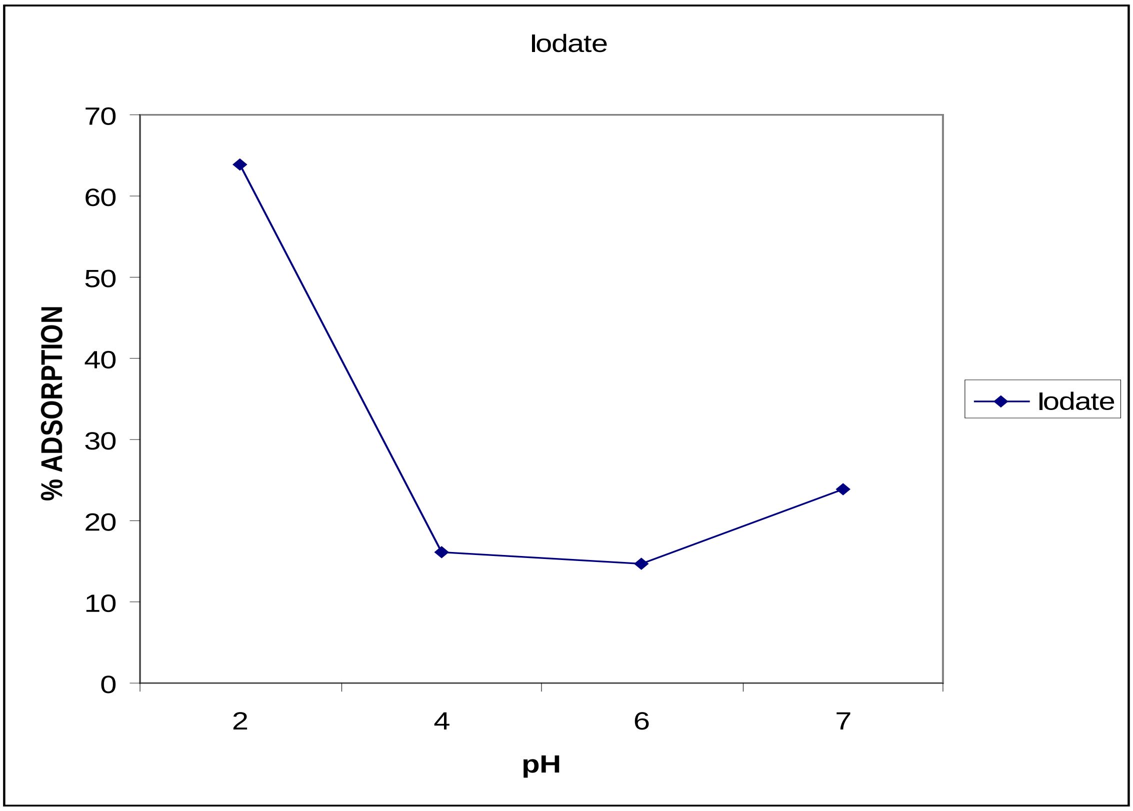


**Fig 4.32: Effects of pH on chlorate adsorption from spiked de-ionised water using waste from the bush tea**

Fig 4.32 above shows the highest adsorption of 63.89 % of the iodate ion at pH 2 while a poor sorption of this ion was obtained at other evaluated pHs. 22.5, 15 and 14.70 % adsorption were obtained at pH 7 4 and 6 respectively. pH 2 seems to favour the sorption of the analyzed metalloids from aqueous system.

Fig 4.32 reveals the sorption efficiency of the pineapple waste as appropriate for the removal of iodate ion from aqueous system. A Quantitative adsorption of 95.02 % occurred at pH 4 while the lowest adsorption of 18.25 % was obtained at pH 7.

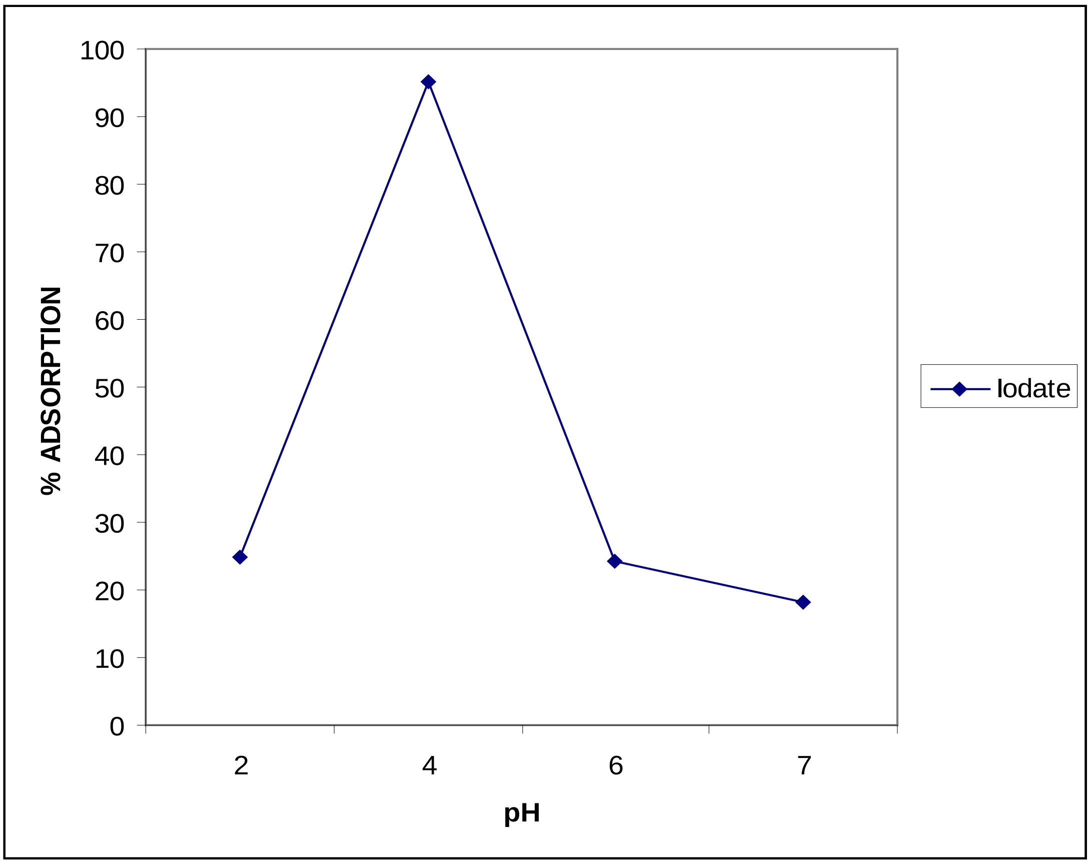


Fig 4.33: Effects of pH on iodate adsorption from spiked de-ionised water Using pineapple peel

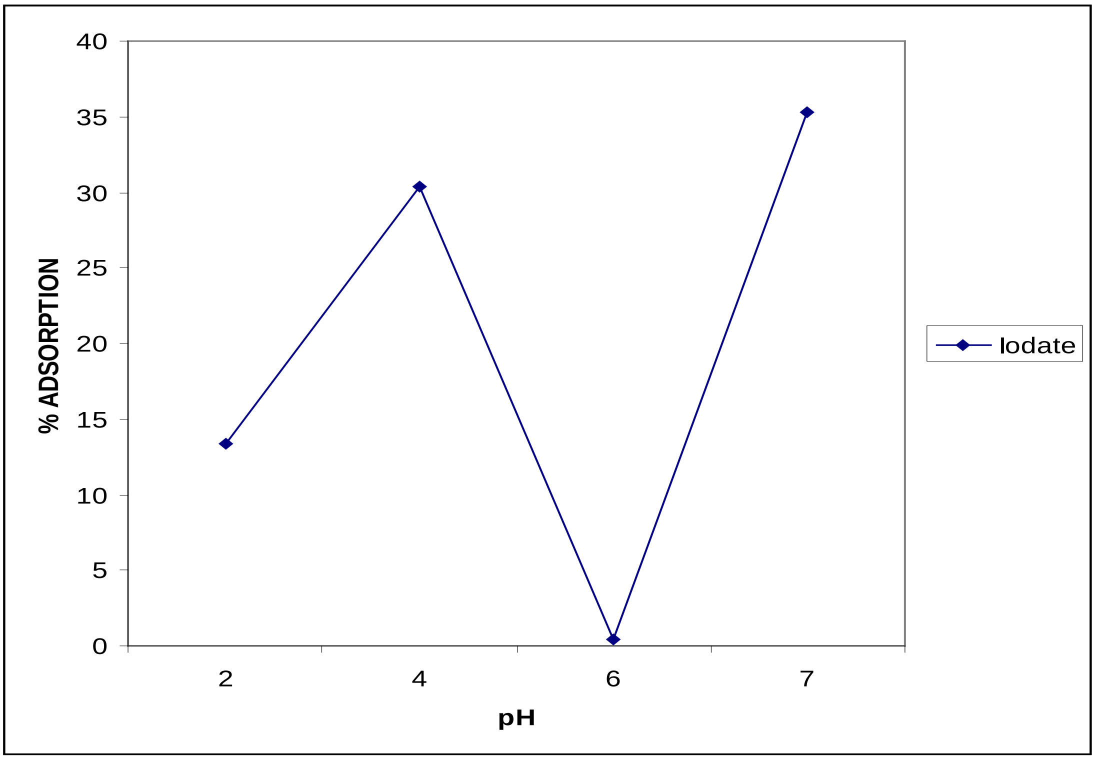


Fig 4.34: Effects of pH on iodate adsorption from spiked de-ionised water

**Using butternut peel (*Juglans* cinerea)**

Generally, poor adsorption of the iodate ion was observed with the waste from butternut peel. As presented in Fig 4.34 above, sorption of 35 % at pH 7; 32 % at pH 4; 13 % at pH 2 and finally 2 % at pH 6. It could be collectively inferred that this waste adsorbent is not suitable for the removal of iodate ion from aqueous media.

## 4.13. Effect of amount of adsorbents on sorption efficiency of the oxyhalides (bromate, chlorate and iodate) from spiked de-ionised water by the evaluated plant-based waste adsorbents (Bush tea (*Athrixia philicoide*), pineapple peel (*Ananas comosus*) and butternut peel (*Cucurbita Moschata*) on.

### 4.13.1: Effect of amount of adsorbent on % adsorption of bromated ion from deionised water.

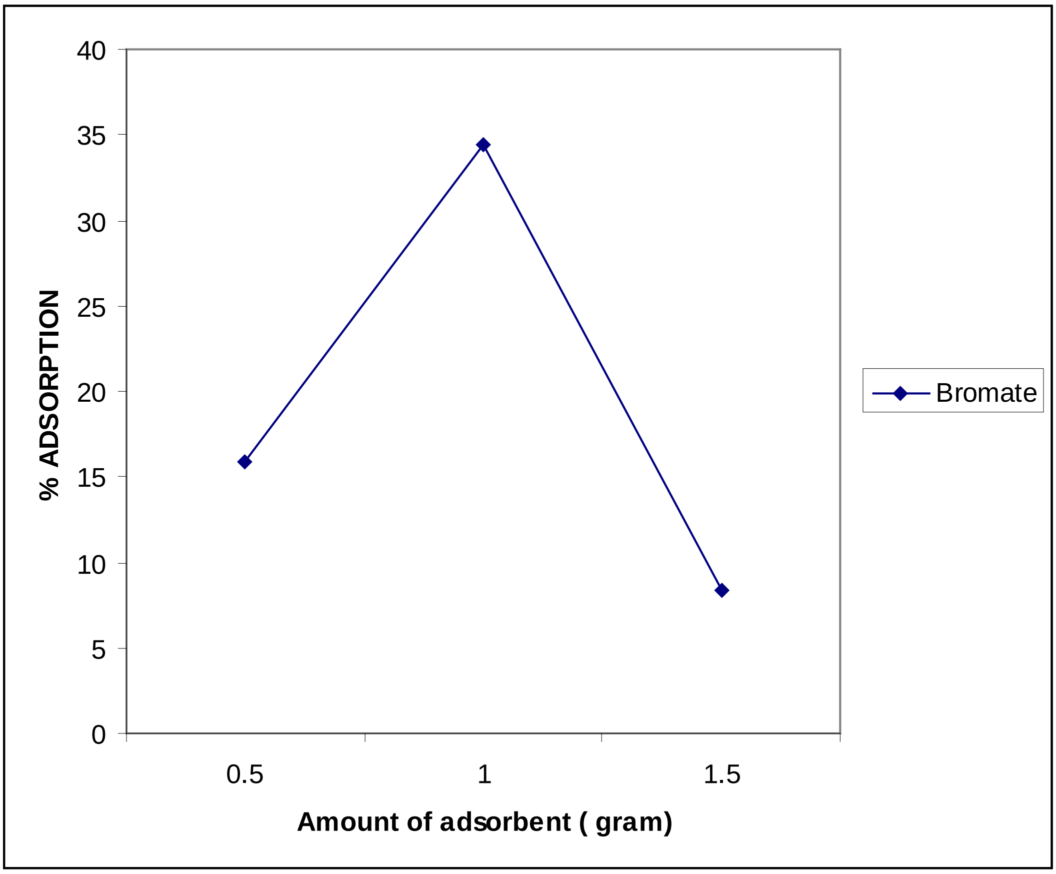


**Fig 4.35: Effect of amount of bush tea on adsorption of bromate ion from Spiked de-ionised water**

From Fig 4.35 above, an adsorption of 34.40 % at pH 7 using the optimsed evaluation parameters was recorded by the bromated using 1.0 g of the plant-based waste adsorbent. This was followed by 15.1 % adsorption with 0.5 g and 8 % with 1.5 g of the adsorbent respectively. It can be inferred that this efficiency of sorption by this adsorbent is 6poor and therefore will not be applicable for the removal of the bromated ion from aqueous medium.

In Figure 4.36 presented below, the highest adsorption of 97.71 % occurred using 1.0 g of the adsorbent and the lowest was 78 % with 1.5 g of the adsorbent. 80.2 % adsorption was however recorded with 0.5 g of the adsorbent.

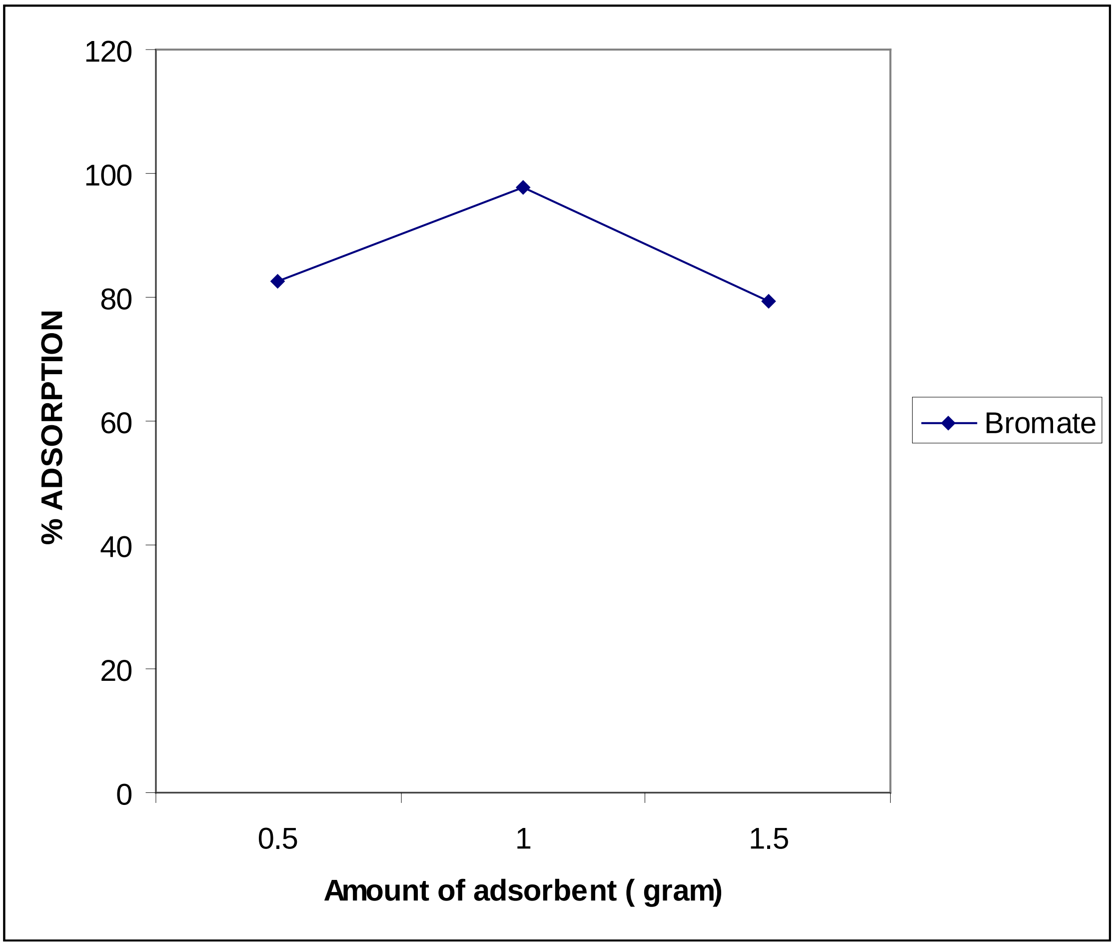


**Fig 4.36: Effect of amount of butternut peel (*Cucurbita Moschata*) on % adsorption of bromate ion from spiked de-ionised water**

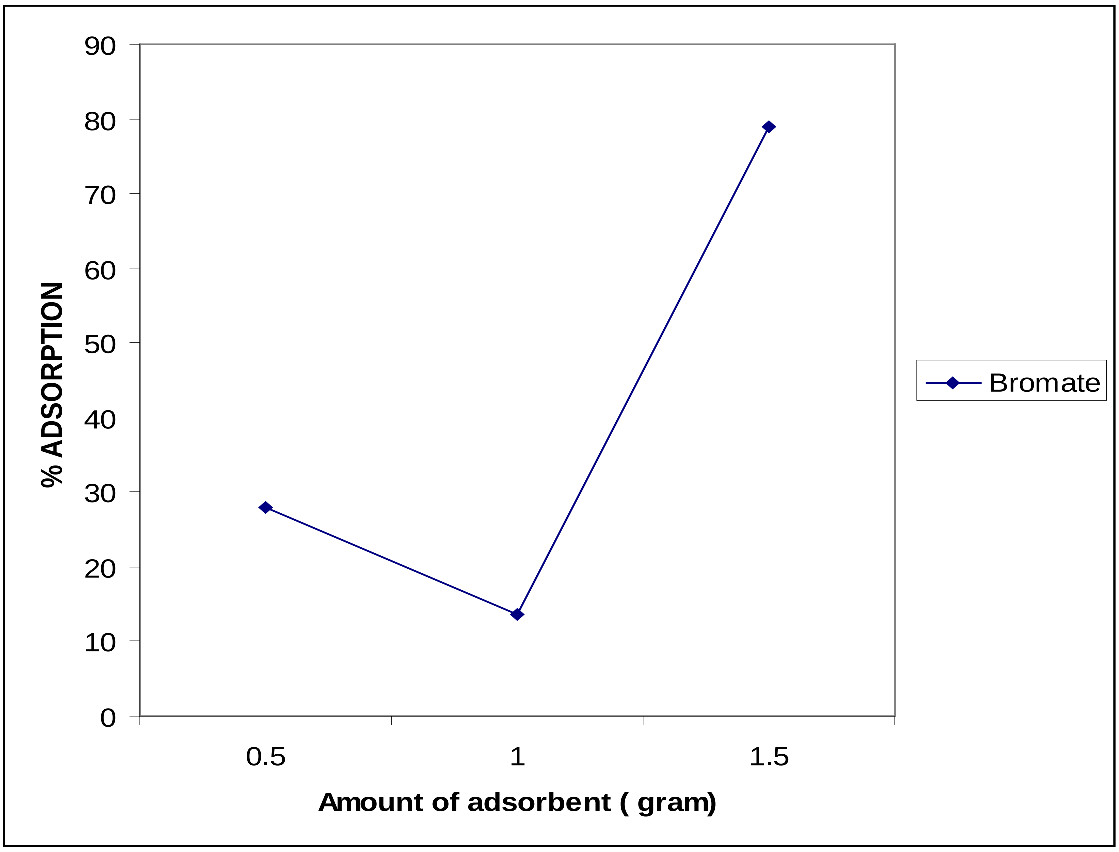


**Fig 4.37: Effect of amount of waste of pineapple peel (*Ananas Comosus*) on % adsorption of bromate ion from spiked de-ionised water**

Fig 4.37 shows that quantitative adsorption of 78.96 % was recorded with 1.5 g of the adsorbent while low sorption was obtained with 1.0 g (13.67 %) and 0.5 g (28 %) of the bromate ion.

### 4.14: Effect of amount of adsorbent on % adsorption of chlorate ion from deionised water using evaluated plant-based waste materials as adsorbents

Figure 4.38 below shows that the highest adsorption of 92.82 % using 0.5g of the adsorbent was obtained. Another quantitative adsorption of 88.2 % was also obtained with 1.0 g of the waste adsorbent while an average sorption of 51.07 % was recorded with 1.5 g of the adsorbent.

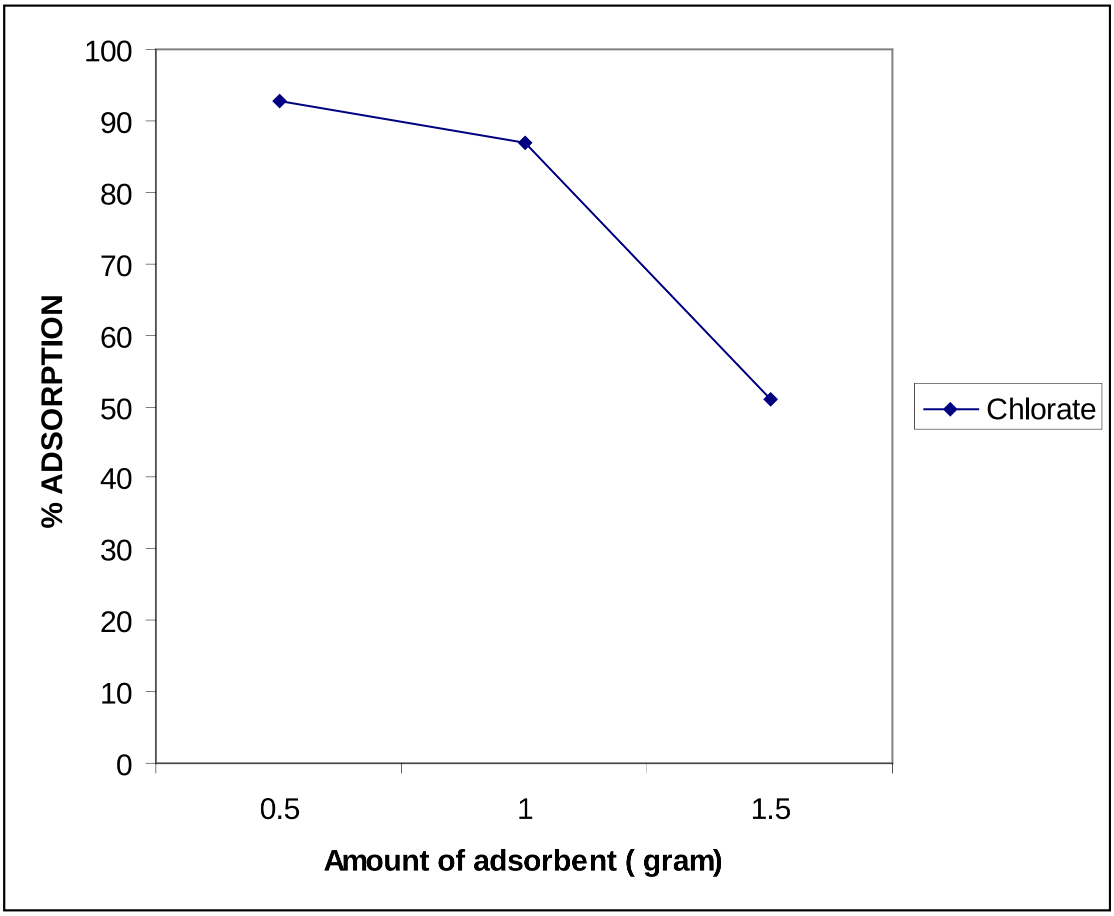


**Fig 4.38: Effect of amount of waste of butternut peel (*Cucurbita Moschata*) on adsorption of bromate ion from spiked de-ionised water**

From Figure 4.39 below, it could be observed that an appreciable quantitative adsorption was obtained with all the evaluated amount of the adsorbent. 98.71 %; 97.2 % and 77.4 % were obtained with 1.0, 1.5 and 0.5 g of the adsorbent respectively. Generally, it could be inferred that this adsorbent is suitable and applicable for the removal of chlorate ions from aqueous system.

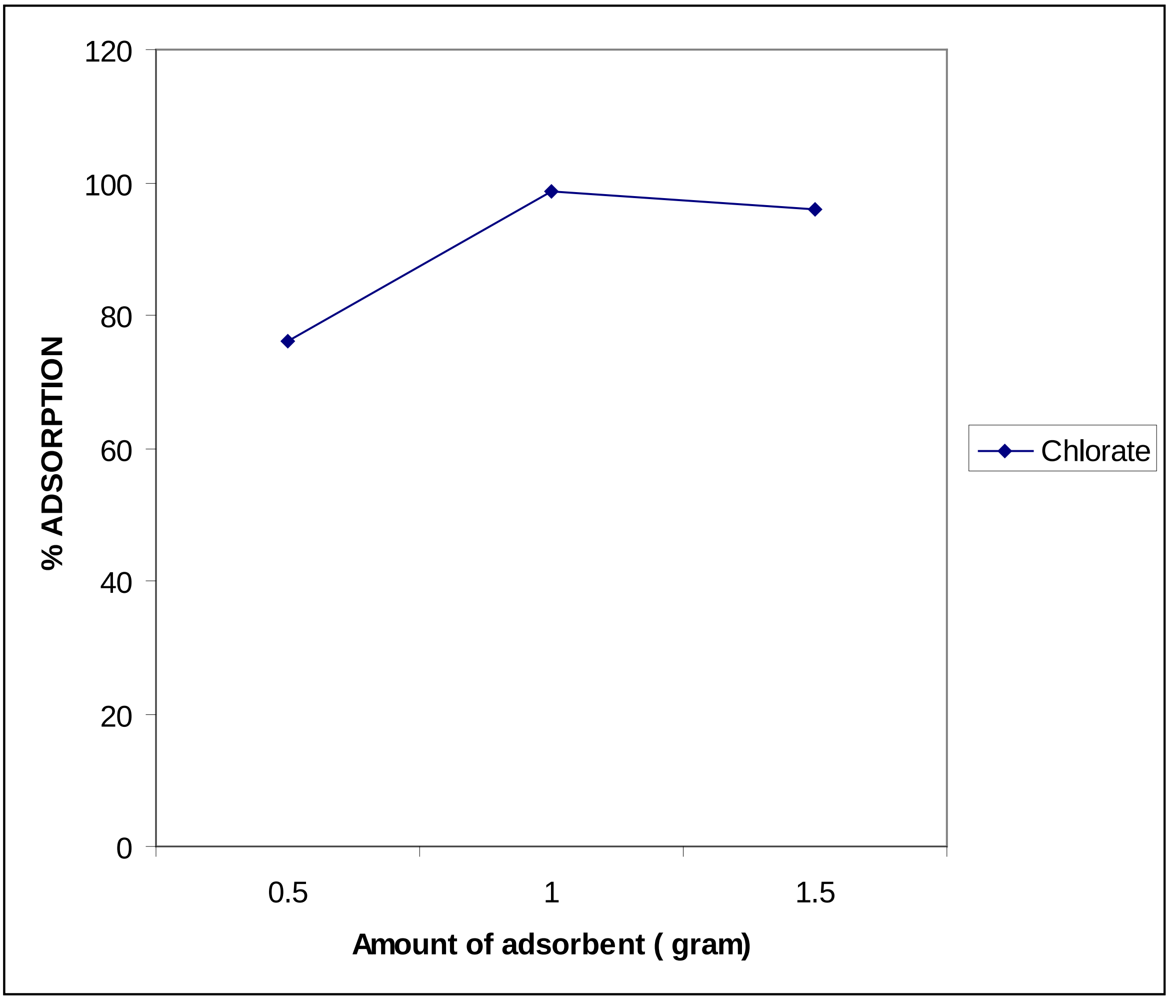


**Fig 4.39: Effect of amount of waste bush tea on adsorption of chlorate ion from spiked de-ionised water**

From Figure 4.39, quantitative adsorption was obtained with all the evaluated amount of the adsorbent. Highest adsorption occurred at 0.5gm with 97.33 %. This is followed by 88.2 % at 1.0 g and 86.88 % adsorption at 1.5 g of the adsorbent.

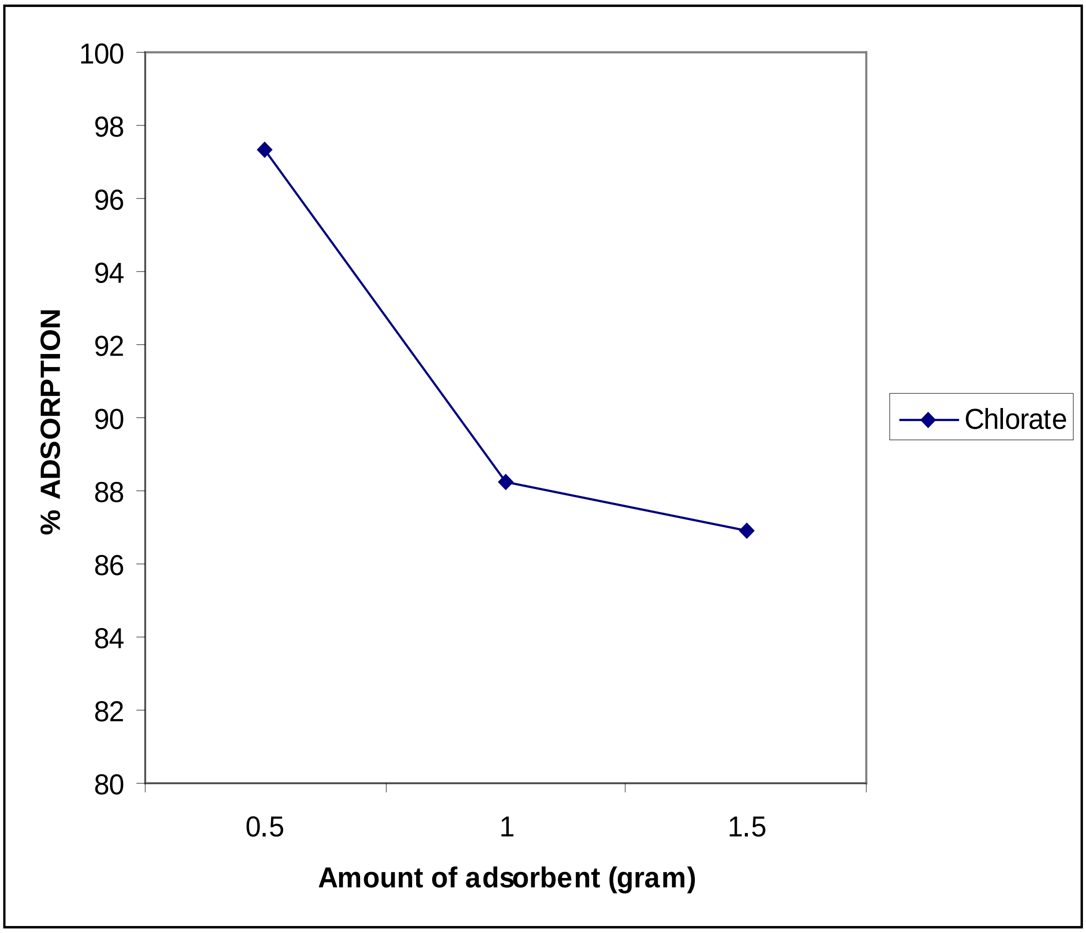


**Fig 4.40: Effect of amount of waste pineapple peel on adsorption of chlorate ion from spiked de-ionised water**

### 4.15: Effect of amount of adsorbent on % adsorption of iodate ion from deionised water using evaluated plant-based waste materials as adsorbents

Figure 4.40, it could be observed that a generally poor sorption of the iodate ion by the adsorbent was obtained. More so, the adsorption value reduces as the amount of adsorbent also reduces. The recorded adsorption follows the pattern of 27.83 %, 18.2 % and 6.44% in the order of 1.5 > 1.0 > 0.5 g of the adsorbent. Generally, it could be concluded that this waste material will not be suitable or applicable for the removal of iodate ion from aqueous system.

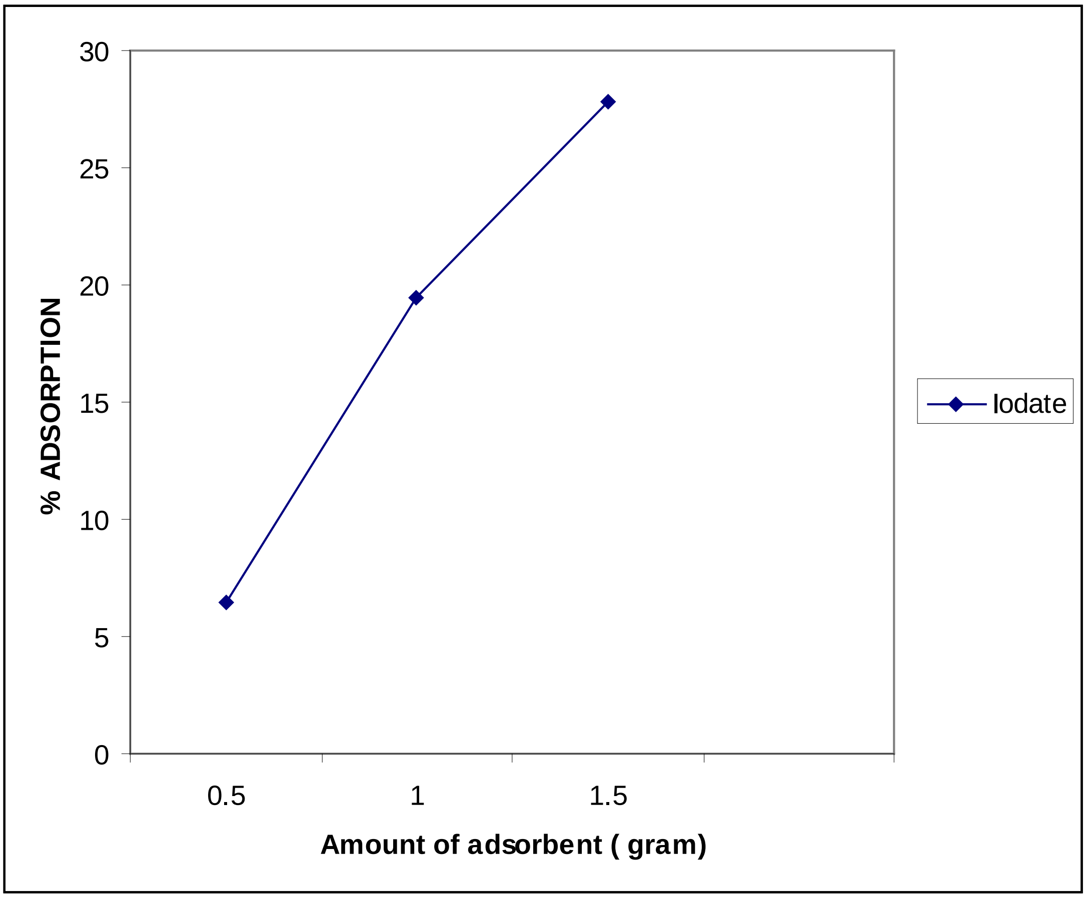


**Fig 4.41: Effect of amount of waste from the bush tea on adsorption of iodate Ion from spiked de-ionised water**

In Figure 4.41, the highest adsorption of 96.56 % occurred using 1.0 g of the adsorbent. This was followed by an adsorption of about 78.3 % at 1.5 g of the waste material while the lowest adsorption of 30.15 % using 0.5 g of the adsorbent was observed.

From the Fig above, similar trend or pattern of downward rate of adsorption from the highest value to the lowest value of amount of adsorbent to that of the bush tea in Fig 4..41 was observed. The highest adsorption rate was obtained for this adsorbent was 63.5 % with 1.5 g of adsorbent. This was followed by 21.2 % with 1.0 g and 6.93 % with 0.5 g of the adsorbent. Although quantitative adsorption was observed using

1.5 g, the value is lower than what was recorded with other evaluated waste adsorbents.

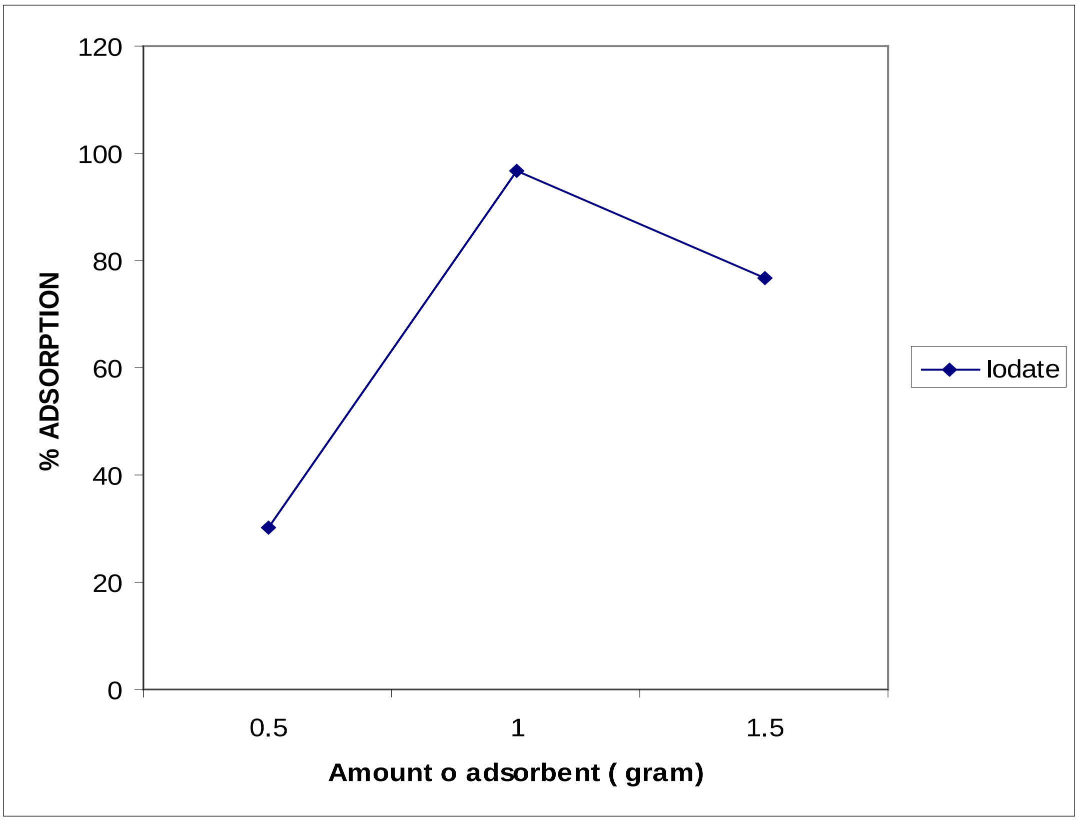


**Fig 4.42: Effect of amount of waste from the butternut peel on adsorption of Iodate ion from spiked de-ionised water**

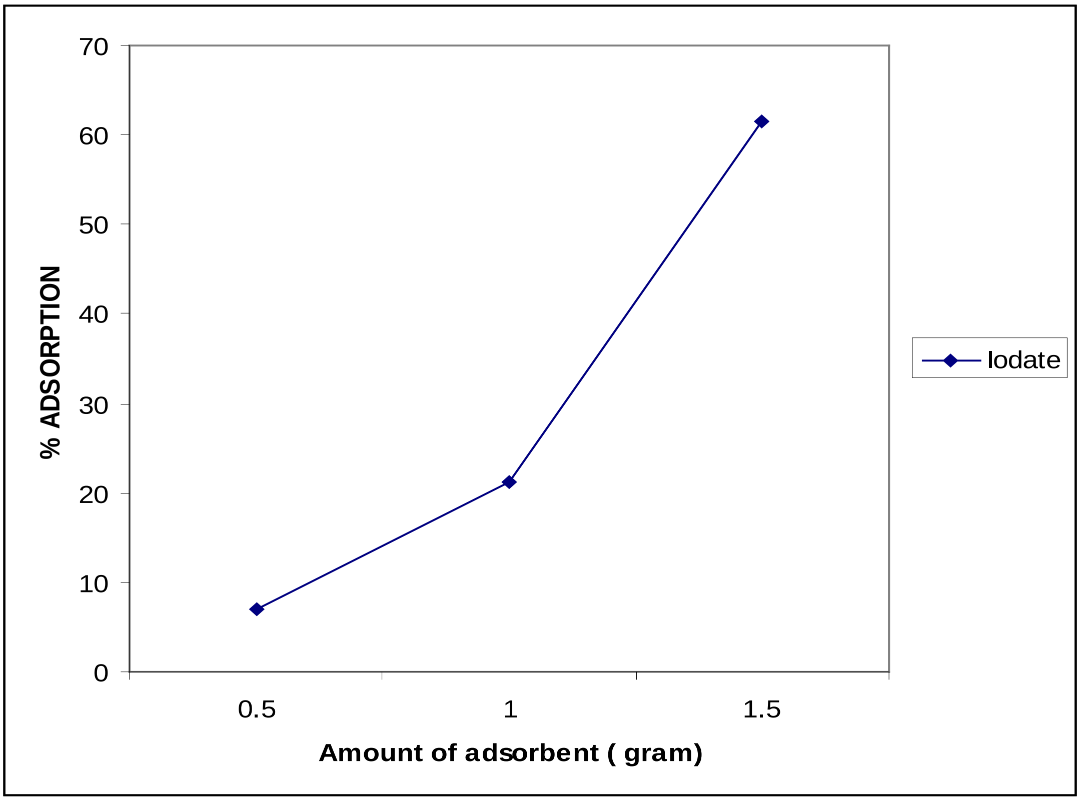


**Fig 4.43: Effect of amount of waste from the pineapple peel on adsorption of Iodate ion from spiked de-ionised water**

## 4.16 Effect of amount of adsorbents on sorption efficiency of the mixture of the evaluated oxyhalides (bromate, chlorate and iodate) from spiked de-ionised water by the evaluated plant-based waste adsorbents.

### 4.1.6.1: Effect of amount of adsorbent on % adsorption of oxyhalide mixture from deionised water using waste from the bush tea (*Athrixia philicoide*).

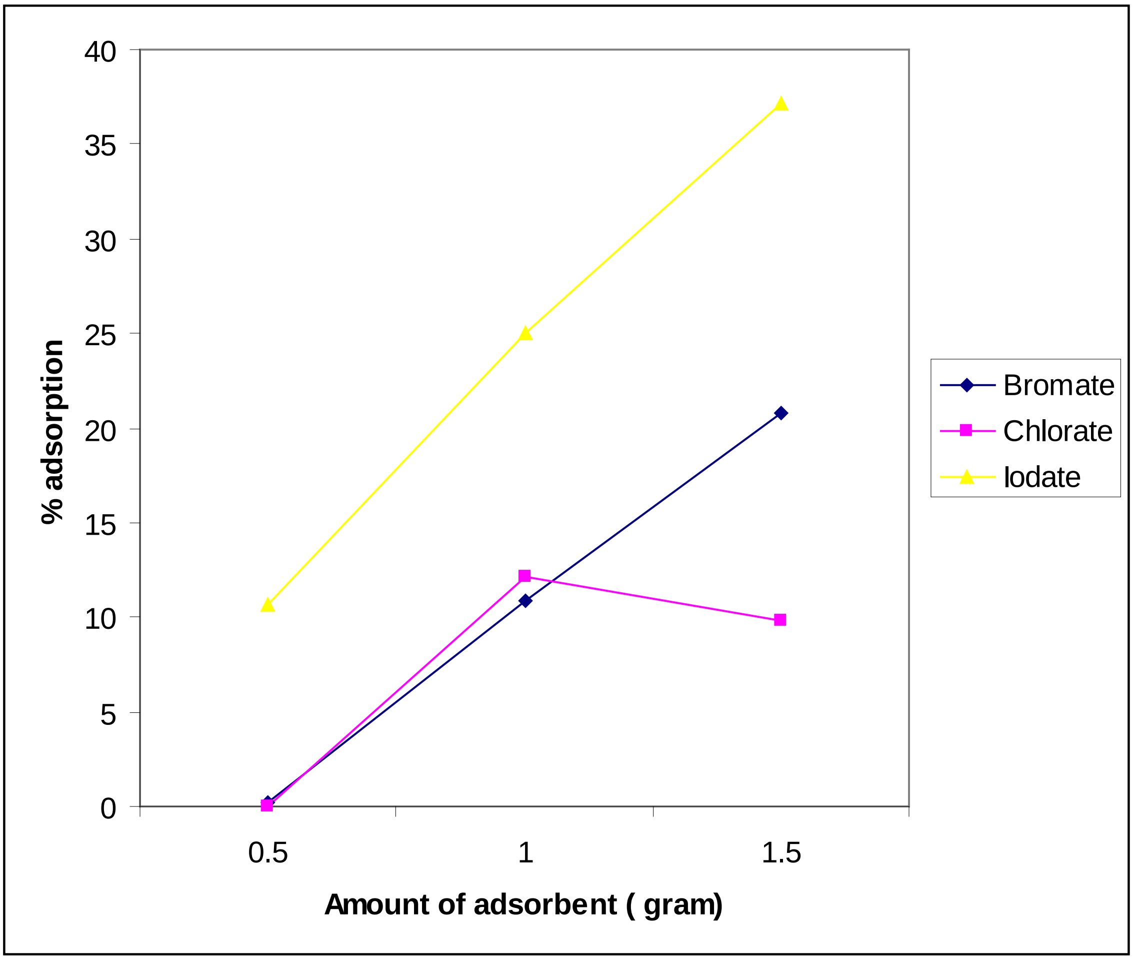


**Fig 4.44: Effect of amount of waste on % adsorption of oxyhalide mixture from deionised water using the bush tea (*Athrixia philicoide*)**

In Figure 4.44, a poor adsorption of all the oxyhalides was obtained. 37.12 %. Adsorption of the iodate was recorded which was followed by the adsorption of bromate at 20.8% that of chlorate at 12.16 %. Generally, it could be concluded that this waste material is not suitable for the removal of the mixture of the oxyhalides from aqueous system as revealed by the general poor sorption of the ions by the waste adsorbent.

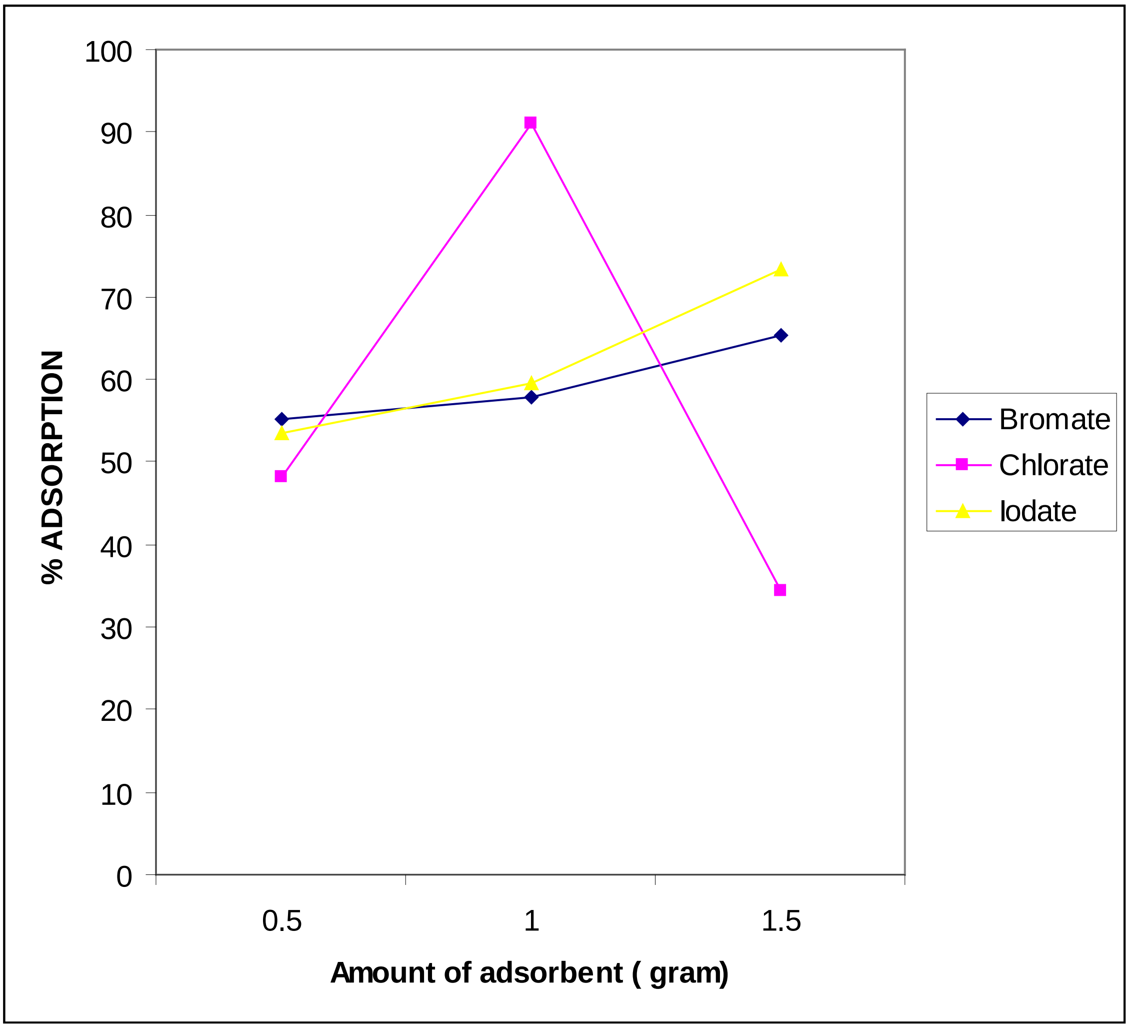


**Fig 4.45: Effect of the amount of waste on % adsorption of oxyhalide mixture from deionised water using waste of the pineapple peel**

In Figure 4.45, the highest adsorbed oxyhalides in the solution was chlorate at 91.03% adsorption using 1.0 g of adsorbent. This was followed by the adsorption of iodate at 73.36 % using 1.5 g of adsorbent and lastly by the adsorption of bromate with 65.40% at 1.5 g of the adsorbent.

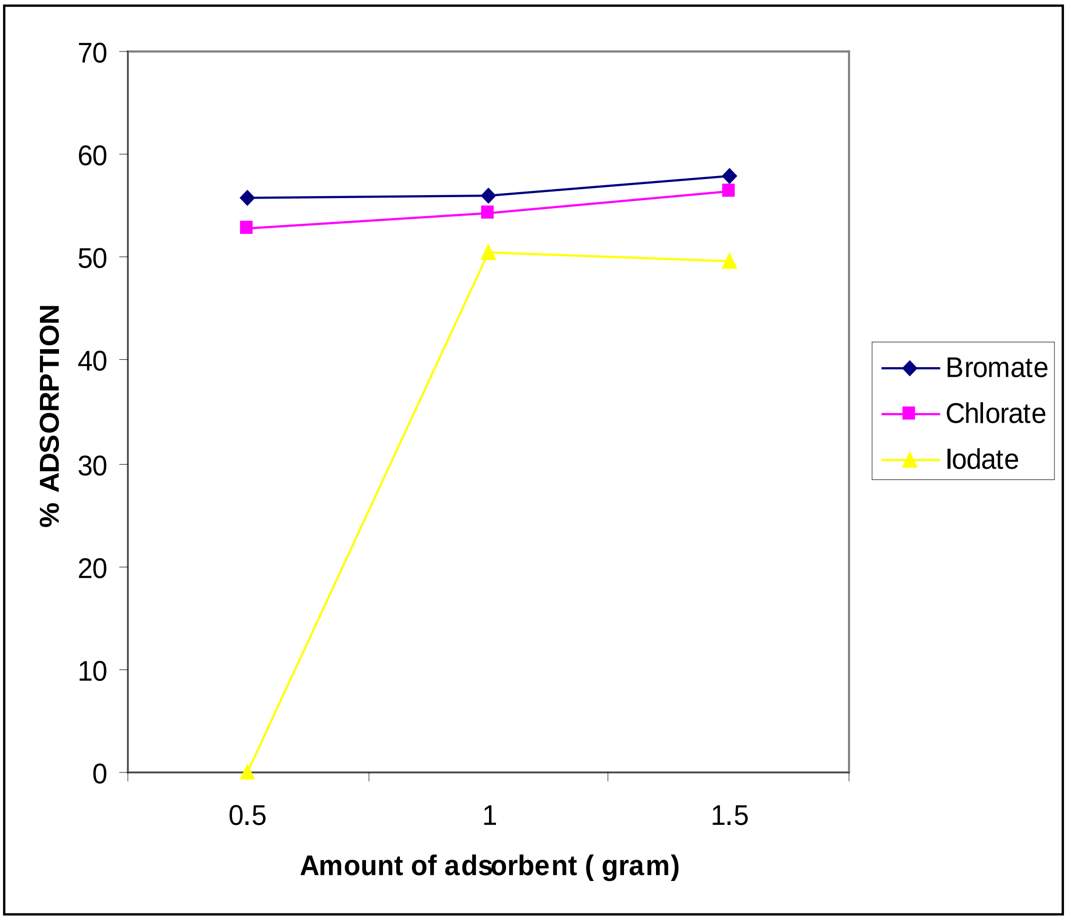


**Fig 4.46: Effect of amount of waste on % adsorption of oxyhalide mixture From deionised water using waste of the butternut peel**

From Figure 4.46 above, the highest adsorbed oxyhalide was bromate with 57.97 % adsorption using 1.5 g of the adsorbent. This was followed by chlorate ion with 56.51% adsorption and lastly by iodate with 50.46 % adsorption at 1.5g of the adsorbent.

## 4.17: Effect of pH on % adsorption of a mixture of the oxyhalides (bromate, chlorate and iodate) using the evaluated plant-based waste materials.

### 4.17.1: Effect of pH on % adsorption of a mixture of the oxyhalides using waste from the pineapple peel.

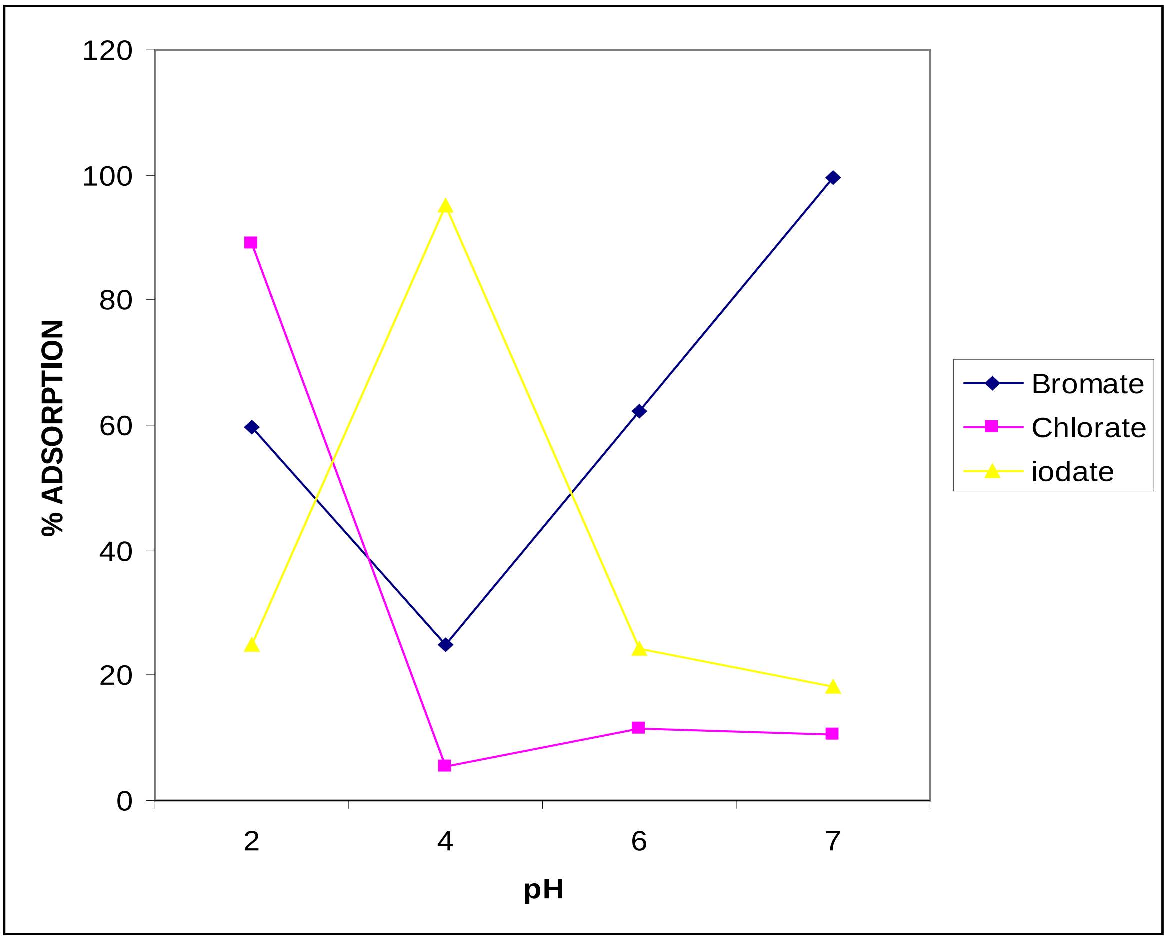


**Fig 4.47: Effect of pH on % adsorption of oxyhalide mixture from spiked deionised water using waste pineapple peel as adsorbent.**

From Fig 4.47, quantitative adsorption of 99.54 % the bromated, 95.02 % of the iodate and 89.05 % of the chlorate ions were obtained at pH 7, 4 and 2 respectively. The lower values obtained at other pHs for the oxyhalides could be as a result of completion for the active sites of the adsorbent by the oxyhalides which probably is responsible for the low sorption at other acidity.

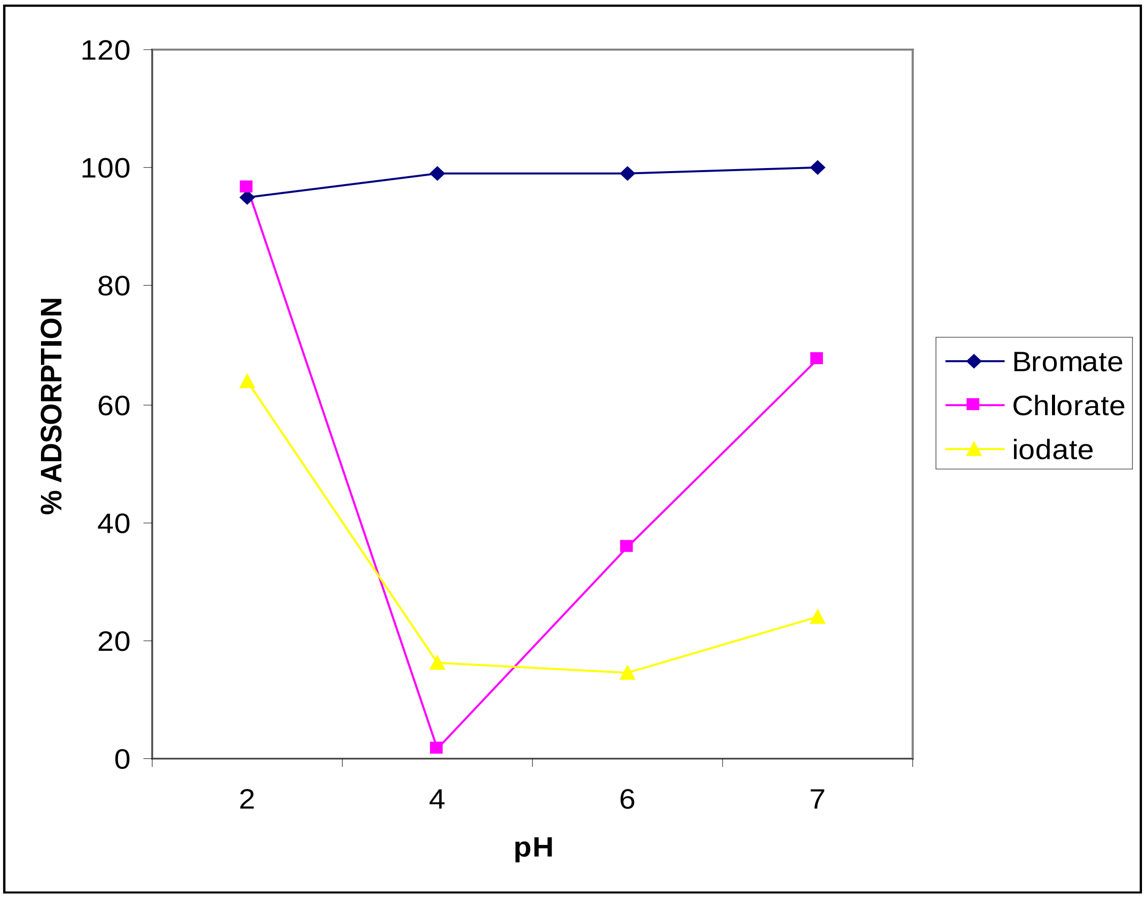


**Fig 4.48: Effect of pH on % adsorption of oxyhalide mixture from spiked deionised water using waste from the bush tea (*Athrixia philicoide*) as adsorbent**

In the Figure 4.48, bromate was quantitatively sorbed by the waste adsorbent across the evaluated pH. The chlorate ion also recorded quantitative sorption at pH 2 which the highest adsorption of iodate ion was 63.89 % at pH 2.

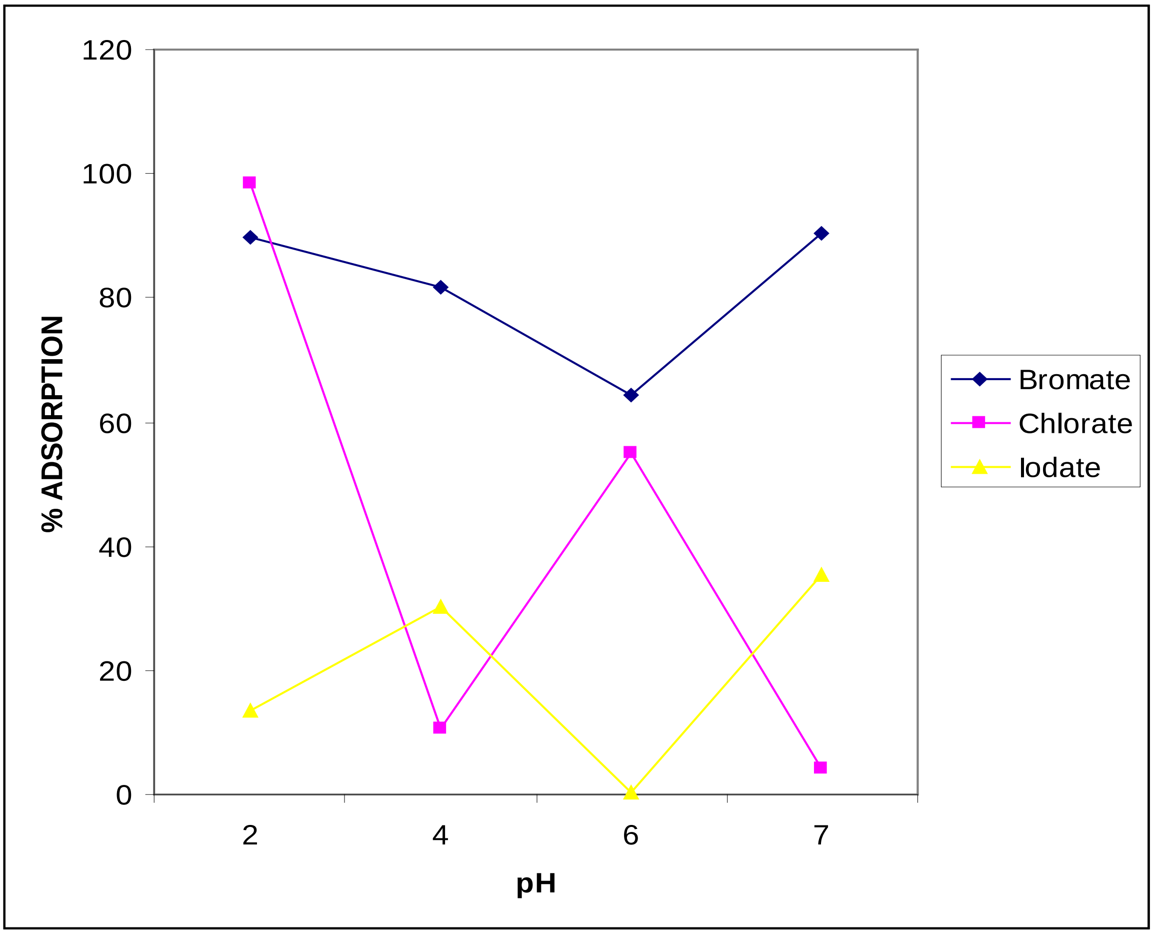


**Fig 4.49: Effect of pH on % adsorption of oxyhalide mixture from spiked deionised water using waste from butternut peel as adsorbent**

In Figure 4.49, chlorate recorded the highest adsorption at pH 2 with 98.43% adsorption follow by bromated with 90.34% at pH 7. Poor adsorption of the chlorate ion was however, recorded with the waste butternut peel with an adsorption of 35.29 % at pH 7.

## 4.18: Effect of contact time on % adsorption of the oxyhalide mixture (bromate, chlorate and iodate) from spiked de-ionised water by the evaluated plant-based waste adsorbents.

### 4.18.1: Effect of contact time on % adsorption of the oxyhalide mixture (bromate, chlorate and iodate) from spiked de-ionised water using waste pineapple peel.

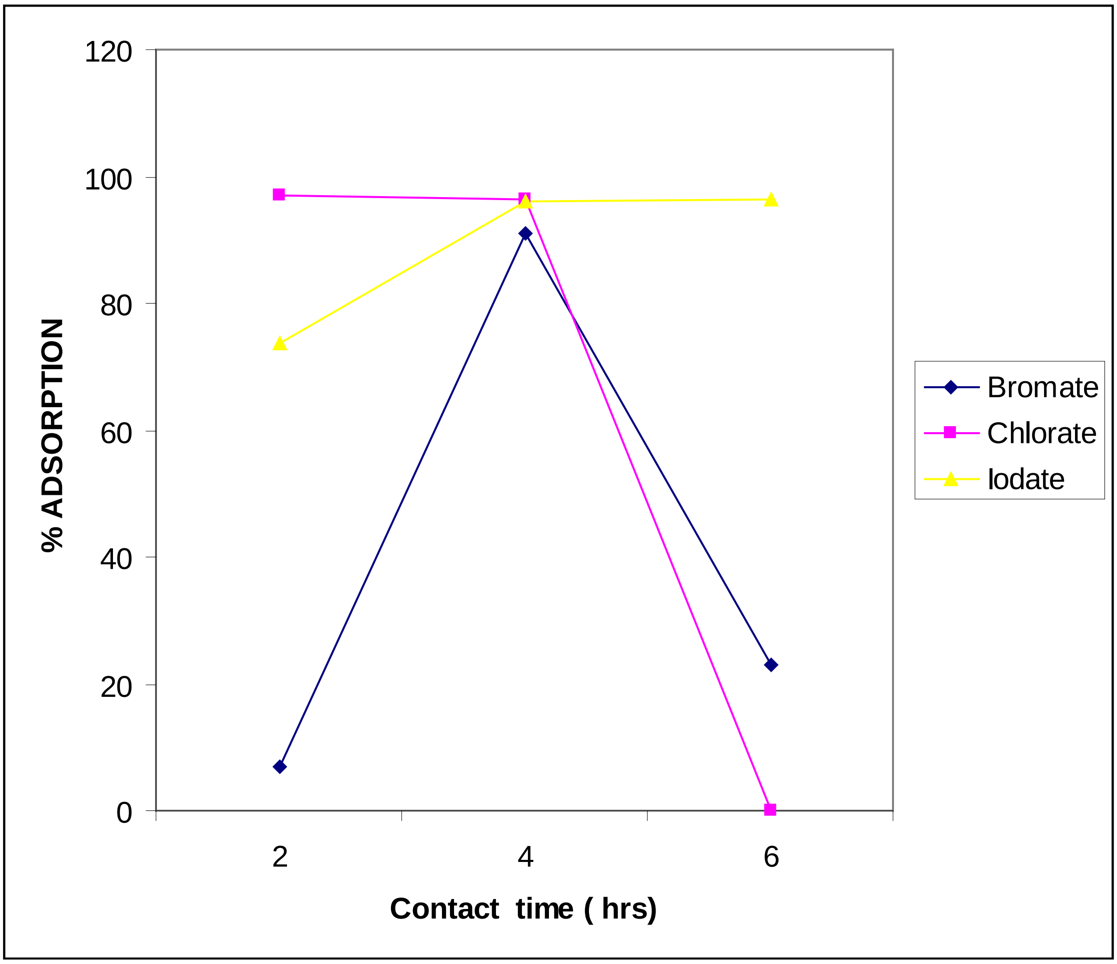


**Fig 4.50: Effect of contact time on % adsorption of oxyhalide mixture from spiked de ionized water using waste pineapple peel as adsorbent**

In the Fig 4.50, chlorate was highly adsorbed at 97 % adsorption with contact period of 2hr. This was followed by the iodate at 96.33 % also at 6 hr contact time while bromate recorded adsorption of 91 % with the contact time of 4hr.

From Figure 4.51, bromated was highly adsorbed at 99.11 % within the 6hr contact time which was followed by iodate with 71 % adsorption at 2hr contact time. Chlorate recorded the lowest adsorption at 50.62 % of the ion adsorbed at 2hr contact time.

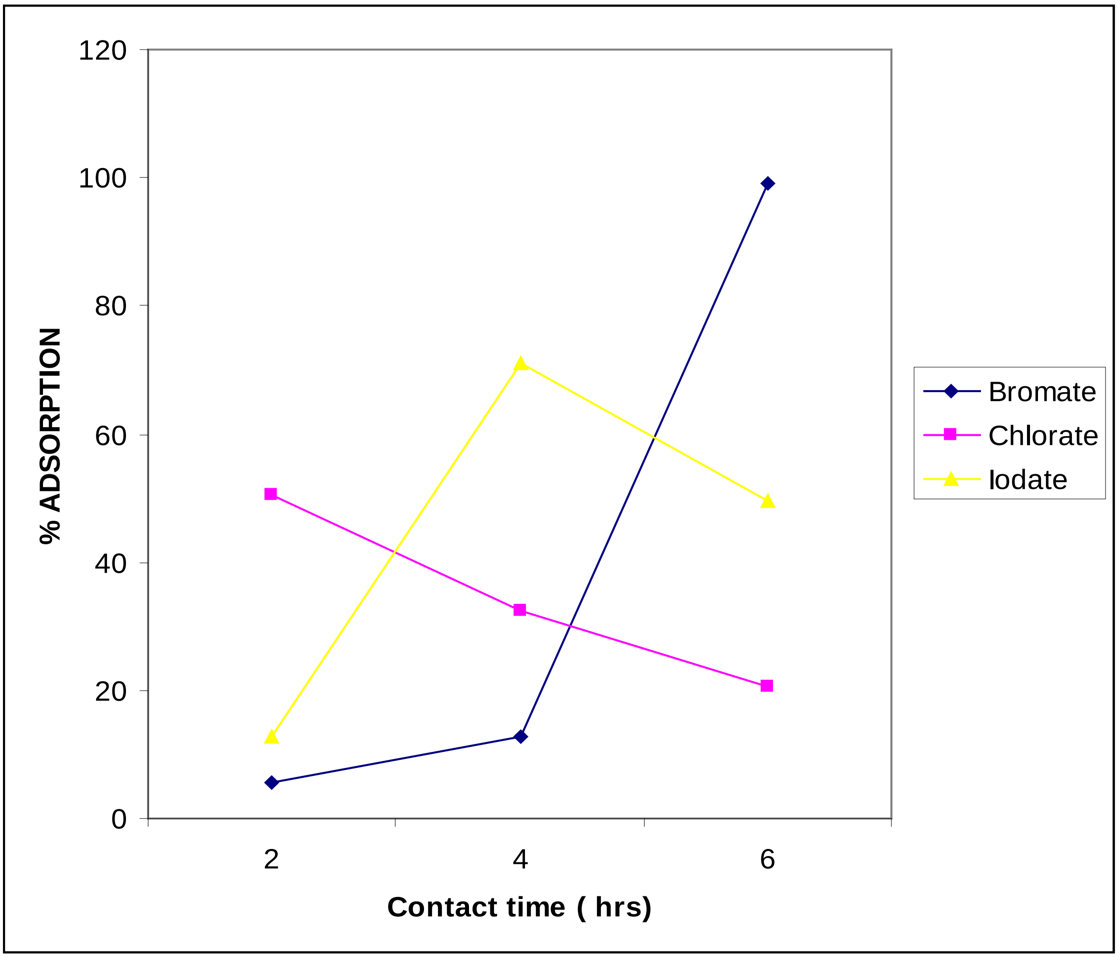


**Fig 4.51: Effect of contact time on % adsorption of oxyhalide mixture from spiked de ionized water using waste from the bush tea as adsorbent**

In Fig 4.52 below, chlorate ions were highly adsorbed in the mixture at 99.8 under the 2hr contact time which was followed by the Iodate was 99.44 % adsorption also within the 2hr contact time. Another quantitative adsorption was recorded by bromated at 99.78 % adsorption within 4 hr contact time.

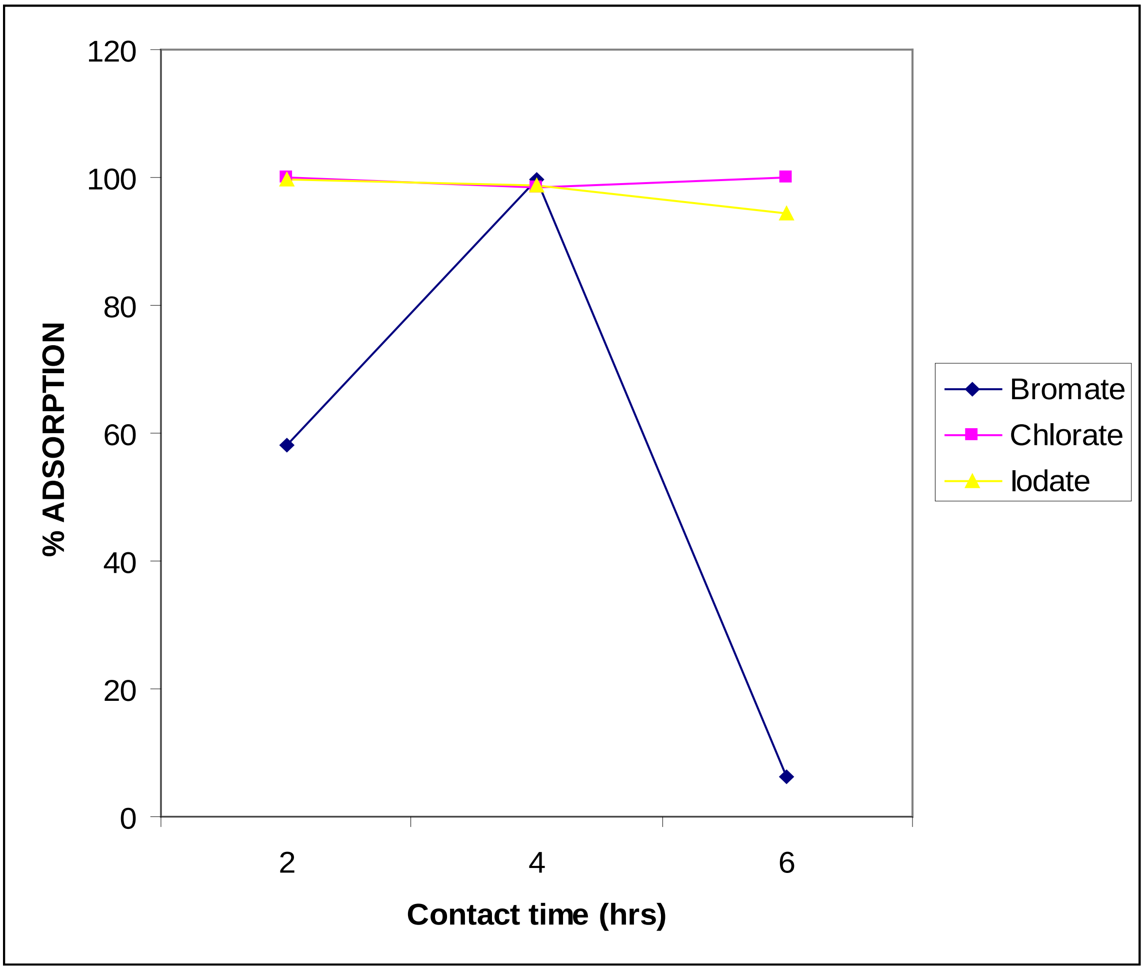


**Fig 4.52: Effect of contact time on % adsorption of oxyhalide mixture from spiked de ionized water using waste from the waste butternut peel as adsorbent**

## 4.19: Effect of the concentration of oxyhalide mixture (bromate, chlorate and iodate) on % adsorption using the three evaluated waste materials (bush tea, pineapple peel and butternut peel).

### 4.19.1. Effect of the concentration of oxyhalide mixture (bromate, chlorate and iodate) on % adsorption using waste from the pineapple peel.

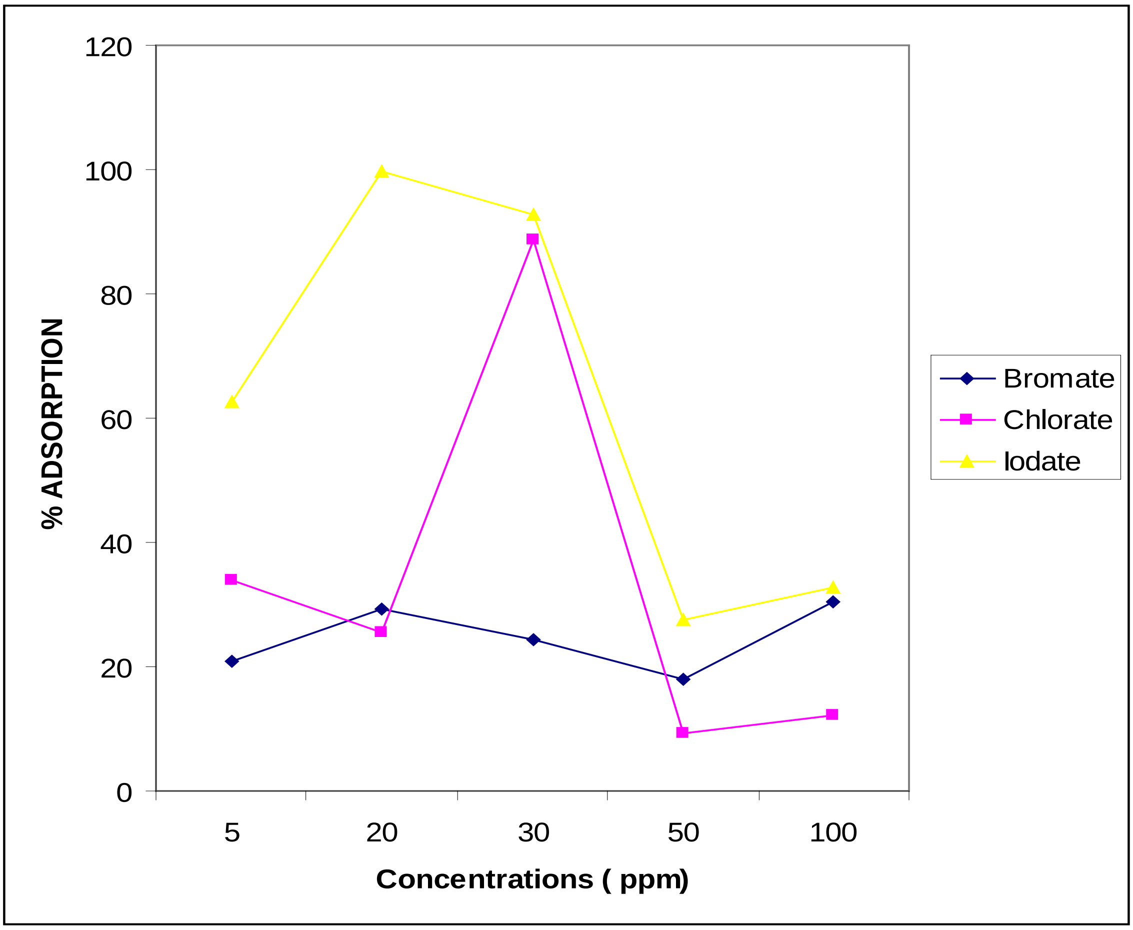


**Fig 4.53: Effect of concentration of oxyhalide mixture on % adsorption from spiked de ionized water using waste from pineapple peel as adsorbent**

From Figure 4.53 above, iodate was highly adsorbed at 99.75 % at 20 ppm concentration of oxyhalides while chlorate adsorption was 88.72 % adsorption at 30 ppm. Bromate was poorly adsorbed at 30.4 % using 100 ppm as concentration of the oxyhalides.

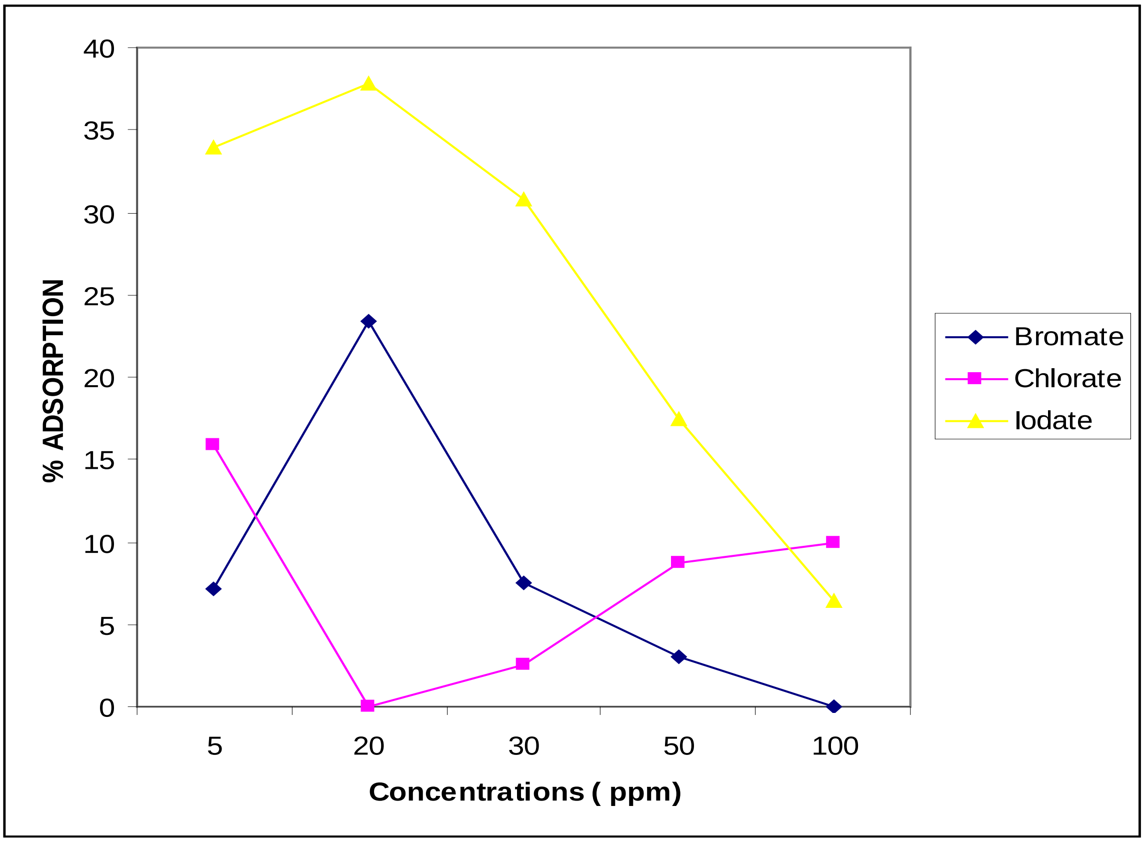


**Fig 4.54.: Effect of concentration of oxyhalide mixture on % adsorption from spiked de ionized water using waste from the bush tea as adsorbent**

In Figure 4.54 above, generally poor adsorption was recorded by all the evaluated oxhyhalides using the bush tea as adsorbent. Iodate recorded adsorption of 33.96% at 20 ppm while bromate was 23.37 % at 20 ppm and chlorate was 15.9 % at 5 ppm concentration of the oxyhalide mixture..

From Figure 4.55, similar pattern of result was shown as in Fig 4.54 with the iodate recording the highest % of sorption of 76.55 % at 5ppm concentration level. All other oxyhalides recorded poor adsorption with respect to the concentration of the adsorbent. Chlorate was adsorbed at the 23.46 % at 5 ppm concentration while the the bromate adsorption was 20.38 % at at the same 5 ppm concentration level of the oxyhalides.

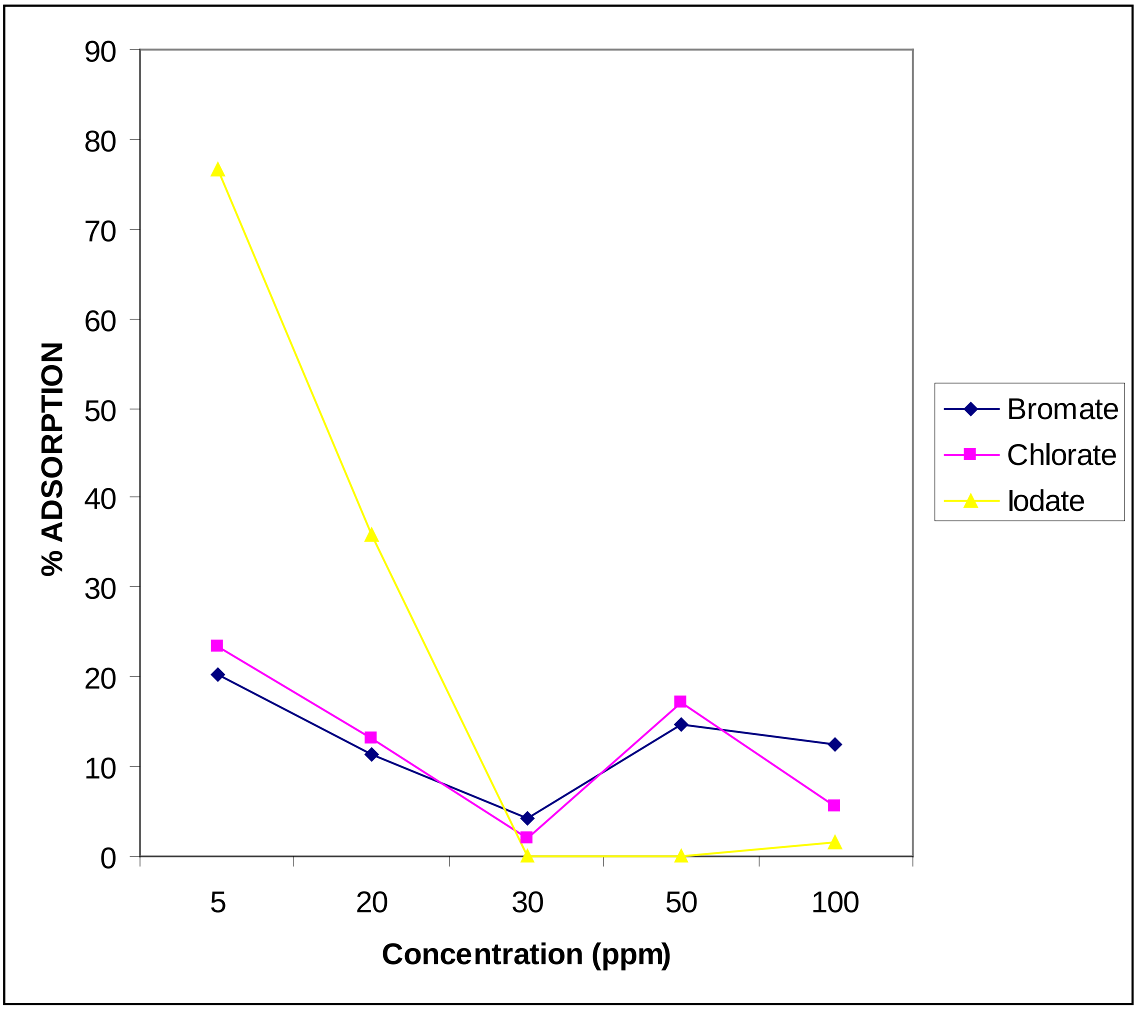


**Fig 4.55: Effect of concentration of oxyhalide mixture on % adsorption from spiked de ionized water using waste from the butternut peel as adsorbent**

## 4.20 REGENERATION OF THE USED ADSORBENTS

Regeneration involves the removal of adsorbed metals from the adsorbent in order to reuse the material for other sorption purposes. It involves the time taken to remove adsorbed metals from the already used adsorbents.

### 4.20.1: Regeneration of the oxyhalides from the used bush tea (*Athrixia philicoide*)

From Figure 4.56, both the cadmium and lead were desorbed at the same pace and this account for Pb overlapping with that of cadmium. The rate of desorption for Mn increases as the contact time between the used adsorbent and the 2M nitric acid decreases.

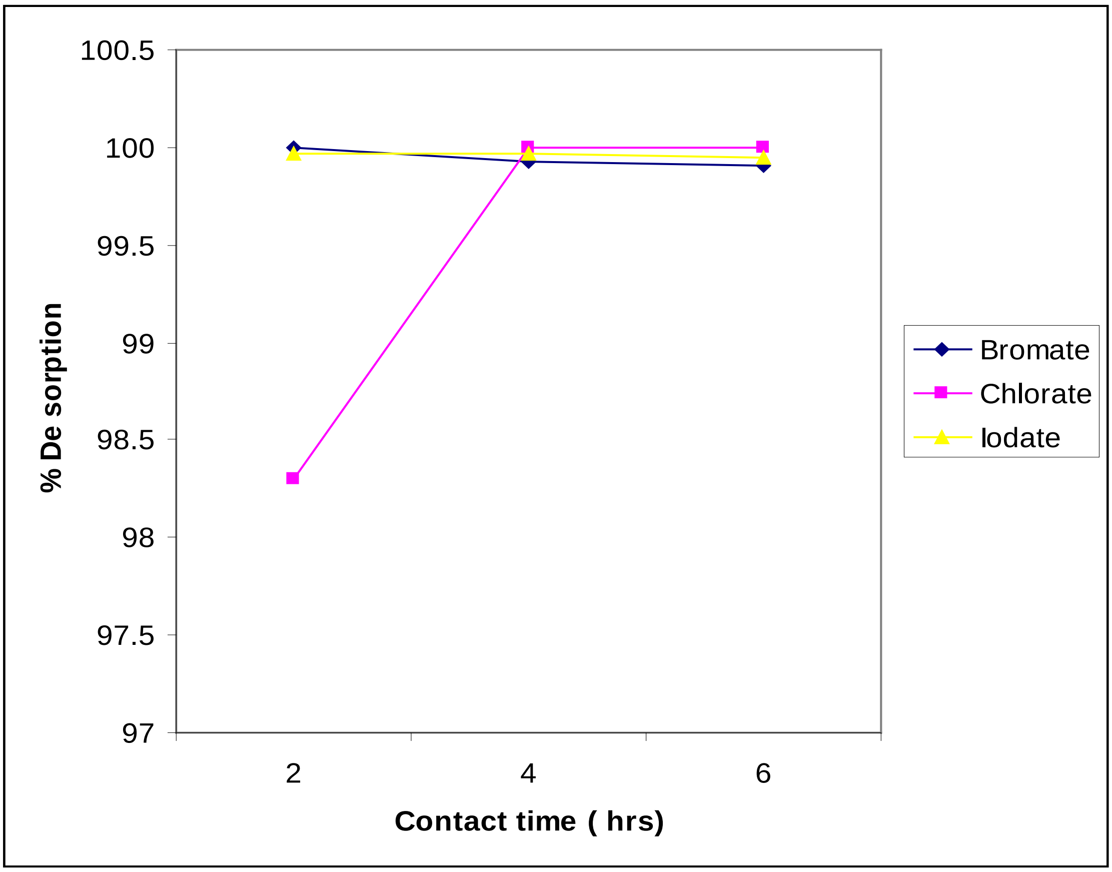


**Fig 4.56: Regeneration of the oxyhalides from used waste bush tea (*Athrixia philicoide*)**

From the Fig 4.56 above Bromate and Iodate was highly de-sorbed 100% between two to four hours contact time while Chlorate was 100% 6hrs contact time while Iodate was 99.97 % adsorbed within 2 to 4hours contact time.

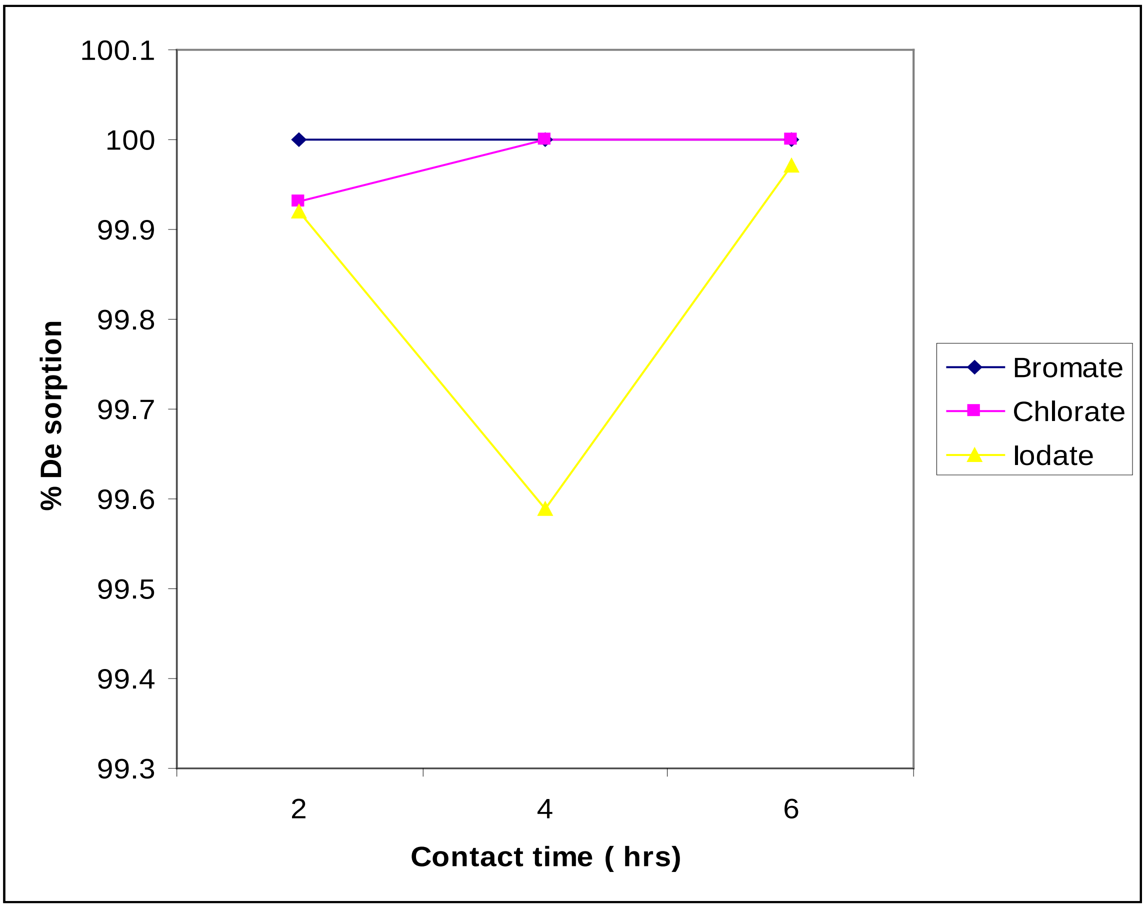
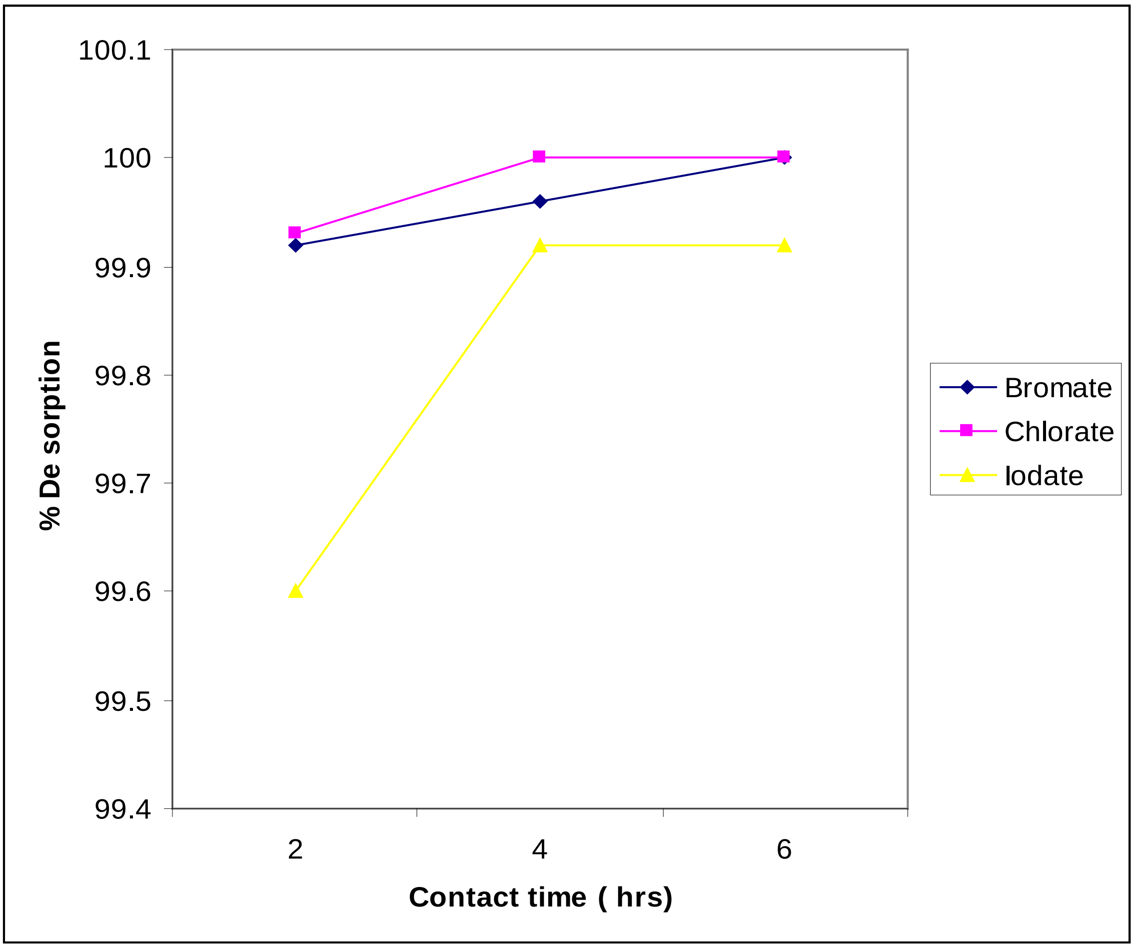


**Fig 4.57: Regeneration of the oxyhalides from used waste butternut peel (*Juglans Cinerea*).**

In the Figure 4.57, desorption of the oxyhalides were quite slow across the contact time using 2M solution of $HNO_3$. However, iodate was desorbed relatively quicker within the 2- 6 hr time period.



**4.58: Regeneration of the oxyhalides from used waste Pineapple peel (*Ananas Comosus*)**

In the Figure 4.58 Bromate and Chlorate were above 99% de – sorbed at between 4 and 6hours contact time, while Iodate was 99.87% adsorbed at 4hours contact time.

## 4.21: Application of the plant-based waste materials; (bush tea (*Athrixia philicoide*), pineapple peel (*Ananas Comosus*) and butternut peel (*Cucurbita Moschata*) for the removal of oxyhalide mixture in environmental waste water sample.

### 4.21.1: % adsorption of a mixture of oxyhalides as a function of pH using waste bush tea as the adsorbent.

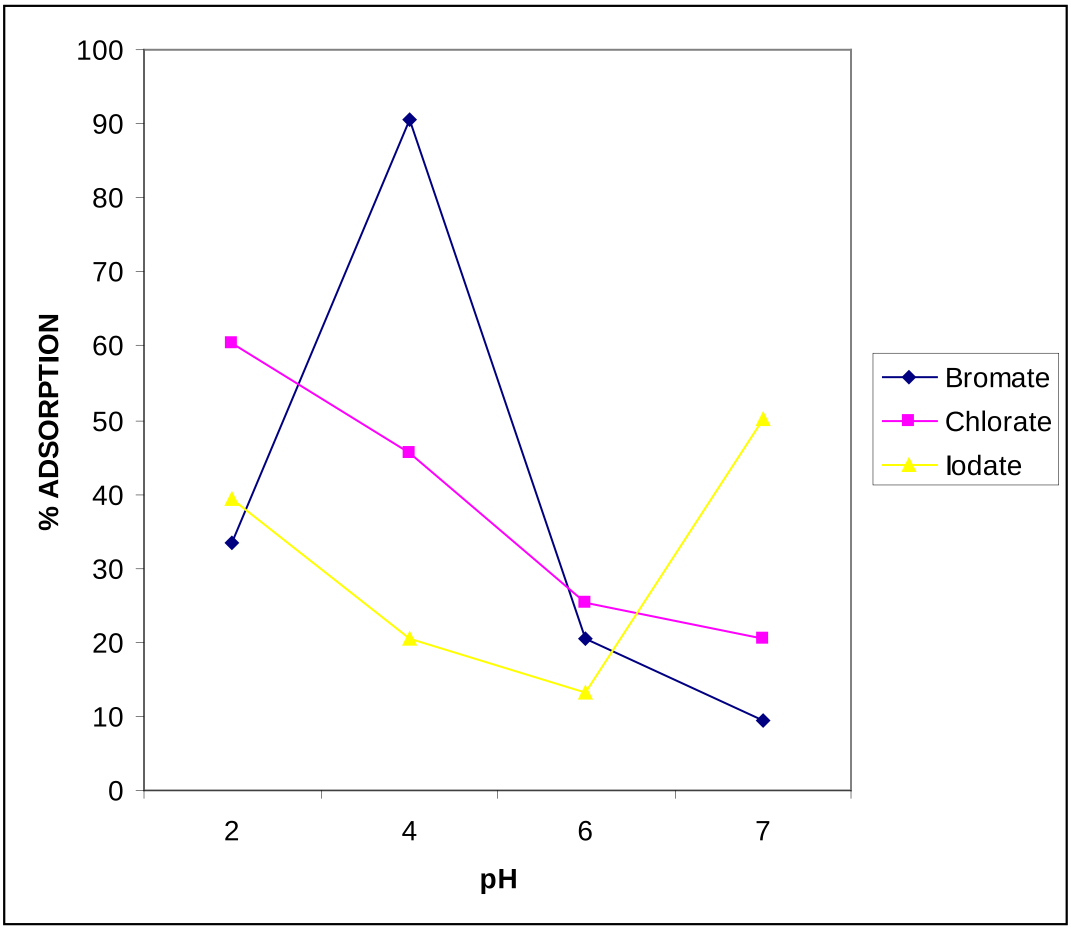


**Fig 4.59: % of oxyhalides adsorbed from spiked waste water using bush tea as adsorbent.**

From the Figure 4.59 above bromate was 90.45% adsorbed while Chlorate was 60.45% at the same pH2 while Iodate was highly adsorbed at pH 7 at 50.14%.

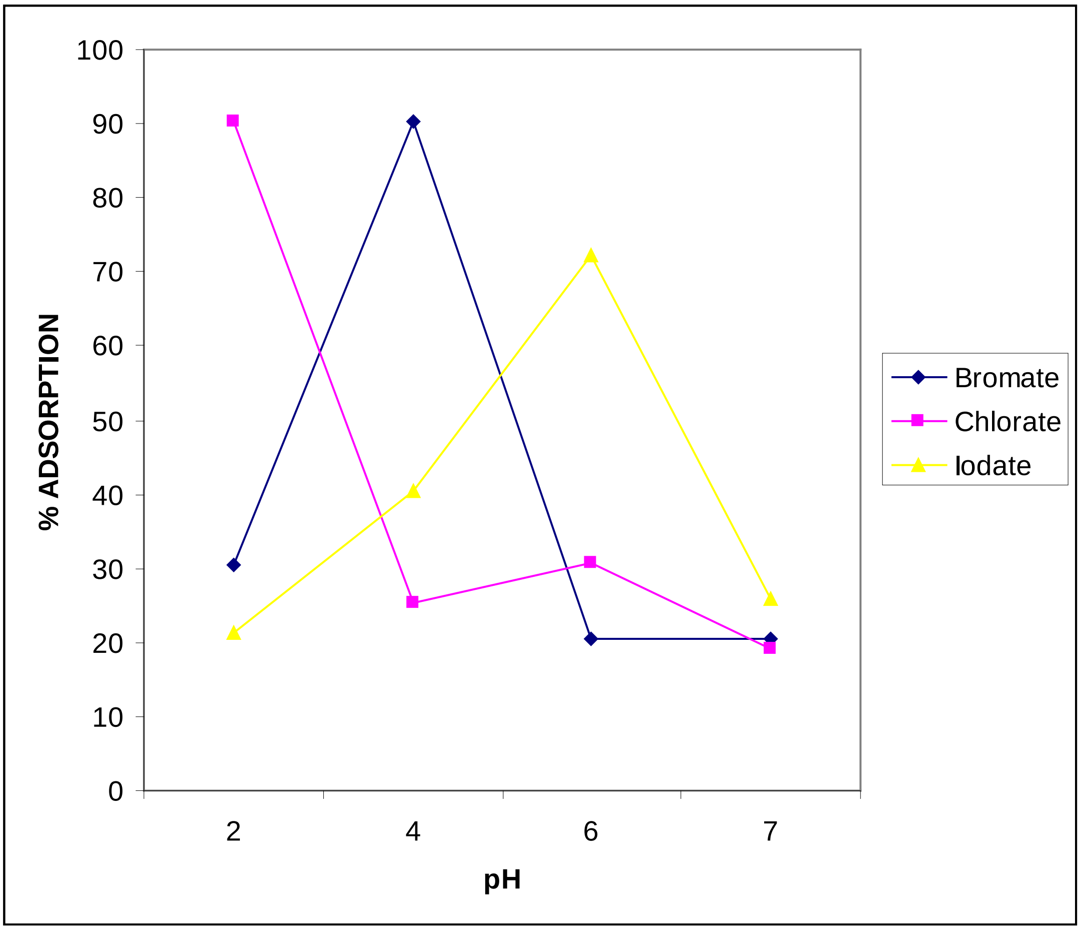


**Fig 4.60: % of oxyhalides adsorbed from spiked waste water using waste pineapple peel as adsorbent.**

In the Figure 4.60 above Bromate was highly adsorbed 90.32% at pH4 while Chlorate was highly adsorbed 90.22% at pH2 while Iodate was 72.36% adsorbed at pH6.

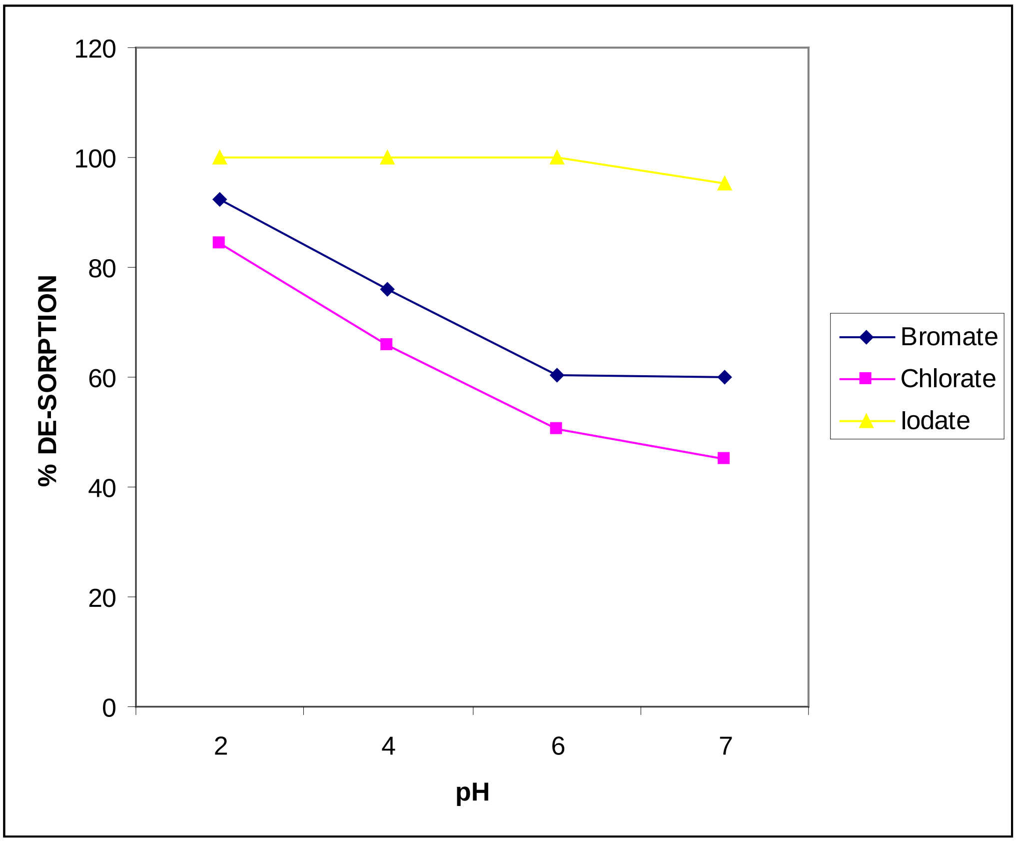


**Fig 4.61: % of oxyhalides adsorbed from spiked waste water using waste Butternut peel as an adsorbent.**

In Figure 4.61 above, iodate was highly desorbed at pH 2 (100%). pH2 favoured the adsorption of all oxyhalides though at different percentages.

## CHAPTER 5: DISCUSSION OF RESULTS

The outcomes of all the experiments carried out in this research work are discussed in this chapter.

### 5.1 The effect of pH on metal adsorption (single metal)

The effect of pH on metal adsorption revealed that the adsorption rate of Lead in bush tea waste materials increased from 14.9 % to 47% for an increase in the pH from 2 to 6. A similar response was observed for butternut waste from 63 % to 93 %. However, a different response was observed for Pineapple peel as the rate of adsorption was constant at 99 % between pH 2 and 4 then with a sharp increase to 98.7 % between pH 4 and 6. Cadmium adsorption using bush tea also recorded a direct proportionality where adsorption decreased as the pH was increasing, starting from 99.15 % adsorption at pH 2 to about 99.0 % adsorption at pH 6. The same pattern was displayed when butternut was used in the adsorption of Cadmium with pH as a factor because at pH 2, it was 18.45 % while the value was 45 % at pH 6. I the case of waste pineapple peel as adsorbent. The highest adsorption rate obtained was at 99.7 % at pH 2 contrary to that of other adsorbents.

**5.2 Removal of Mn from the spiked de ionised water using bush tea**. The outcome of this experiment showed that the adsorption rate of manganese increased as the pH increased from 28.5 % at pH 2 to 33.7 % at pH 6. The rate of adsorption of Manganese with the butternut peel, also increased as the pH increased from 99.86 % at pH 2 to 99.92 % at pH 6. The adsorption of pineapple peel displayed a different pattern though with a slight difference. It increased as the pH increased from pH 2 (99.84 %) to pH 6 (99.90 %).

## 5.3. The effect of pH in the removal of metals in spiked de ionised water using the three evaluated adsorbents (Bush tea, Butternut peel and Pineapple peel).

Manganese was highly adsorbed at 99.90 % at pH 6 followed by the Lead with 98.34 % adsorption at the same pH6 while Cadmium was lowly adsorbed 43.94 % at the same 6pH. The result of the study on the mixture of the metals with Bush tea showed that Cadmium was highly adsorbed at 100 % at pH2 while Lead was 38 % adsorbed at pH6 and Manganese was 28 % adsorbed at pH4.

## 5.4 Removal of metals from the spiked de ionised water using butternut peel as the adsorbent:

The pH had no appreciable effect on the adsorptive ability of butternut on Cadmium and manganese because both were 100 % adsorbed from pH 2 to pH 6 while Lead was highly affected by the change in pH as it was 64.5 % adsorbed at pH 2 and was > 99.5 % adsorbed at pH 6. With respect to the efficiency of bush tea on the removal of the three (3) metals from aqueous medium, pH 2 favoured the adsorption of Mn from the three evaluated metals. The rate of adsorption increased as the pH increased from pH 2 to 6. The same trend was observed with cadmium, where the rate of adsorption of Pb increased from 93 % at pH 4 to 98.7 % at pH 6.

## 5.5. Effect of pH on oxyhalides from spiked deionised water using the adsorbent

**Bush Tea**: Bromate displayed an adsorption of 95 % at pH2, 99 % at 4pH and 100 % at pH7. Chlorate was totally adsorbed at pH2, 28 % adsorbed at pH6 while it was 64 % adsorbed at pH7. Iodate was 63.89 % adsorbed at pH2, 15 % at pH4 and 14.70 % at pH 7. This shows that both Chlorate and Iodate adsorption decreased as the pH increased.

**Pineapple peel**: Bromate was 60 % adsorbed at pH2, 22 % adsorbed at pH4 and 100 % adsorbed at pH7. Chlorate was 90 % adsorbed at pH 2, 5 % adsorbed at pH4 and 10 % adsorbed at pH7. The adsorptive rate was reduced as the pH increased. Iodate was 24 % adsorbed at pH 2, 95.02 % adsorbed at 4pH and 18.25 % adsorbed at pH7.

**Butternut peel**: Bromate was 90 % adsorbed at pH2, 80 % at pH 4; 60 % at pH 6 and 89 % at pH7. Chlorate was 98 % adsorbed at pH 2, 5% at pH 4, 48 % at pH 6 and 3 % at pH7. Iodate was 12.5 % adsorbed at pH2, 30 % adsorbed at pH 4, 25 % at pH 6 and 35 % at pH 7.

## 5.6 Effects of the amount of adsorbent used on the removal capability of the waste materials

**Bush Tea:** Lead was 100 % adsorbed when the amount of adsorbent was 0.5 g and increased to 1.5 g, it was totally adsorbed. Manganese was affected by the change in the amount of adsorbent used for adsorption. It was 82 % adsorbed at 2.0 g of adsorbent and 70 % adsorbed at 1.0 g. Cadmium was 15 % adsorbed at 1.0g and 7 % adsorbed at 2.0 g.

**Butternut peel:** Cadmium and Manganese were 100 % adsorbed from 1.0 g amount of adsorbent to when the amount was increased to 2.0 g, so the adsorption of the two metals is independent of the amount of adsorbent used for the adsorption. Adsorption of Pb was decreasing as the amount of adsorbent was increasing, it was 82 % adsorbed at 1.0g while 78 % adsorbed at 2.0 g.

**Pineapple peel**: In this case, Lead was 100 % adsorbed during the increment of the amount of adsorbent from 1.0gram to 2.0g and Cadmium was 100 % adsorbed at 1.0 g of adsorbent, 50 % adsorbed at 1.5 g and 85 % adsorbed at 2.0 g. Manganese was 8 % adsorbed at 1.0gram, 39 % adsorbed at 1.5 g and 5 % adsorbed at 1.0 g.

### 5.7: Effect of amount of adsorbent on metal spiked de ionized water adsorption using individual metal

**Bush tea with Cadmium**: the rate of adsorption of Cadmium reduced as the amount of adsorbent increased; it was 12 % adsorbed at 1 g, 10 % adsorbed at 1.5g and 5 % adsorbed at 2g.

**Pineapple peel with Cadmium**: It was 100 % adsorbed at 1.0gram, 50 % adsorbed at 1.5g and 80 % adsorbed at 2g.

**Butternut With cadmium**: It was totally adsorbed at 1.g and 58 % adsorbed at 1.5g and 85 % at 2g just like the pattern of the absorption of the pineapple peel.

**Bush Tea with Manganese**: It was 70 % adsorbed at 1.0g, 13 % adsorbed at 1.5g and 89 % adsorbed at 2.g. With Butternut, the adsorption of Manganese increased as the amount of adsorbent increased. It was 99.0 % adsorbed at 1.0g, 99.98 % at 1.5g and 99.99 % at 2g. the adsorption of Manganese with pineapple peel was 10 % at 1.0g, 36 % at 1.5g and 32 % at 2g.

**Bush Tea adsorbing Lead from the wastewater**: lead was 98.82 % adsorbed at 1.0gram, 98.96 % adsorbed at 1.5g and 99.45 % adsorbed at 2g, the rate of adsorption was increased as the amount of adsorbent increased. In Butternut on lead, the rate of adsorption decreased as the amount of adsorbent increased; 87.5 % was adsorbed at 1.0 g, 83.62 % adsorbed at 1.5 g and 72.70 % at 1.5 g.

**Pineapple peels adsorbing lead from the wastewater**. Lead was 99.84 % adsorbed at 1.0gram, 99.96 % at 1.5gram and 99.88 % at 2.0gram.

## 5.8: Effect of amount of adsorbents on mixture of oxyhalides in the spiked de ionised water.

**BUSH TEA**: Using 0.5 g of adsorbent, 0.22 % of Bromate was adsorbed while chlorate was not adsorbed at all and Iodate was 10.66 % adsorbed also. When 1.0 g of the adsorbent was used there was an improvement in adsorption of Bromate to 10.9 % while Chlorate was 12.16 % adsorbed and Iodate 24.97 % adsorbed. But when 1.5g of the adsorbent was used, 20.8 % of the bromate was adsorbed while 9.85 % of Chlorate was adsorbed and 37.128 % of Iodate was also adsorbed.

**PINEAPPLE PEEL**: Using 0.5g of the ground adsorbent, 55.30 % of the Bromate was adsorbed, 48.2 % of chlorate and 53.49 % of Iodate was adsorbed. When 1.0g of the adsorbent was used, 57.78 % of Bromate was adsorbed while Chlorate was highly adsorbed at 91.03 % and Iodate was adsorbed at 59.48 %. At 1.5g, 65.40 % Bromate was adsorbed, 34.48 % chlorate and 73.36 % Iodate were adsorbed.

**BUTTERNUT**: At 0.5g, 55.7 % of Bromate was adsorbed while 52.84 % of Chlorate and Iodate was not adsorbed at all.

## 5.9: Effects of contact time on metal adsorption from the spiked de ionized water.

**Pineapple peels on the metals using contact time:** Cadmium was 99.95 % adsorbed in 60 minute contact time while it was 90 % adsorbed in 30 minutes. The rate of adsorption increased as the contact time increased. Manganese adsorption also increased as the contact time between the adsorbent and the metal increased. It was 99.80 % adsorbed in 30 minutes and 99.85 % adsorbed in 60 minutes. Lead was 99.80 % adsorbed even when the contact time was increased.

**Bush Tea:** 100 % adsorption of at Lead was observed in the first 30 minutes. The absorption rate was consistent despite the increased contact time. Cadmium adsorption decreased as the contact time increased. It recorded an 80 % adsorption in 30 minutes, 78 % in 45 minutes and 65 % in 60 minutes. Manganese adsorption increased as the contact time increased though with a slight increment; 2 % in 30 minutes contact time, 27 % in 45 minutes and 47 % in 60 minutes contact time.

**Butternut peel:** Lead was 100 % adsorbed and Cadmium 98 % adsorbed in the 30 minutes contact time. A different response was observed in Manganese which was 20 % adsorbed in the first 30 minutes. All the three metals were however 100 % adsorbed from the solution within 45 to 60 minutes of contact time.

## 5.10: EFFECT OF CONTACT TIME ON OXYHALIDES SPIKED IN DE IONISED WATER.

Three different contact times (2, 4 and 6 hours) were used for this purpose.

**Pineapple peel**: It was observed that Bromate was 7.04 % adsorbed in 2 hours, 91.04 % adsorbed within 4 hour contact time and 22.92 % adsorbed within 6 hour contact time. Chlorate was 97.012 % adsorbed in 2 hours and 96.455 % adsorbed in 4 hours while none was adsorbed within 6 hour contact time. With Iodate, the rate of adsorption increased with an increase in contact time; 73.83 % adsorbed in 2 hours contact time, 96.10 % adsorbed in 4 hours and 96.33 % in 6 hours.

**Bush Tea**: The rate of adsorption of Bromate increased as the contact time increased. It was 5.50 % adsorbed in 2 hours, 12.92 % adsorbed in 4 hours and 99.11 % adsorbed in 6 hours. In the case of Chlorate the rate of adsorption reduced with an increase in contact time; 50.62 % adsorption in 2 hours contact time, 32.52 % adsorption in 4 hours contact time and 20.43 % adsorption in 6 hours contact time. When Bush tea came in contact with Iodate, it was 12.63 % adsorbed in 2 hours, 71.05 % adsorbed in 4 hours but the rate of adsorption reduced to 49.65 % in 6 hours.

**Butternut peel**: within 2 hours contact time, 58.23% of the bromate was adsorbed while 99.78 % of the Bromate was adsorbed in 4hours contact time and at 6 hours contact time the rate of adsorption drastically reduced to 6.156 %.

### 5.11. Effects of concentration on metal adsorption from the spiked de ionised water.

**Pineapple peel on single metal:** The adsorption of Lead recorded an increase as the concentration of the metal increased from 98.72 % at 5ppm to 99.80 % at 30ppm and 99.97 % at 100ppm. The adsorptive capacity of pineapple with Manganese reduced when the concentration of the metal increased; 99.70 % at 5ppm 93.70 % at 50ppm and 94.70 % adsorbed at 100ppm concentration. Cadmium was 99.92 % adsorbed at 5ppm, 99.97 % adsorbed at 30ppm and 99.87 % adsorbed at 100ppm.

**Pineapple peel with the three metals**. All the three metals were totally adsorbed when the concentration was 5ppm, at 20ppm Cadmium and Lead were still totally adsorbed and they remained adsorbed as the concentrations increased to 100ppm. Manganese was 52 % adsorbed at 20ppm, 95 % adsorbed at 30ppm and 100 % adsorbed at 100ppm**.**

**Bush tea with single metals.** The adsorption of Lead increased as the concentration of the metal increased. It recorded an adsorption of 25.86 % at 5ppm, 87.30 % 30ppm and 96.99 % at 100ppm. Manganese was 25 % adsorbed at 5ppm, 63 % adsorbed at 50ppm and 36 % adsorbed at 100ppm. Cadmium however showed an increase in adsorption as the concentration of the metal increased in the solution; 99.76 % adsorbed at 5ppm, 99.96 % adsorbed at 30ppm and 99.99 % adsorbed at 100ppm**.**

**Bush tea with the three metals**. Cadmium was totally adsorbed from the solution, right from when the solution was 5ppm and when the concentration were being increased the Cadmium was being totally removed, for lead the rate of adsorption was increasing as the concentration of the metal was increasing 22 % adsorbed at 5ppm, 84 % adsorbed at 30ppm and 98 % adsorbed at 100ppm. Manganese was not predictive in its adsorption, because it was 22 % adsorbed at 5ppm, 22 % adsorbed again at 30ppm and 40 % adsorbed at100ppm.

**Butternut peel with single metals.** Lead displayed an increase adsorption as the concentration of the metal increased. It was 99.92 % adsorbed at 5ppm, 99.956 % adsorbed at 30ppm and 99.99 % adsorbed at 100ppm. The rate of adsorption of

Manganese increased as the concentration of the metal increased but a slight drop was observed in the rate of adsorption when it got to 100ppm. It was 99.82 % adsorbed at 5ppm, 99.99 % adsorbed at 50ppm and 99.98 % at 100ppm**.**

**Butternut with the three metals:** Lead and Manganese were 100 % adsorbed in the solution from 5ppm concentration to 100ppm concentration. Cadmium adsorption increased with an increase in the concentration of the metal. It was 22 % adsorbed at 5ppm, 80 % adsorbed at 20ppm, 90% adsorbed at 50ppm and 98 % at 100ppm.

## 5.12 EFFECT OF CONCENTRATION ON OXYHALIDE ADSORPTION FROM THE SPIKED DE IONISED WATER

**Butternut with single oxyhalide**: The rate of adsorption of Chlorate fluctuated irrespective of the change in concentration; it was 4.16 % at 5ppm, 99.165 % at 20ppm, while 95.87 % at 30ppm, 62.126 % at 50ppm and 99.547 % at 100ppm. Iodate recorded its best adsorption rate of 89.75 % at 50ppm and the least 5ppm which was 5ppm. Bromate exhibited 99.65 % adsorption at 20ppm with the least adsorption rate at 100ppm which was 65.67 %.

**Butternut with the three oxyhalides**: At 5ppm Bromate was 20.38 % adsorbed, chlorate was 23.46 % adsorbed and Iodate 76.55 % adsorbed. At 20ppm bromate was 11. 45 % adsorbed, chlorate was 13.07 % adsorbed and Iodate 35.91 % adsorbed.

**Pineapple peel with single oxyhalides**: Bromate was highly adsorbed 99.348 % at 50ppm but was least adsorbed at 100ppm at 78.625 %. Chlorate was 99.08 % adsorbed at 100ppm while it was least adsorbed at 20ppm.

**Pineapple with the three oxyhalides:** 100ppm concentration favoured the adsorption of Bromate with a 30.4 % adsorption, while a 30ppm concentration favoured the adsorption of Chlorate at 88.72 % and Iodate at 92.82 %.

**Bush tea with single oxyhalides.** An increase in Bromate adsorption was observed when the concentration of the metal increased; it was 78.52 % adsorbed at 5ppm, 86.58 % adsorbed at 30ppm and 96.99 % adsorbed at 100ppm. Chlorate too was highly adsorbed as the concentration of the metal increased; 40.62 % at 5ppm, 94.406 % at 50ppm and 97.704 % at 100ppm. Iodate reacted differently from the others with 4.52 % adsorption.

**Bush tea with the three oxyhalides.** Bromate was highly adsorbed at 20ppm which was 24 % adsorbed, chlorate was highly adsorbed at 5ppm and 16 % adsorbed while Iodate was 38 % adsorbed at 20ppm**.**

## 5.13. EFFECT OF ADSORBENT ON WASTE WATER CONTAINING OXYHALIDES

**BUSH TEA WITH WASTEWATER:** Bromate was highly adsorbed in the wastewater (90.45%) when tested as a single oxyhalide. It however presented the highest adsorption rate when the three oxyhalides were mixed. It was 7.14% at 5ppm while the highest rate for Chlorate and Iodate were 15.9% at 5ppm was 37.80% at 20ppm respectively. This was followed by Chlorate adsorption (60.45%) at pH 2 while Iodate was 50.14% at pH 7.

**PINEAPPLE PEEL WITH WASTEWATER:** Bromate was highly adsorbed at pH 4 (90.32%), Chlorate was highly adsorbed at pH 2 (90.22%) and Iodate was 72.36% at pH 6.

**BUTTERNUT PEELS WITH WASTEWATER:** Iodate was 100% adsorbed at pH 2 while bromate was 98.57% adsorbed at the same pH 2 and Chlorate was 91.2% adsorbed at the same pH2.

## 5.14. EFFECT OF ADSORBENT ON WASTEWATER CONTAINING TOXIC METAL

**BUSH TEA.** A complete adsorption of Cadmium and Manganese was observed (100%) at pH 2 and pH 7. Lead was absorbed at 82.5% at pH 4 but was not adsorbed at pH 6.

**PINEAPPLE PEEL.** Manganese was 100% adsorbed at pH 7, 84.5% of Cadmium was adsorbed at pH 2 while Lead was adsorbed 64.3% at pH 7.

**BUTTERNUT PEEL**. Cadmium and Manganese were highly adsorbed at pH 4. Cadmium was 78.76% adsorbed, Manganese was 94.5% adsorbed in the wastewater and Lead was 96.5% adsorbed in the wastewater.

## 5.15. REGENERATION OF ADSORBENT USED IN ADSORBING TOXIC METAL.

**PINEAPPLE PEEL**. Within two hours contact time, the used pineapple peel in 2M Nitric Acid desorbed the Cadmium and lead that had been adsorbed by the pineapple peel, even when the contact time between the acid and the nitric acid was increased. On the other hand, manganese continuously de-sorbed as the contact time increased and was 99.65% adsorbed in 2 hour contact time, 99.80 in 4 hours and 100% adsorbed in 6 hours.

**BUSH TEA**. Cadmium was totally de-sorbed within the first 2 hour contact time with Nitric Acid, manganese was 93% de-sorbed within the contact time, and totally de-sorbed within 6 hours contact time. Lead de-sorption reduced as the contact time increased; 97% de-sorbed in 2 hours contact time, and 92% de-sorbed in 6 hours contact time.

**BUTTERNUT PEEL**: Lead and Cadmium were totally de-sorbed from the used adsorbent in the first 2 hours contact time between the used adsorbent and 5M Nitric Acid. Manganese was 100% adsorbed in 4 hours contact time.

## 5.16. REGENERATION OF ADSORBENT USED IN ADSORBING OXYHALIDE

**PINEAPPLE PEEL:** Bromate de-sorption increased with an increase in contact time; it was 99.92% de-sorbed while at 4 hours it was 99.96% de-sorbed and 100% de-sorbed at 6 hrs. Chlorate was 99.93% de-sorbed at 2 hours contact time between the used adsorbent and 5M Nitric acid but was completely de-sorbed at 4 hours contact time. Iodate de-sorption decreased as the contact time increased. It was 99.60% de-sorbed at 2 hours contact time, at 4 hours it was 99.92% de-sorbed but remained the same at 6 hours.

**BUTTERNUT PEEL:** Bromate was totally de-sorbed at 2 hours contact time and remains constant throughout irrespective of the contact time. Chlorate was 98.30% de-sorbed at 2 hours contact time but when the contact time increased to 4 hours all the chlorate was completely de-sorbed. Iodate was 99.97% de-sorbed at 2 hours contact time remained the same at 4 hours but the de-sorption decreased to 99.95% at 6 hours contact time.

**BUSH TEA**. the de-sorption of Bromate decreased as the contact time increased, it was 100% de-sorbed at 2 hours contact time, at 4 hours contact time it was 99.93% de-sorbed and 99.91% de-sorbed at 6 hours. The de-sorption of Chlorate on the other hand increased with an increase in the contact time. It was 98.30% desorbed in 2 hours contact time, totally de-sorbed at 4 hours contact time but remained constant even after 6 hours. Iodate adsorption reduced as the contact time increased, it was 99.97% adsorbed at 2 hours contact time, remained the same at 4 hours contact time but the adsorption dropped to 99.95% at 6 hours contact time.

## CONCLUSIONS AND RECOMMENDATIONS

**Pineapple peels.** From the present project, pineapple peels perform betters than other materials investigated in the removal of Cadmium from the wastewater at pH 2 for individual metals with increased contact time, even when the metals were mixed together, cadmium was still better adsorbed. Manganese was better adsorbed at a high pH by the pineapple peel; a low pH favoured the adsorption of Iodate from the wastewater. An Increase in the concentration of the oxyhalides increased the adsorption rate of Bromate in pineapple peels. The increase in pH increased the adsorbed rate of lead and Iodate and a low pH increased the adsorbed rate of chlorate. Pineapple peels exhibited a very good potency in the adsorption of Iodate at pH2, as an increase in the concentration of the oxyhalides facilitated the adsorption of Bromate and Chlorate. As regards pineapple peel with wastewater, Bromate was highly adsorbed at pH 4 (90.32%) while Chlorate was adsorbed at 90.22% at pH 2 and Iodate 72.36% adsorbed at pH 7.

**Bush Tea:** During the research, bush tea was observed to be good in the adsorption of Lead at a high concentration and at pH 6. The best contact time for this was 30 minutes and the amount of adsorbent was around 0.5g, more so when the amount of adsorbent was increased. It was however observed that it was not that favourable for the adsorption of Cadmium unlike the pineapple peel. Nevertheless, when Cadmium was mixed with other metals it was totally adsorbed from the solution and the increased in contact time really facilitated the adsorption capacity of cadmium.

At pH 7, Bromate and Chlorate were highly adsorbed especially with increased concentration of the oxyhalides. On the other hand, the adsorption of Iodate was not encouraging. When analysing Bush tea with wastewater, it was observed that bush tea possessed a better adsorption capacity of Bromate than the other oxhyhalides. **Butternut peel:** This adsorbent exhibited a very good capacity in the adsorption of Lead and Manganese at 6pH. On a single metal, the adsorption of lead was good at a high concentration and very good in the adsorption of Manganese at 50ppm but not too good in the adsorption of Iodate. When the three metals were combined, Lead and Manganese were totally adsorbed unlike Cadmium so it suffices to conclude that Butternut peel will not really favour the adsorption of Cadmium.

Butternut is very good in the adsorption of Bromate and Chlorate, but not encouraging with the adsorption of Iodate. During the analysis of the experiment on Butternut with the wastewater, it was observed that butternut was favourable for the adsorption of Iodate, Chlorate and Bromate in wastewater, and also good in the adsorption of Lead and Manganese when analysing with toxic metals.

In light of the analysis and conclusions of this research study it is recommended that future researchers may wish to make use of acidified form of the three materials used for the study in order to determine the adsorbability of the toxic metals.

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