ADDIS ABABA UNIVERSITY

NATURAL AND COMPUTATIONAL SCIENCES

DEPARTMENT OF CHEMISTRY

ADSORPTION EFFICIENY OF GROUNDNUT SHELL, LENTIL HUSK AND ORANGE PEEL IN THE REMOVAL OF SELECTED HEAVY METALS IN WASTEWATER

By

HERMON BERHANE

Advisor: Dr. MERID TESSEMA

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A thesis submitted to the Department of Chemistry, Addis Ababa University in partial fulfillment of the requirements for the Degree of Master of Science in Chemistry

July 2020

Addis Ababa

DECLARATION

I, the undersigned, hereby declare that this research study is my own original work and that all references have been correctly recorded and acknowledged, and that it has not previously been submitted in full or in part to any university for academic qualification. The thesis “Adsorption efficiency of groundnut shell, lentil husk and orange peel in the removal of selected heavy metals in wastewater “ is conducted under the supervision of Dr. Merid Tessema, Department of Chemistry, Addis Ababa University, Ethiopia.

Name: Hermon Berhane

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This thesis has been submitted for examination with my approval as university advisor.

Advisor’s Name ____

Signature____

Place and date of submission: Natural and computational sciences
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APPROVAL OF THE THESIS

Approved by the examining committee

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ABSTRACT

Huge amount of metal contaminated wastewater is discharged in Addis Ababa. Owing to the associated problem of disposal, wastewater presents a very severe environmental challenge. The present work focused on the removal of Cr $^{3+}$, Cd $^{2+}$ and Ni $^{2+}$ from wastewater using groundnut, lentil husk and orange peel as adsorbents. The adsorption efficiency of these agricultural waste products for the metals in tannery wastewater was measured. Batch adsorption experiments were performed at different adsorbent mass (0.025 – 3.5 g), different contact time (30- 240 min), pH of solution ranging from 4 – 9, and constant concentration. The concentration of the selected heavy metals (Cr $^{3+}$, Cd $^{2+}$ and Ni $^{2+}$) in wastewater and standard solutions were determined by flame atomic absorption spectrophotometer. Maximum adsorption efficiency of groundnut shell for the metals Cr $^{3+}$, Cd $^{2+}$ and Ni $^{2+}$ were found to be 90.01%, 97.50%, and 96.79%, of lentil husk 88.82%, 98.15%, and 95.20%. The maximum adsorption efficiency of orange peel were 96.13%, 98.27%, and 92.67% respectively. The present study demonstrated that groundnut shell, lentil husk and orange peel could be employed as effective low cost adsorbents for the adsorption of Cr $^{3+}$, Cd $^{2+}$ and Ni $^{2+}$ in the wastewater sample.

KEYWORDS: heavy metals, adsorption, groundnut shell, lentil husk, orange peel, chromium, cadmium, nickel, adsorbent, adsorbate.

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List of Abbreviations

AAS	Atomic absorption spectroscopy
BDH	British drug house
BDL	Below detection limit
CSA	Central statistical agency
DM	Dry matter
DNA	Deoxyribonucleic acid
EC	European communities
FAAS	Flame Atomic absorption spectrometry
FAO	Food and Agriculture Organization of the United Nations
GS	Groundnut shell
GSDW	Groundnut shell in distilled water
ICP-OES	Inductively coupled plasma atomic emission spectroscopy
IU	International unit
LH	Lentil husk
LHDW	Lentil husk in distilled water
MCL	Maximum contaminant level
MW	Microwave
NPN	Non-protein protease
OP	Orange peel
OPDW	Orange peel in distilled water
PIs	Protease inhibitors
PN	Protein nitrogen
SD	Standard deviation
USDA	United States Department of Agriculture
USEPA	United states environmental protection agency

1 INTRODUCTION

Wastewater is a mixture of liquid or water-borne waste disposed from residential, commercial, and industrial premises along with groundwater, surface water and rainwater (EC 2001; Florescu et al. 2013). It includes some undesirable elements, including organic, inorganic and toxic substances, as well as pathogenic or disease-causing micro-organisms, due to the wide range of inputs in the sewers. Several pollutants from natural and anthropogenic sources worldwide have confirmed pollution of both surface water and groundwater (Tzou et al. 2007). Pollution and toxicity problems are generally associated with metals such as cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), nickel (Ni), lead (Pb) and zinc (Zn) (O'Connell et al. 2008).

Due to the ever increasing industrialization, excessive disposal of radioactive metals into water bodies has become a major environmental issue in recent years. Many rivers and streams act as receptacles for industrial effluent containing dangerous materials and heavy metals, due to inadequate industrial effluent treatment techniques. Because of their high solubility, heavy metals have an immense adverse impact on river water quality and associated marine life. These heavy metals include cadmium, chromium, copper, mercury, nickel, lead and zinc which are highly toxic when taken into the body from the food web (Ahalya et al. 2003).

Figure 1: Wastewater disposal and treatment

The wastewater from industrial tannery is a significant source of heavy metal pollution in our environment as shown in Figure 1. Heavy metals are the most important contaminants in the world, and are of economic significance in industrial use. Environmental heavy metal contamination has become a significant threat to living species within an ecosystem (Siddiquee 2015; Su 2014).

Since large volumes of metal contaminated wastewater are discharged, heavy metal bearing industries are the most dangerous of the chemical intensive industries. Heavy metals can be consumed by living organisms because of their high solubility in the marine environments. Large concentrations of heavy metals can accumulate in the human body once they reach the food chain. If the metals are ingested above the permissible concentration, they may cause serious health problems (Babel and Kurniawan 2004). Domestic waste mostly has a lower level of heavy metals than industrial waste. Due to heavy urbanization and the introduction of untreated industrial wastewater into municipal wastewater systems, hazardous metals can be found in municipal wastewater (McGrath et al. 2000). Two classes of heavy metals can be classified on the basis of the relative toxicity to plants and animals. The first class that consists of chromium, cadmium, mercury and lead is extremely toxic to humans and animals but less toxic to plants. The second class comprising zinc, nickel and copper is more harmful to plants than to humans and animals when present in excess concentration (Gowrek and Ratenska 2009).

1.1 Objectives of the study

1.1.1 General objective

To measure the adsorption efficiency of agricultural wastes for metals in tannery wastewater.

1.1.2 Specific objectives

1. To explore the use of agricultural wastes as adsorbents for metals in wastewater.
2. To investigate the removal of heavy metals in wastewaters using agricultural wastes as adsorbents.
3. To evaluate the efficiency and selectivity of adsorbents for wastewater treatment.

1.2 Statement of the problem

As the world population grew, and industrial applications evolved, environmental pollution became a significant problem. One of the ways that the environment is polluted is through wastewater. Wastewater contains liquid as well as solid waste. In recent years, concentrations of heavy metals have risen in many parts in addition to other contaminants, to reach unsafe levels for living environments. There are also research reports on methods for treating tannery wastewater. Owing to their large quantity and problem of disposal, wastewater present a very severe environmental challenge. Owing to industrialization and urbanization, the unregulated release of heavy metals into the atmosphere has posed a major problem worldwide. In recent years the presence and removal of toxic and polluting heavy metals from industrial effluents, water sources and mine waters in wastewaters has gained much attention. The amount of heavy metals that industrial wastewaters frequently contain is substantial, and if discharged without proper treatment, will endanger public health and the environment. Heavy metals which are usually associated with toxicity and natural components of the Earth's crust cannot be degraded or destroyed. They reach our bodies, to a small extent, through food, drinking water, and air. Some heavy metals are important as trace elements to maintain human body metabolism. They can however lead to poisoning at higher concentrations. There are no local trials to the researcher's awareness of removing heavy metals from wastewater using agricultural wastes. Among them, this study considered only chromium (Cr), cadmium (Cd), and nickel (Ni).

1.3 Scope of the study

As mentioned, this study focused on the treatment of tannery wastewater using agricultural wastes to remove heavy metals and to determine the adsorption efficiency for Cr^{3+}, Cd^{2+} and Ni^{2+}. To estimate the reliability of the tests, adsorption experiments were conducted in triplicate and average tests were reported in all cases. Batch experiments for the adsorption of Cr^{3+}, Cd^{2+} and Ni^{2+} metal ions on groundnut shell, orange peel and lentil husk were conducted. The primary parameters examined included adsorbent mass, contact time and pH. Liquid phase characterization was performed using FAAS.

2 LITREATURE REVIEW

2.1 Groundnut

Groundnut (*Arachis hypogaea L.*), also known as peanut, earthnut, monkey nut, and goobers, is a variety of oil seeds and legume grains. It is one of the largest oilseed crops in the world (Upadhyaya et al. 2010), ranked 4th most important oilseed crop, and 13th most important food crop (Surendranatha et al. 2011). The word groundnut, *Arachis hypogaea* L., was derived from two Greek words, *Arachis* means a legume and *hypogae*a meaning below ground which refers to the formation of pods or pegs (Figure 2), the structure which carries the young embryo down into the soil. It is cultivated in nearly 100 countries on six continents, accounting for more than 97% of the world's groundnut area and 95% of total production (FAOSTAT 2018).

Groundnut or peanut is one of the world's most valuable crops of food and oilseeds. It is a mainly self-pollinated, annual legume crop. Groundnut is a rich source of oil (45–56%), protein (25–30%), carbohydrates (9.5–19.0%), minerals (P, Ca, Mg, and K), and vitamins (E, K, and B); (Gulluoglu et al. 2016). Groundnut is grown on 27.66 million ha globally, with a total annual production of 43.98 million tons. The world's leading groundnut production countries are India (20.97%), China (16.35%), Nigeria (9.68%), and Sudan (8.37%); (FAOSTAT 2018).

Figure 2: Raw and shelled groundnuts

2.1.1 Botany

The groundnut belongs to the family *Leguminosae*, subfamily *Papilionoidae*, tribe *Aeschnomeneae*, sub-tribe S*tylosanthinae*, genus *Arachis* and species *hypogaea* (Isleib et al. 1994). The genus *Arachis* consists of 80 described species (Krapovickas and Gregory 1994) and is divided into nine taxonomic sections: *Trierectoides, Erectoides , Procumbentes , Rhizomatosae ,Heteranthae, Caulorrhizae, Extranervosae, Triseminatae and Arachis*. These divisions were made based on sexual compatibilities, morphological and cytogenetic features and geographic distributions. The sexual compatibility data available from a large number of crossing experiments is very informative as to the barriers between gene pools in the genus (Krapovickas and Gregory 1994).

2.1.2 Uses of groundnut

Groundnut is an important annual monoecious legume used worldwide for oilseeds, food and animal feed (Upadhyaya et al. 2006). Recently it has also been used as a supplement for milk during fasting days in Ethiopia in the preparation of Macchiato. Groundnut is also used in the preparation of food for children (FAFFA), and is used regularly as a roasted snack. In general, it is used in various forms as a healthy source of calcium, iron and vitamins. Groundnuts are also an excellent source of cash income in developing countries, significantly contributing to food security and poverty alleviation (Smart et al. 1994). Groundnuts enhance soil fertility by fixing nitrogen and thereby increasing other crops' productivity when used in rotation or intercropping (Ajeigbe et al. 2015). Increasing demand on both the domestic and export markets may also provide a cash source for smallholder producers. Given this fact, groundnut productivity is still low at 1.7535 ton / ha in Ethiopia (FAOSTAT 2018). Low rates of adoption of productivity enhancing technologies are among the reasons for low level of productivity.

2.1.3 Composition of groundnut

Groundnut contains 40–50% fat, 20–50% protein, and 10–20% carbohydrates. It is packed with many essential B-complex groups of vitamins including Riboflavin, Niacin, Thiamin, Pantothenic Acid, Vitamin B6, and Folates, are listed in Table 1. It is also a rich source of minerals such as copper, manganese, potassium, calcium, iron, magnesium, zinc, and selenium. Groundnut, is also rich in fat, providing 656 calories Kcal 100 g. Its high energy value, protein content, and minerals make them a rich nutritious source at low prices. It also has environmental benefits for the producers, in addition to nutritional values. (USDA 2019).

Table 1: Nutritional composition of 100 g groundnut

Name	Amount
Energy (Kcal)	656
Protein (g)	25
total lipid(fat) (g)	56.25
Carbohydrates (g)	18.75
Fiber, total dietary (g)	6.2
Sugars (g)	6.25
Calcium (mg)	0
Iron (mg)	2.25
Sodium (mg)	16
Vitamin C (mg)	0
Vitamin A (IU)	0
Fatty acid, total saturated (g)	9.38
Fatty acid, total brans (g)	0
Cholesterol (mg)	0

USDA National nutrient database for standard reference, 2019

2.1.4 Profile of groundnut in Ethiopia

Groundnut is one of the five oilseed crops commonly cultivated in Ethiopia (Wijnands et al. 2009). Groundnut is grown in Ethiopia under rain-fed for extraction of oil and confectionary. In addition, it generates substantial cash income for many small scale producers and foreign exchange earnings through country exports (Geleta et al. 2007). Groundnut is the second important warm climate lowland oilseed in Ethiopia. It is relatively new in comparison with sesame. Italian explorers officially introduced groundnut into Ethiopia in the 1920s (Adugna 1991). It was first introduced to Hararghe, Eastern Ethiopia, and later spread to western Wollega, Gamo Gofa, Illubabor, Gojam, Shoa, and Wollo lowlands (Adugna 1991). Groundnut is the second lowland oil crop after sesame, both in terms of area and production (CSA 2019), according to the central statistical agency agricultural sample survey.

The fact that Ethiopia has varying climatic conditions contributes to the growing of a large variety of oil crops such as groundnut. Although groundnut was introduced into Ethiopia in the early 1920s (Daniel 2009), it currently accounts for 13.64 % of the total oil seed produced. According to the Central Statistical Agency (2019), groundnut covered approximately 84,237.01 hectare of land at the national level in 2018/2019 production year. Groundnut is grown in the lowlands in Ethiopia, it plays an increasing role as an alternative oil crop to an increasing number of smallholder farmers. The largest area of groundnut production is located in the regional states of Oromia (50,121.08 ha), Benishangul-Gumuz (17,174.96 ha) and Harar (2,222.13 ha) (CSA 2019), are given in the Table 2. Groundnut production and productivity in western Oromia is growing year by year. Groundnut is commonly produced in Ethiopia for food, cash income, and animal feed. It is grown primarily by smallholder farmers in the lowland and drought prone areas of the country, under dry land conditions (Guchi et al. 2014). The CSA report for annual yield of groundnut for the years 2014/2015 to 2018/2019 is shown in Figure 3.

Table 2: Area, production and yield of Groundnut for private peasant holdings for 2018/2019

Variables	Benshangul	Harar	Oromia
Area (Ha)	17,174.96	2,222.13	50,121.08
Production (qin)	348,628.02	15,558.68	815,968.88
Yield (qin/Ha)	20.3	7.00	16.28

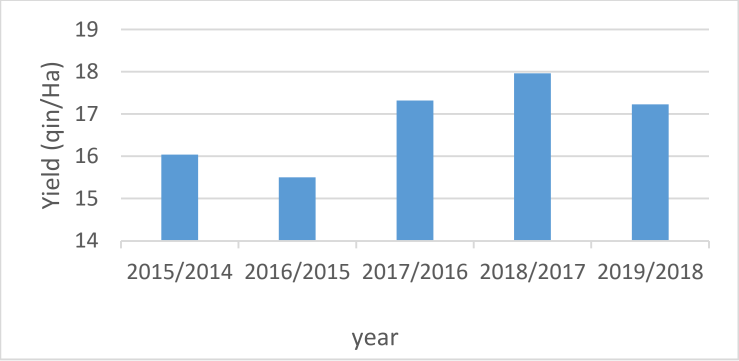


Figure 3: Yield of groundnut for private peasant holdings for Meher (harvest) season of 5 years (CSA 2014-2019)

2.1.5 Micronutrients

Micronutrient availability in soils is regulated by soil pH, exchange capacity of cations and anions, nutrient interactions, soil physical and chemical properties. Groundnut includes the seven known plant essential micronutrients: boron (B), chlorine (Cl), copper (Cu), iron (Fe), manganese (Mn), molybdenum (Mo) and zinc (Zn). Groundnut's potential for symbiotic assimilation of dinitrogen produces different demands not only on molybdenum and Copper, but also for boron and zinc nutrition. The most frequently limiting micronutrient for groundnut production is boron, due to its role in kernel quality and flavor. In groundnut kernels, boron deficiency results in the "hollow-heart" phenomenon. Deficiencies of zinc and molybdenum can be expected in soils with high lime content, specifically when high levels of phosphorous have been applied. At low soil pH, the availability of manganese and zinc can increase to toxic levels. Liming very acidic soils to pH 5.5 lowers manganese solubility and uptake to remove toxicity sufficiently (Smith et al. 1994).

2.1.6 Groundnut shell

Groundnut shells are the leftover product obtained after groundnut seed has been removed from its pod. It is the abundant agricultural waste product that has a very slow rate of degradation under natural conditions (Zheng et al. 2013). The groundnut shells are discarded as an agrowaste after separating the usable component (pods). These shells are therefore abundant in certain substances, and may therefore be used for various purposes. The chemical composition of groundnut shell is as follows: 65.7% of cellulose, 21.2% of carbohydrates, 7.3% of protein, 4.5% of minerals and 1.2% of lipids (Shehu et al. 2014). Commercially, it is used as a feedstock, food, and filler in fertilizer and even in bio-filter carriers. But most of the deserted groundnut shells are burnt or buried resulting in environmental pollution.

2.2 Lentil

One of the ancient crops, cultivated lentil (*Lensculinaris Medik*), is a fast cooking and nutritious staple legume grown in more than 70 countries and consumed globally in whole, dehulled and split form (Nosworthy et al. 2017). Its seeds are lens shaped and have a wide variety of seed coat colors (green, tan, brown, grey, white and black) and patterns (marbled, dotted, spotted, complex and unpatterned) as depicted in Figure 4 (Vandenberg 1990). Lentil seeds are usually rich in protein, dietary fiber, complex carbohydrates, and essential micronutrients such as the complex iron, zinc, and vitamin B (Khazaei et al. 2017). The seeds are also highly antioxidant compared to other grain legume species mainly due to specific phenolic compounds (Grela et al. 2017).

Figure 4: Four kinds of lentil and unthreshed lentil harvest

2.2.1 Origin, taxonomy and production

It is thought that the cultivated lentil originated and was first domesticated in western Asia and then introduced in the Indogenetic plain around 2,000 BC (Cubero 1981). Lentil has also rapidly spread to Egypt, Central and Southern Europe, the Mediterranean basin, Ethiopia, Afghanistan, India, Pakistan, China and later to the new world, including Latin America, Mexico, Chile, Argentina, Colombia and more recently Canada (Cokkizgin and Munqez 2013). Lentil belongs to the family *Legumnosae (Fabaceae)* genus *Lens* of the *Viceae* tribe, generally known as the legume family (Fikiru et al. 2007). In 1787 Medikus, a German botanist and physician (Hanelt 2001) gave the plant the scientific name *Lens culinaris*, (microsperma) and large seeded (macrosperma) (Sharma et al. 1995). This is an annual bushy herb with a slender stem and has many branches with an erect, semi-erect or widespread habit (Sandhu and Singh 2007). Lentil plants are typically short, but can range from 20-75 cm in height, depending on growing conditions (Saskatchewan 2000). After germination, the cotyledons remain under ground. The first two nodes on the stem grow below, or at the surface of the soil, and are known as nodes of scale (Oplinger et al. 1990; Randy 1993). Lentils continue to flower until they experience some form of stress, such as drought, heat, frost, deficiency in nitrogen, mechanical damage or chemical desiccation. This indeterminate habit of growth is most prevalent in late maturing varieties, but all current varieties of lentils have indeterminate habit. Lentil flowers are self-pollinated (Risula 2010), and can abort the first few flowers on the main stem. This happens when conditions favor excessive vegetative growth over seed germination, such as good humidity combined with high fertility to nitrogen (Anonymous 2012).

2.2.2 Production environments

Lentil is one of the most cool season food legumes. It is grown in Ethiopia as a winter crop, and is particularly important in Oromia, Amhara and some parts of the South Nationalities Nations and Peoples and Tigray regions (Korbu 2009). It is one of the less abundant legumes in terms of climate and soil features (Cokkizgin and Munqez 2013). It is typically well suited to different types of soil, ranging from sand to clay loam when good internal drainage occurs (Ozdemir 2002). It works best on rich, sandy loam soils with a high content of phosphorus and potassium. It is widely grown in areas with an altitude range of 1,700- 2,400 meters above sea level with annual rainfall in Ethiopia ranging from 700- 2,000 mm (Korbu 2009). As indicated from Table 3, lentil is mainly grown in the Ethiopian highlands where rainfall is generally high (Jarso et al. 2009). The CSA report for annual yield of lentil for the years 2014/2015 to 2018/2019 is shown in Figure 5.

Table 3: Area, production and yield of lentil for private peasant holdings for 2018/2019

Variables	Amhara	Oromia	S.N.N.P	Tigray
Area (Ha)	68,265.62	21,431.65	399.46	9.609.46
Production (qin)	935,842.28	344,202.40	4114.64	123,962.85
Yield (qin/Ha)	13.71	16.06	10.30	12.9

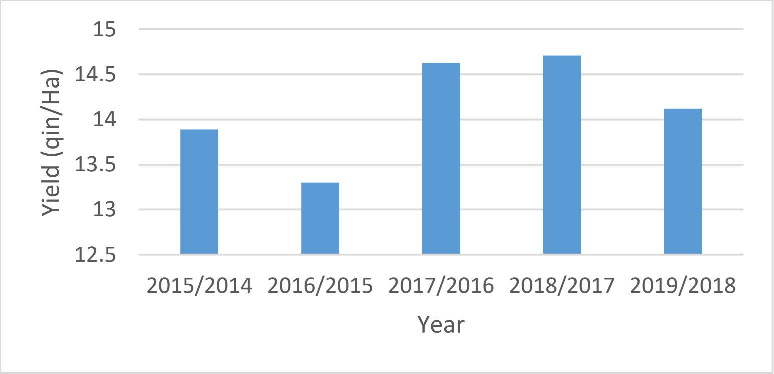


Figure 5: Yield of lentil for private peasant holdings for Meher (harvest) season of 5 years (CSA 2014-2019)

2.2.3 Nutritional composition of lentil

Lentils are becoming increasingly popular, with important vegetable protein sources. The main attributes that make lentils valuable legume crops are high protein content 22-34.6% and 55% starch, low anti-nutrient levels, high fiber content and the ability to grow under low water stress conditions. Lentils also contain significant amounts of mineral elements such as Ca, Mg, Fe, Mn, Cu, Co, Ni, B and Se (Salunkh and Kadam 1989). Lentils accumulate metals at different levels depending on environmental factors, metal species and the heavy metals available types. Most plants are found to take up significant quantities of other elements from the atmosphere and are referred to as heavy metal hyper accumulators (Olajire and Ayodele 2003). The nutritional composition and individual nutrients of whole and split lentils are clearly described in Table 4 (USDA 2019).

Table 4: Nutritional composition of lentil

Composition	Whole lentil	Split lentil	Dietary reference value
Water	10.4	11.8	-
Energy (KJ)	1,477	14,435	2000
Protein (g)	25.8	25	50
Lipid (Fat) (g)	1.1	2.2	65
Ash (g)	2.7	1.9	To
Carbohydrates (g)	60.1	59.2	300
Calcium (mg)	56	41	1,000
Iron (mg)	7.5	7.6	18
Magnesium (mg)	122	72	400
Phosphorous (mg)	451	294	100
Potassium (mg)	955	578	3,500
Sodium (mg)	6	7	2,400
Zinc (mg)	4.8	3.9	15
Copper (mg)	0.5	1.3	2
Manganese (mg)	1.3	1.4	2
Selenium (μg)	8.3	8.2	70
Vitamin A (μg)	2	3	-
Vitamin C (mg)	4.4	1.7	60
Vitamin E (mg)	0.5	-	30
Vitamin k (μg)	5.0	-	80

USDA National nutrient database for standard reference, 2019

2.2.3.1 Macronutrients

Lentils are considered as a good source of proteins. This high protein content in lentils and other pulses makes them an important and affordable source of nutritious food for developing countries (Hoover et al. 2010). Lentils are sources for some protein storage which is described as biologically active protein. These proteins have been traditionally referred to as "anti-nutritional'' compounds such as lectins and protease inhibitors (PIs) (El-Adawy et al. 2003). In addition, the protein fraction of total lentil nitrogen or protein nitrogen (PN) is significantly high (4,49 g N/100 g DM), representing approximately 89% of total nitrogen, while the non-protein nitrogen (NPN) part accounts for the remaining component, which indicates better usability of nitrogen in lentils than in high NPN foods (El-Adawy et al. 2003). Total carbohydrates are the major component of lentil seeds with starches comprising the majority of the carbohydrate mass (Padovani et al. 2006). In addition, lentils are valuable sources of total dietary fibres, with insoluble dietary fibers of around 93–99.7% (Bednar et al. 2001). Lentils have relatively low fat content, and thus low energy content (Table 4) (USDA 2019; Padovani et al. 2006).

2.2.3.2 Micronutrients

Lentil ash content is relatively high, with a range value of 3–5 g/100 g DM. In addition, the lentil mineral content consists of relatively high levels of magnesium, phosphorous, calcium, and sulphur. Furthermore, lentils have low sodium content and relatively high potassium content, with a K: Na ratio of about 30:1–90:1 (Demirbas 2005). Iron is also considerably present in lentils (Demirbas 2005). Because natural chelating agents present in the pulses could adversely affect the bioavailability of iron from lentils, this adverse effect could be minimized by cooking, germinating and fermenting lentils before ingestion (Umeta et al. 2005). Furthermore, lentils contain zinc which ranges from 3.2- 6.3 mg/100 g. Lentils also contain certain trace minerals including Copper, Manganese, Molybdenum, and Boron (Demirbas 2005).

2.2.3.3 Bioactive components

Unsurprisingly, bioactive phytochemicals were detected and quantified in lentil seeds, making them major sources of phytochemicals in the diet. Bioactive components and essential nutrients could be categorized into various functional compounds according to their chemical structure in lentil seeds (Issa et al. 2006).

2.3 Orange

Oranges probably originated in South East Asia, and were grown in China by 2500 BC (Nicolosi et al. 2008), where they were called "Chinese apples" (Ehler 2011). Today, due to their high nutritional values, and other uses oranges are grown almost all over the world as a source of food for humans. In terms of production volume, citrus ranks as the world's second largest fruit crop with over 75,413,374 million tons after banana (FAOSTAT 2018). Sweet orange (*Citrus sinensis L. Osbeck*) usually referred to as orange (Figure 6) is a member of this family and a significant source of vitamin C, folacin, calcium, potassium, thiamine, niacin, and magnesium (Angew 2007).

Figure 6: Citrus fruit plantation in winter time

2.3.1 Botany and origin of orange

The subgenus Citrus (*Swingle*), the *Rutaceae* family and the *Aurantioideae* subfamily are of three types: Citrus, Fortunella (Kumquat), and Poncirus Trifoliata. There are three genera and eighteen species described, but there are many natural mutations resulting in various hybrids spreading widely across the world (Guo and Deng 2001). Sweet orange (*Citrus sinensis L. Osbeck*) (to differentiate it from closely related species such as sour orange, *C. aurantium C. reticulata* and *mandarin* orange), is an evergreen tree 7.5 m high and often up to 15 m high. It originated in southern China, where it has been cultivated for many years, but is now commercially grown in tropical, semi-tropical and some warm temperate regions around the world to become the world's most widely planted fruit tree (Nicolosi et al. 2000; Ehler 2011).

The origin center of most citrus cultivars is perhaps unknown, but the ancient citrus relatives are native to China, Southeast Asia, the Archipelago of Malaysia, New Caledonia and Australia (Atta et al. 2012). The genetic history of sweet orange is not clear, although it is suspected to be derived from some primitive citrus species' interspecific hybridization (Xu et al. 2013).

Its many cultivars are therefore grouped into three major categories or varieties by origin (Mediterranean and Spanish oranges) and taste. The navel oranges named for their form (segmented skin looks like a human navel) appeared in a Brazilian monastery in 1820 as a single mutation. Since they do not produce seeds, every single navel orange originates from it, and spread is through cuttings of graft. These oranges continued to grow in popularity resulting in their worldwide success. The Valencia orange was named after William Wolfkill, an agronomist known for his orange production in the Spanish city of Valencia (Ehsani et al. 2007). Depending on the fruit, blood oranges named for their crimson flesh range from sweet to tart. There are three types of oranges in this category: moro, tarocco and sanguinello, each with a different taste, size and roots. Blood oranges are used for making sorbets, marmalades, and beverages.

2.3.2 Uses of orange

Citrus fruits are the main source of essential phytochemical nutrients, and their good nutritious and antioxidant properties have long been valued for. It is scientifically known that vitamin and mineral rich oranges have many health benefits. In addition, it is now recognized that many biologically active, non-nutrient compounds present in citrus fruits such as phytochemical antioxidants, soluble and insoluble dietary fibers are known to help reduce the risk of cancer, many chronic diseases such as arthritis, obesity and coronary heart disease (Crowell 1999).

As antioxidant: A high quality orange is mature with a uniformly distributed strong color intensity over the air. These oranges must be solid, with a relatively smooth texture and shape characteristic of the variety, free of rot, and other defects. There have been studies of the biological activity and health effects of citrus flavonoids as antioxidants (Tripoli et al. 2007). Oranges as an excellent source of vitamin C contain powerful natural antioxidants, folates, dietary fibers and other bioactive components, such as carotenoids and flavonoids, which prevent cancer and degenerative diseases (Ejaz et al. 2006).

Anti-inflammation: Citrus flavonoids contain anti-inflammatory activity compounds due to the presence of regulatory enzymes (protein kinase C, phosphodiesterase, phospholipase, lipoxygenase, and cyclooxygenase) that regulate the formation of biological mediators responsible for activating endothelial cells and specialized inflammatory cells. Flavonoid suppression of the immune response and inflammation may be related to their suppression of these enzymes (Tripoli et al. 2007).

Anti-Cancer and anti-Arteriosclerosis: With selective cytotoxicity, antiproliferative actions and apoptosis, citrus flavonoids can prevent cancer (Elangovan et al. 1994; Hirano et al. 1994). Flavonoids are antimutagenic, and their ability to absorb ultraviolet light protects the DNA from damage (Stapleton and Walbot 1994). When they are produced near DNA, they neutralize free radicals which promote mutations. That was seen in x-ray irradiated mice (Shimoi et al. 1994).

Anti-Obesity: Sweet oranges have low calories and do not have saturated fats or cholesterol, but are high in dietary fiber, pectin that is very powerful in obese people. Pectin as a bulk laxative protects the mucous membrane from exposure to toxic compounds, as well as from binding in the colon to cancer that causes chemicals. Pectin has also been shown to decrease blood cholesterol levels by reducing its colon reabsorption by binding to bile acids (Sinclair et al. 1945).

Wholesome health: Oranges also contain very good amounts of vitamin A, and other antioxidant flavonoids such as alpha and beta carotenes, beta-cryptoxanthin, zeaxanthin and lutein, compounds with antioxidant properties. Orange fruit also contains quite a lot of minerals such as potassium and calcium. Potassium is an essential part of cell and body fluids helps to regulate blood pressure and heart rate. Vitamin A is also required for the maintenance of healthy mucous membranes and skin, and is important for vision. Consumption of flavonoid rich natural fruits helps the body defend against lung and oral cervical cancers. In the orange, the alkaline properties stimulate the digestive juices, thus reviving constipation. Regular orange juice consumption decreases the chances of formation of calcium oxalate that triggers the kidney stones. Polyphenols found in oranges prevent infection by viruses. Oranges protect the skin against damage caused by free radicals, helping you look young and keep your skin healthy and bright (Tsuda et al. 2004).

2.3.3 Orange in Ethiopia

The majority of the Ethiopian orange (fruits) were produced in gardens and small-scale commercial types. The manufacturing aim is mainly for home consumption. Some farmers grow orange (fruits) for the local markets in areas where it is ideal for orange (fruit) production. Commercial processing of orange (fruits) is a young industry in Ethiopia and has begun in the last six decades. There are very few commercial orange orchards (fruits) in the country and most of them are owned by state sectors (Gebremariam 2003). As seen in table 5, orange was one of Ethiopia's most important fruits with a total area coverage and total production of 2758 ha and 25,902 tons respectively (FAOSTAT 2018), Oromia (2,042.12), S.N.N.P (1,145), Amhara (1,018.42), and Somali (467.64) have the largest areas of orange production (CSA 2019). The CSA report for annual yield of orange for the years 2014/2015 to 2018/2019 is shown in Figure 7.

Table 5: Area, production and Yield of Oranges for private peasant holdings for 2018/2019

Variables	Amhara	Oromia	S.N.N.P	Somali
Area (Ha)	1,018.42	2,043.12	1,145	467.64
Production (qin)	72,359.17	132,402.08	116,045.91	72,648.28
Yield (qin/Ha)	71.05	64.80	101.33	155.35

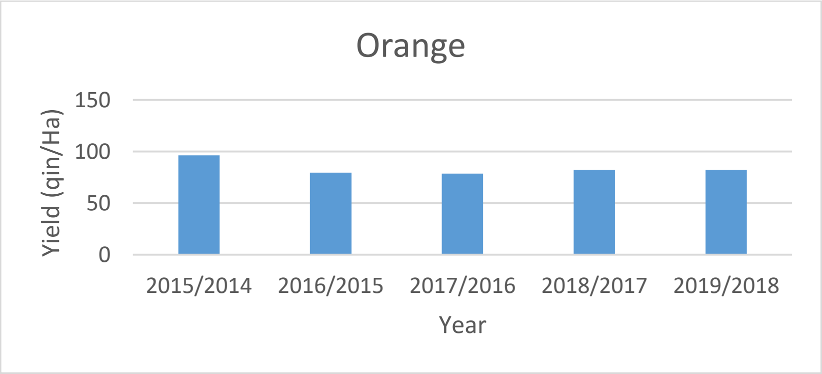


Figure 7: Yield of orange for private peasant holdings for Meher (harvest) season of 5 years (CSA 2014 2019)

2.3.4 Nutritional composition of orange

The human diet contains important micronutrients namely vitamins C and E, carotenoids and flavonoids, essential for maintenance of human health are presented in Figure 6. Multiple dietary sources of these compounds are present virtually in all plant material (Di Majo et al. 2005). The nutritional importance of orange is due to the presence of these functional food ingredients and antioxidant nutraceuticals or phytochemicals. Phytochemicals are found in edible fruits and vegetables and thus prevent chronic and degenerative diseases when eaten potentially modulate human metabolism in a favorable manner (Tripoli et al. 2007).

Table 6: Nutritional composition of sweet orange

Composition	Amount
Energy (KJ)	197
Sugar (g)	9.35
Dietary fiber (g)	2.4
Fat (g)	0.12
Protein (g)	0.94
Water (g)	86.75
Vitamin A (μg)	11
Vitamin C (mg)	53.2
Vitamin E (mg)	0.18
Calcium (mg)	40
Iron (mg)	0.1
Magnesium (mg)	10
Manganese (mg)	0.025
Phosphorous (mg)	14
Potassium (mg)	181
Zinc (mg)	0.07

** Tripoli et al. 2007

2.3.5 Orange peel

Orange peel (OP) is a substance composed of many constituents, consisting mainly of cellulose, pectin, hemicellulose, lignin, chlorophyll pigments and other hydrocarbons of low molecular weight (Feng et al. 2009). These components contain different functional groups such as carboxyl and hydroxyl which make orange peel a potential adsorbent material to remove metal ions from aqueous solutions. OP is an attractive and inexpensive alternative for the removal of dissolved metals from adsorption, at a low cost.

2.4 Heavy metals

Heavy metals are non-biodegradable, permanent, and accumulate in nature, and thus are the causes of pollutants to the environment. Specific anthropogenic sources such as industrial effluents, wastewater pollution (Praveena et al. 2008), agricultural return flows (Conceic¸a ˜o et al. 2013) and domestic sewage release heavy metals into the aquatic environment (Hejabi et al. 2010). Because of their major impact on ecological quality (Sastre et al. 2002), heavy metals are considered to be one of the key causes of contamination in the world. The release of heavy metals into wastewater through human and industrial activities has become a significant human as well as aquatic problem (Wang et al. 2013). The most concerned heavy metals from different industries include lead (Pb), zinc (Zn), copper (Cu), arsenic (As), cadmium (Cd), chromium (Cr), nickel (Ni) and mercury (Hg) (Mehdipour et al. 2015). Because of their toxicity, inseparability and adverse physiological effects on the environment and animals, heavy metals are contained with high density in the industrial wastewaters and are regarded as a serious concern worldwide. Heavy metals are not decomposed and accumulate in the body of species like plants and animals, slowly. The heavy metals deposit and accumulate in human fatty tissues, muscles, bones and joints and can cause neural disorders and carcinogenicity (Iyer et al. 2005).

2.4.1 Heavy metal effects on plants

The toxicity of heavy metals is also known to affect processes of plant photosynthesis (Wang et al. 2009). The presence of excess metals in plants will directly impede both photosynthetic electron transport and photosynthetic metabolism (Burzyhski and Zurek 2007). Toxic elements can also join the photosynthetic apparatus by decreasing the chloroplast structure of the photosynthetic pigment and causing changes in the lipid and protein composition of the thylakoid membrane resulting in lipid peroxidation associated with the generation of toxic oxygen species (Wang et al. 2009). There are also known impacts of heavy metals on soil ecosystems. The impact of pollution from heavy metals on soil is mostly felt by plants which grow in these environments. Some of these impacts include decreased seed germination and lipid content, decreased enzyme activity and plant growth, photosynthesis inhibition, reduced seed germination, decreased development of chlorophyll and plant growth; which can be caused by cadmium, chromium, copper or mercury, nickel and lead, respectively (Gardea-torresdey et al. 2005).

2.4.2 Mobility of heavy metals

Another risk of environmental pollution is detected by the leaching of heavy metals from soil to groundwater. The risk increases with time as metals remain in soils for a longer period of time and many metals are not biochemically degraded thus raising the risk of metals becoming bio-available and leaching to the groundwater table (Gadepalle et al. 2008).

2.4.3 Environmental effect of heavy metal polluted wastewater effluent

The presence of heavy metal contaminants act as great threats to soil and plants growing on such soils, with the ingestion of such plants by animals and humans due to their entry into the food chain through bio magnification and bioaccumulation, leading to significant detrimental effects (Saidi 2010). Intake of toxic metals in vegetables and corn products is reported to accumulate in the kidney, leading to dysfunction. Some studies relate skeletal damage (osteoporosis) to heavy metals in humans, such as high levels of selenium (Abdullahi 2013). The nature of polluted wastewater effluent from heavy metals on humans can be toxic (acute, chronic or sub-chronic), neurotoxic, cancerous, mutagenic or teratogenic (Duruibe et al. 2007). Although individual metals are known to have different signs of toxicity, the signs associated with cadmium, lead, arsenic, mercury, zinc, copper and aluminum poisoning are gastrointestinal disorders, diarrhea, stomatitis, tremor, hemoglobinuria that cause rust red color to stool, ataxia, paralysis, vomiting and epilepsy, depression and pneumonia when volatile vapors are inhaled. (Duruibe et al. 2007).

2.4.4 Adverse health effects of heavy metals

Due to its existence outside certain limits, heavy metal contaminants are harmful to both humans and other living creatures (Tare and Chaudhari 2015). Because of their non-biodegradable composition the heavy metals are the most toxic and dangerous pollutant. The reason for these parameters' higher values can be attributed to the disposal of sewage estates, waste from metal processing industries and household refuses (Lokhande and Kelkar 2001). Due to their presence beyond specified limits, heavy metal pollutants cause direct toxicity to both humans and other living organisms. Many of these metals are bio-accumulative, and hazardous to human health.

2.4.5 Removal of heavy metals by chemical methods

In recent years, various treatment techniques for wastewater laden with heavy metals have been developed, both to reduce the amount of wastewater generated and to improve the quality of the treated effluent. Chemical precipitation, ion exchange, flotation, coagulation-flocculation, membrane filtration, electrotreatment and adsorption are different treatment methods used to remove heavy metals (Fu and Wang 2011). Except for adsorption, these methods are non-economical with drawbacks such as incomplete metal removal, high reagent costs, energy requirements and the production of hazardous sludge or other waste products requiring further disposal or treatment. Due to its effectiveness and low cost the adsorption technique remains the preferred method (Li et al. 2007).

2.4.5.1 Chemical precipitation

Chemical precipitation usually requires a chemical reaction by which precipitating agents bind to insoluble metal precipitates with dissolved heavy metal ions (Fu and Wang 2011). The resulting precipitates may then be separated by either sedimentation or filtration from the surface, after which the treated water is decanted and discharged accordingly. The efficacy of the chemical precipitation process depends on factors such as the concentration of ionic metals in the solution, the presence of other constituents which may impede the precipitation process and the precipitant used (Oncel et al. 2013). In practice, the minimum achievable concentrations of residual metals often depend on the type and composition of the organic matter in the wastewater, as well as the temperature. This approach is therefore inappropriate for large quantities of solutions with very small metal ion concentrations. The precipitation of hydrous metal oxides with lime and soda (NaOH) is used in heavy metal removal. Despite its benefits, chemical precipitation needs significant quantities of chemicals to reduce metals to an appropriate level for discharge (Jüttner et al. 2000).

2.4.5.2 Coagulation–Flocculation

Coagulation requires the aggregation to form large aggregates of insoluble and/or dissolved organic particles (Renault et al. 2009). The process of coagulation neutralizes the charges which hold colloidal particles apart and thereby destabilize them. If the force responsible for separating them has been neutralized, the suspended particles can remain together and can then be separated by sedimentation, filtration and flotation processes (Fu and Wang 2011). In wastewater treatment systems, many widely used coagulants such as aluminum sulphate, ferric chloride and ferric sulphate have been used, impurities and particulates have been effectively eliminated by neutralizing the charging of the particles. This technique involves pH-adjustment. Coagulation is hindered by the inability to control the existence of the hydrolysis species created by adding the coagulant to the solution (Bratby 2006) and generating a large amount of sludge. Alzheimer's disease is also caused by residual aluminum salts in the treated water. Besides the water's pH, the operating process also depends on the temperature, mass and type of coagulant (Saritha et al. 2015).

Polymeric materials are used in flocculation processes to build bridges between the flocs and tie the particles together to form large aggregates (Fu and Wang 2011; Sher et al. 2013). Like coagulation, they are eventually separated by sedimentation, filtration and flotation until the suspended particles are bound together into large clumps. Polymeric flocculants have some advantages over coagulants in that they are capable of producing large, dense and compact flocculants which are stronger and have good settling characteristics compared to those produced by coagulation. High efficiency for removal can be achieved with a small amount of flocculant. Polymeric flocculants destabilize particles and colloidal matter by compressing electrical double layers, neutralizing the charging and subsequently forming a particle – polymer – particle bridge, which in turn produces a small volume of sludge (Renault et al. 2009). Unlike coagulation, pH depends less on this process.

2.4.5.3 Membrane filtration

The membrane filtration method is a promising technique which can remove organic and inorganic pollutants and suspended solids, nitrogen, phosphorus and bacteria (Blšt'áková et al. 2009; Parmar and Thakur 2013). Different forms of membrane filtration methods are used to remove heavy metals from wastewater depending on the particle size that can be retained. These include ultrafiltration, nanofiltration, reverse osmosis and electrodialysis.

2.4.5.4 Flotation

Flotation is used with the bubble attachment to separate solids or dispersed liquids from a liquid phase. Flotation uses bubble fixing to isolate solids or liquids scattered from a liquid phase (Fu and Wang 2011; Parmar and Thakur 2013). By adhering the surface of growing bubbles, the suspended particles are isolated from the heavy metal suspensions. Pretreatment of chemicals is important for successful flotation. It is better used after coagulation/flocculation instead of sedimentation, since the operating period is shorter than the latter. Notably, there are different types of flotation: dissolved air, dispersed air, vacuum air, biological, and electro-flotation (Parmar and Thakur 2013).

2.4.5.5 Ion exchange

Ion exchange is a unit process in which ions of a given species in solution are displaced by ions of a different species from an insoluble exchange medium. It is one of the most commonly used therapies due to its various benefits including high ability to remove and fast reaction rates (Fu and Wang 2011). The possibility of ion-exchange depends on the exchanger's selective ability to remove the heavy metal and competing ion concentrations. For the ion exchange, low concentrations of competing ions and a high selective ability of an exchanger are required (Hui et al. 2005). The most commonly used exchanger are synthetic insoluble substances, called resins (Fu and Wang 2011). Ion exchange can be used for heavy metal recovery as well. Metals may be recovered either by elution with appropriate reagents after separation of the charged resin (Kurniawan et al. 2006) or by incineration of metal saturated resin (Hui et al. 2005).

2.4.5.6 Electrochemical treatment

Electrochemical water treatment has been implemented in the UK since 1889, but has not been used widely and steadily for reasons ranging from spending a relatively large capital to expensive electricity supply (Chen 2004). Owing to the increasingly strict environmental regulations on wastewater discharge, electrochemical treatment methods have recovered their attractiveness in the last two decades. Electrochemical heavy metal removal treatment process includes different technologies such as electrocoagulation, electroflotation, electrooxidation and electrodeposition (Chen 2004; Fu and Wang 2011).

2.4.5.7 Adsorption process

Adsorption is a process of mass transfer in that a component is moved to the solid phase from the liquid phase. It is the mechanism of accumulating substances on a correct interface, which are in solution. The adsorbate is the material which is separated at the interface from the liquid phase. The adsorbent is the layer of solid, liquid, or gas that the adsorbent accumulates upon. The term adsorption is often used to describe the two forms of contact forces between the adsorbent and the adsorbate. Such forces of interaction are commonly called physisorption (physical adsorption) and chemisorption (chemical adsorption) (Rouquerol 1999).

Adsorption is an easy, inexpensive and versatile process for the removal of heavy metals in wastewater. Its advantages include low capital costs, suitability at very low concentrations, low output of sludge, ease of operation and sorbent regeneration through an effective desorption process due to potential process reversal (Fu and Wang 2011). Sorbents can also be quickly incorporated into waste management systems and are applicable both for batch and continuous processes (Pyrzńska and Bystrzejewski 2010). An adsorbent is called "good" if it has a porous structure which gives rise to a large surface area and has a fast adsorption kinetics (Gupta et al. 2009).

2.4.6 Toxic heavy metals

Heavy metals are elements with an atomic density greater than 5 g/cm^3; they are among the most common wastewater contaminants. Also called trace elements and are the metallic elements of the periodic table. Arsenic, lead, arsenic, cadmium, chromium, copper, nickel, silver, and zinc are the commonest toxic heavy metals in wastewater. The introduction of large concentrations of heavy metals into water sources causes significant health and environmental issues which could lead to a rise in the cost of handling wastewater. Heavy metals also occur naturally in small amounts, and can penetrate the aquatic environment by leaching rocks, airborne dust, forest fires and vegetation (Mwita et al. 2011).

The heavy metals may cause irreversible brain damage at higher doses. Children may receive higher doses of metals from food than adults, because they consume more food than adults for their body weight. Wastewater regulations have been established to minimize exposure to hazardous chemicals from human and environmental sources. That includes limitations on the types and concentration of heavy metals that may be present in the wastewater discharged. The MCL standards (Table 7), set by USEPA for these heavy metals (Babel and Kurniawan 2003).

Table 7: The MCL and permissible limits for most of the hazardous heavy metals

Heavy metal	MCL (mg L^{-1})**	Toxicities
As	0.05	Skin Manifestation, Visceral cancers, vascular disease
Cd	0.01	Kidney damage, renal disorder, human carcinogen
Cr	0.05	Headache, diarrhea, nausea, vomiting, carcinogenic
Cu	0.25	Liver damage, Wilson disease, insomnia
Pb	0.06	Damage fetal brain, disease of the kidney's, circulatory system and nervous system
Hg	0.00003	Rhematoidarithis and disease of the kidney, circulatory system and nervous system
Ni	0.20	Dermatis, nausea, chronic asthma, coughing, human carcinogen
Zn	0.80	Depression, lethargy, neurological sign and increased thirst

** Babel and Kurniawan 2003.

2.4.6.1 Chromium

Chromium as a heavy metal ranking among the top sixteen toxic substances with adverse human health effects (Gardea-torresday et al. 2000). High mass of chromium has been reported to cause damage to the human kidney and liver (Khambhaty et al. 2009); and it causes skin irritation and ulceration at low concentration (Karthikeyan et al. 2005). Exposure to high concentrations of chromium often induces cancer in the digestive tract and in the lungs (Ofudje et al. 2014). Accordingly, indiscriminate discharges of heavy metals into marine bodies and potable water supplies must be controlled by the implementation of legal requirements and a stringent mechanism for environmental protection. (Garg et al. 2004). Chromium in trace concentration is an important item of the diet, as it controls the human body's glucose metabolism. Due to its carcinogenic effect, the excess amount of chromium absorption is very dangerous. Chromium inhibits plant development in soils (Shanker et al. 2003), is non-essential for micro-organisms and other types of life, and exerts toxic effects on them after cellular absorption when in excess amounts. Cr (VI) enters the cell more readily compared to Cr (III) but is eventually reduced to Cr (III) after it leaves the cells. Sulphate and phosphate carrier system Cr (VI) is transported through mammalian cell membrane with the aid of carboxylate.

2.4.6.2 Cadmium

Cadmium is a highly toxic heavy metal. It is harmful at extremely low levels of exposure, and has acute and chronic health and environmental consequences. Cadmium is not degradable in nature, and will thus remain in circulation until released into the environment. New releases contribute to the already existing natural deposits of cadmium. Compared with other heavy metals, cadmium and cadmium compounds are easily soluble in water. Cadmium is typically present as impurity in deposits of zinc (Zn) or lead (Pb), and is therefore formed primarily as a by-product of smelting zinc or lead. Human exposure to cadmium primarily occurs through inhalation or ingestion. Depending on the particle size, 10-50 % of inhaled cadmium dust is absorbed. For people with an iron, calcium, or zinc deficiency, intestinal absorption is greater (Nordberg et al. 2007). Cadmium is considered a poisonous metal and is both harmful to human and wildlife. It functions as a mitogen in many tissues and encourages cancer. This also stimulates cell growth, prevents restoring DNA, and prevents apoptosis. It causes cell death that results in tissue damage in the kidney. Cadmium at low concentration causes apoptosis in cell culture systems, and it becomes evident with increased concentration necrosis. In addition, cadmium affects renal function when exposed to the environment (Templeton and Liu 2010).

2.4.6.3 Nickel

The heavy metals constitute main portions of the periodic table and include metals from the periodic table from groups IIA (most of the alkaline earth metals) to certain chalcogens (such as selenium, polonium, tellurium etc.). Nickel is regarded as an industrial and occupational health risk among environmental heavy metal pollutants, because many nickel compounds are accessible in the human environment (Macholz et al. 1978). The average nickel concentration in the Earth's crust is about 75 mg/kg and makes up about 0.016 % of the total mass. Pentlandite ($(FeNi)_9S_8$), millerite (NiS) and garnierite ($(NiMg)_6Si_4O_{10}(OH)_8$) are the principal ores. It only happens in meteorites, as the natural metal. It is used in metal processing, nickel plating for corrosion resistance and in battery manufacturing (e.g. nickel-cadmium batteries) (Dojlido and Best 1993).

2.5 Flame atomic absorption spectrophotometry

2.5.1 Basic principles

Flame atomic absorption is a quick and precise method of study. Determinations of analyte concentrations are common for most elements in the mg L^{-1} concentration area. The need for trace metal analysis at μg L^{-1} and even sub μg L^{-1} rates, however, demands a more sensitive technique. Atomic absorption spectroscopy (AAS) is regarded, with few interferences, as a very basic technique. Probably there will never be an ultimate analytical method which is absolutely free of any interference from the nature of the sample. FAAS is a technique used to measure the quantity of chemical elements present in environmental samples by measuring the radiation absorbed by the chemical element of interest. The wavelengths of light emitted by the sample are determined by a detector and compared to the wavelengths originally passed through the sample as shown in the Figure 8. AAS is commonly used in a wide range of substances to classify elements present. (García and Báez 2012).

Atoms of different elements absorb characteristic wavelengths of light. Analyzing a sample to see if it contains a particular element means using light from that element. In FAAS, the sample is atomized, i.e., converted into ground state free atoms in the vapor state and a beam of electromagnetic radiation emitted from excited atoms is passed through the vaporized sample. Some of the radiation is absorbed by the atoms in the sample. The greater the number of atoms there is in the vapor, the more radiation is absorbed. The amount of light absorbed is proportional to the number of atoms. First, via the nebulization process, we aspire the sample to the burner chamber, where it mixes with the fuel and oxidant gases as a fine aerosol. At this point, the metals in the droplets of fine aerosols are still in solution. When these small droplets pass through the heat of the flame, the evaporation or desolvation process eliminates the solvent and leaves small solid particles of sample material. When more heat is added, liquefaction occurs and extra heat vaporizes the sample. At this point the metal of interest, called the analyte, is still connected to some anion to form a molecule that does not demonstrate the phenomenon of atomic absorption that we wish to test. By adding even more heat energy, this molecule dissociates itself into the individual atoms that make it up (García and Báez 2012).

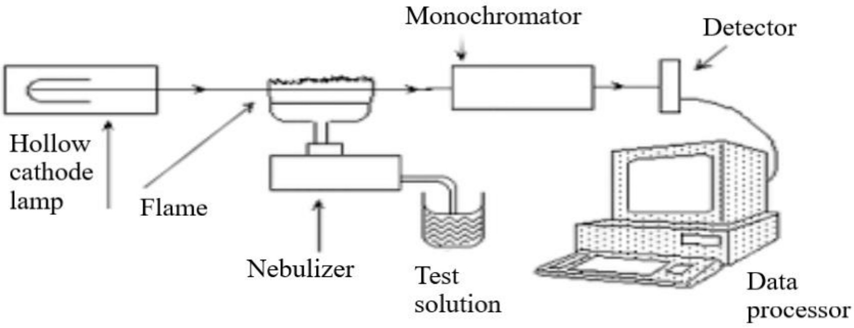


Figure 8: Components of Atomic Absorption spectrophotometer

2.6 Sample decomposition

Decomposition requires the release of the analyte (metal) of interest by using a reagent (mineral / oxidizing acids or fusion flux) and/or heat from an interfering matrix. The use of reagents (acids) and external heat sources can in itself cause problems. These problems are specifically based in the elemental analysis on the risk of contamination and loss of analyte. It should be recalled that complete digestion may not always be needed as atomic spectroscopy frequently uses a hot source, e.g. flame or inductively coupled plasma, which provides a secondary method of sample dissolution. Methods which require sample dissolution can therefore be equally useful (Dean 2003). The various methods of decomposition could be classified as dry ashing, wet digestion and digestion by microwave (Mustafa et al. 2006).

2.6.1 Dry ashing techniques

Dry ashing is a typically convenient method of sample preparation to be used in food materials for subsequent trace metal determination. Dry oxidation or ashing removes or minimizes the effects of organic materials on determination of mineral elements. It consists of the combustion of organic compounds in a muffle furnace by air at ambient pressure and at relatively elevated temperatures (450-550 °C). Ash residues resulting from this dissolve in a suitable solution. Dry ashing presents several useful features: (1) treatment of large sample amounts and dissolution of the resulting ash in a small acid volume resulted in element preconcentration; (2) complete destruction of the organic matter, which is a prerequisite for some detection techniques (e.g., ICP-OES); (3) simplification of the sample matrix and the final solution condition (clearness, colorless and odorless); (4) application to a variety of samples (Welna and Szymczycha-Madeja 2011).

2.6.2 Wet ashing techniques

Wet digestion is used to oxidize the organic component of the samples or to remove elements by concentrated acids or their mixtures from inorganic matrices. It is usually performed in open vessels (in tubes, in beakers, on a hot plate, in a heating block) or in closed systems at high pressure (digestion bombs) using different sources of energy: thermal, ultrasonic and radiant (infrared, ultraviolet and microwave) (Sneddon et al. 2006). Wet digestion presents a wide range of varieties compared to dry ashing, including the choice of reagents as well as the instruments used. Nonetheless, before analysis, consideration should be given to the sample nature and its composition, as well as the composition and concentration of the reactive mixture. It includes: strength of the acid, its oxidizing and boiling point, resulting salt solubility, reagent safety and purity. In general, organic materials, alloys, minerals, soils, rocks, and silicates are used with HNO_3, HCl, H_2SO_4, H_3PO_4, $HClO_4$, HF, and H_2O_2. Concentrated HNO_3 is the most suitable oxidant for organic matter degradation. Unfortunately it can lead to incomplete digestion of materials with organic rich matrices due to relatively low oxidation potential (Welna and Szymczycha-Madeja 2011).

2.6.3 Microwave assisted digestion

MW assisted sample preparation with HNO_3 or its mixtures with HCl or H_2SO_4 (with or without added H_2O_2) is these days predominantly used for decomposition of a variety of inorganic and organic materials. The interaction of microwave radiation with samples and reagents results in fast heating of reaction mixtures and their efficient decomposition. The use of small amounts of reagents decreases signals from the blank and increases accuracy of results. Usually, a mixture of HNO_3 and H_2O_2 is used for botanic, biological and food samples, while a mixture of H_2SO_4 and H_2O_2 is mainly used for oily samples. Acid mixtures are recommended for inorganic materials such as metals, alloys, minerals and for extracts from soils and sediments. Two different systems for MW assisted digestion are used: pressurized closed vessels and open focused vessels. MW assisted digestion in closed vessels under pressure is the most commonly applied. It offers safety radiation, versatility, energy control and possibility for addition of solutions during digestion. The only limitation is time required for cooling before vessels can be opened (even hours). In case of open focused MW system loss of volatile elements can occur. Results for low-level elements might also be affected by higher amounts of reagents used (increased risk of sample contamination). Both drawbacks can be, however, minimized by using vapor phase acid digestion, which has been proven to be very effective in minimizing the residual carbon content (Sneddom et al. 2006).

3 EXPERIMENTAL

3.1 Description of the study area

The present study was conducted in Addis Ababa University, Addis Ababa Ethiopia. Addis Ababa is the capital city of Ethiopia with longitude of 38° 44' 48.80" E coordinates and latitudes of 9° 01' 29.89" N. The study was done in the Department of Chemistry, Analytical chemistry laboratory from December 2019 to June 2020.

3.2 Apparatus and instruments

Electronic balance (ZSA 120) with a precision of ± 0.0001 g was used for accurate measurements of adsorbent mass. 250 mL Round bottomed flasks fitted with a reflux condenser were used in Kjeldahl apparatus (Gallenkamp, England) and whatmann (150 mm) filter paper were used. pH meter (HACH, sension^{TM} + mm150, South Africa) was used for measurements of pH. Hot plate (IKA®RET, China) was used for the digestion of wastewater. The concentration of metal ions was analyzed using Flame Atomic Absorption Spectrophotometer (Analytikjena, Germany). A convection oven (J.P.SELECTA, Spain) was used for drying adsorbents. Plastics bags (Ziploc, USA) were used for storing adsorbents until use.

3.3 Chemicals and reagents

All chemicals and reagents used in the present work were of analytical grade. All glass wares and plastic containers used were washed with detergent solution followed by soaking in 37 % (v/v) nitric acid and rinsed with distilled water. The stock solutions of Cd^{2+} and Ni^{2+} were prepared from $Cd(NO_3)_2.4H_2O$ (Hopkin and Williams LTD, England) and $Ni(NO_3)_2.6H_2O$ (Analytical reagent, US) and then diluted to appropriate concentrations. Cr^{3+} solution was diluted from 1000 mg L^{-1} of standard solution (BDH reagents, England). 0.1 mol L^{-1} HCl and 0.1 mol L^{-1} NaOH were used for pH adjustment. HNO_3 and $HClO_4$ were used for acid digestion of the adsorbents and wastewater. Distilled water was used in the entire experiments.

3.4 Methods

3.4.1 Wastewater collection

Sample of wastewater was collected from local tannery located at Asko Road, Addis Ababa. The color of the wastewater was black, while it had pH value of 7.65 ± 0.13. The wastewater was taken from three times which is before treatment. The wastewater was mixed well to make it homogenized and filled in plastic containers.

3.4.2 Collection of adsorbent samples

Groundnut, lentil and orange were purchased from the local market in Addis Ababa. The adsorbents from the different places were mixed well to homogenize adsorbent samples. Samples from different areas may have different adsorption abilities, therefore, mixing samples from different areas will help to homogenize this ability. Though the study is based on adsorbent types found in the areas where the indicated samples are collected it does not intend to correlate specific adsorbent ability to specific sample area.

3.4.3 Preparation of adsorbents

Groundnut shell (GS), lentil husk (LH) and orange peel (OP) were used as the raw material for the preparation of the adsorbents. The GS, LH and OP which were prepared from the items purchased from local markets, were washed with distilled water several times to remove dust, adsorbed impurities and other contaminants. Then they were washed with distilled water and were dried in sunlight for two weeks. The GS, LH and OP were dried at 177 ℃, 70 ℃ and 93 ℃ respectively inside a convection oven for 25 - 30 min to remove any moisture left. The dried GS, LH and OP were crushed and sieved with 0.30 mm sieve to obtain smaller particles and were kept in Ziploc plastics.

3.4.4 Preparation of wastewater samples

For the determination of the total concentration of metals, acid digestion using 55% nitric acid was performed to decompose organic matter and to dissolve larger particles in the sample. First the wastewater samples were filtered and 100 mL of each sample was taken into a 250 mL beaker and 10 mL of concentrated nitric acid was added, then the sample was evaporated to near dryness on a hot plate. The sample was then cooled and another 1 mL of concentrated nitric acid was added, until digestion was complete. This digestion decomposed the organic matter. The beaker was then washed down with distilled water and the sample was filtered into a 100 mL volumetric flask to remove silicate and other insoluble materials. Then each sample was made up to the mark with distilled water.

3.4.5 Standard metal solution preparation

Standard metal stock solutions (1000 mg L^{-1}) were prepared by dissolving 0.274 g $Cd(NO_3).4H_2O$ and 0.512 g $Ni(NO_3)_2$ in distilled water then diluted to 100 mL. Standard solution was prepared for each metal for calibration of the instrument for each element being determined. Working standards were prepared from stock solution of 1000 mg L^{-1}.

3.4.6 Optimization of digestion

Wet acid digestion is one of the methods used to get free metals ions in solution from complex organic matrix based on adjusting various parameters such as volume ratio of reagents added, sample mass, digestion temperature and time duration. Wet acid digestion is commonly conducted using Kjeldhal apparatus in which organic components are assumed to decompose into various gaseous forms leaving metallic elements in the solution. Therefore, if the solution is clear and colorless, digestion is expected to be complete.

In this study, for the digestion of GS, LH and OP samples, different parameters such as digestion time, volume ratio of reagents, mass of adsorbent, digestion time, and digestion temperature were tested to achieve optimum conditions. For optimization varying masses of homogenized GS, LH and OP samples were transferred into a round bottomed flasks. Then different volume mixtures of HNO_3 (69- 72%), $HClO_4$ (70%) were added and the mixtures were digested in the Kjeldahl digestion apparatus by setting different temperatures (30-300 ℃) for varying times (0:30 – 3:00 hrs). Then after, the digested solution was allowed to cool for 10 min without dismantling the condenser from the flask and for 5 min after removing the condenser. Deionized water was added to the cooled solution in order to dissolve the precipitate formed on cooling. Then the solution was poured into 50 mL volumetric flask. The volumetric flask was filled to the 50 mL mark with distilled water. Blank solutions were prepared following the same digestion procedure as for the sample. Triplicate samples and blanks were digested.

A series of procedures involving some changes in reagent volume, adsorbent mass and digestion temperature and digestion time were tested. Accordingly, thirty-four procedures were tested for the digestion of each GS, LH and OP samples.

The optimized procedure was selected depending on: clarity of digests, minimal reflux time/digestion time, minimal reagent volume consumption, absence of undigested GS, LH and OP samples. As wet digestion is used, it was necessary to prepare reagent blanks for each digestion employed. Reagent blanks were also prepared and digested using the same procedure as for the samples.

3.4.7 Digestion of adsorbents

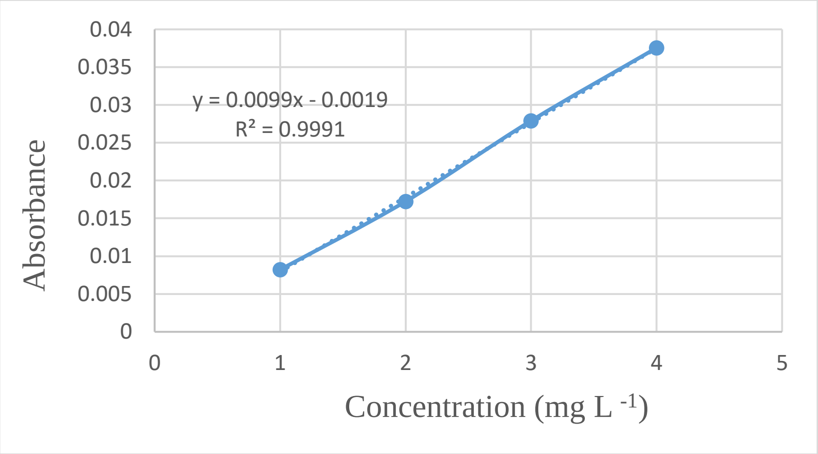
Applying the optimized conditions 0.25 g, 0.25 g and 0.25 g of powdered GS, LH and OP samples respectively were transferred into a 250 mL round bottomed flask. Then 6 mL, 6 mL and 7 mL of a mixture of HNO_3 and $HClO_4$ with a volume ratio of 2:4, 4:2 and 4:3 (v/v) respectively was added to the samples. The corresponding solutions were then digested on Kjeldhal digestion apparatus fitted to a reflux condenser by setting the temperature at 270 ℃, 240 ℃ and 300 ℃ respectively until a clear and colorless solution was obtained. The digested solution was allowed to cool for 10 min without dismantling the condenser from the reflux. In order to dissolve the precipitate formed on cooling, 5 mL of distilled water was added to the cooled solution, and the mixture was gently swirled and filtered into 50 mL volumetric flask to remove any suspended matter. The clear solution was then diluted up to 50 mL with distilled water. Each sample was analyzed in triplicate and blank digests were processed similarly.

3.4.8 Instrument calibration

The qualities of the results obtained for analysis of heavy metals using FAAS are seriously affected by calibration and standard solution preparation procedures. Calibration curves were prepared to determine the concentration of metals in the sample solution. The instruments were calibrated using a series of working standards. Concentration of the working standards, calibration equation and correlation coefficient value for each of the metals is listed in Table 8. The calibration curve of each of the metals of interest is shown in Figure 9. The calibration graphs and correlation coefficient of each of the elements were determined by plotting absorbance versus working standards concentration of metals.

Table 8: Calibration of the instrument

Metals	Concentration of standards (mg L^{-1})	Calibration equation	Correlation Coefficient
Cr	1, 2, 3, 4	Y= 0.0099x - 0.0019	0.9991
Ni	1, 2, 3, 4	Y= 0.0044x + 0.0024	0.9998
Cd	0.25, 0.50, 0.75, 1.0	Y= 0.0045x + 2E-05	0.9963



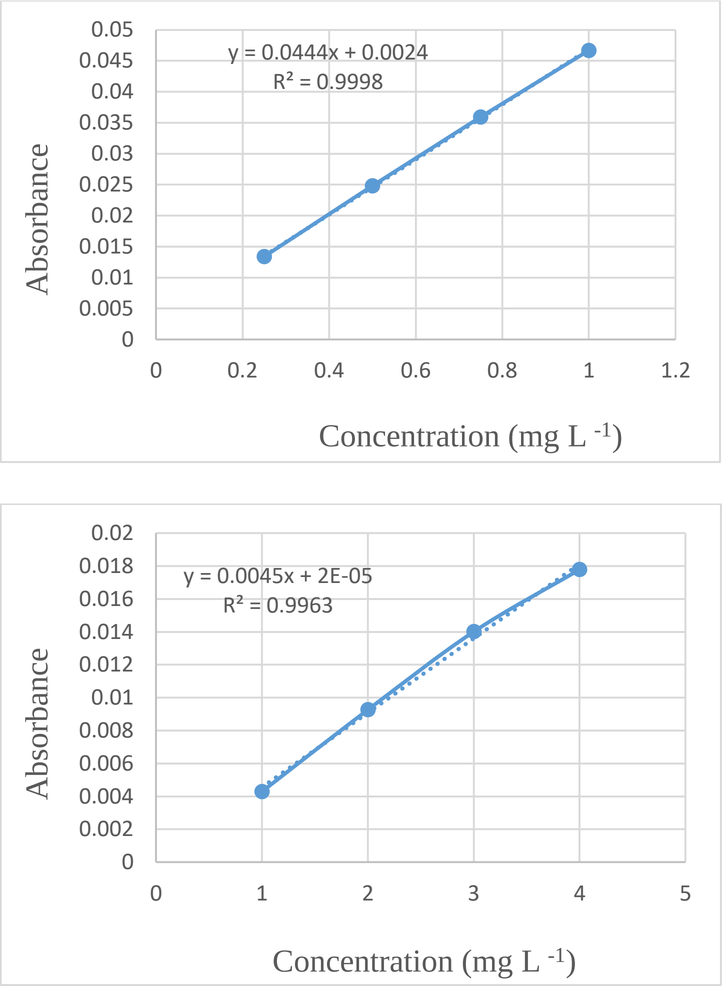


Figure 9: Calibration curve of standard solutions of Cr $^{3+}$, Cd $^{2+}$ and Ni $^{2+}$

3.4.9 Adsorption studies

Batch adsorption experiments were carried out by mixing adsorbents with 100 mL of wastewater and standard solutions (Cd $^{2+}$ and Ni $^{2+}$) in a desired concentration in 100 mL conical flask. The effect of the pH of the solution on the Cr $^{3+}$, Cd $^{2+}$ and Ni $^{2+}$ equilibrium adsorption was investigated between 4 and 9. The adsorption time ranged from 15 to 240 min and 0.2-3.5 g of adsorbent mass were used in adsorption studies. After the specified contact time was reached, the samples were extracted and analyzed using flame atomic absorption spectrophotometry for the concentration of the residual ions. The selected heavy metal ions removal was calculated by the following equation:

$$\boldsymbol{R = \frac{Co-Ce}{Co} \times 100} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(1)}$$

The amount of metal ions adsorbed onto GS, LH and OP, Qe (mg/g) was calculated by the following equation:

$$Qe = \frac{(Co - Ce)V}{m} \text{ ....(2)}$$

Where R is the adsorption efficiency of metal ions adsorbed by adsorbent, C_o and C_e are the initial and final concentration of metal ions (mg L^{-1}). V is the volume of metal ions solution (L) and m is the mass of adsorbent used (g).

3.4.9.1 Effect of adsorbent mass

The effect of adsorbent mass in the removal of the selected heavy metals was investigated for different masses ranging from 0.025-3.5 g. Solutions of the same initial concentration, the same contact time and temperature at the selected optimum pH were used. The samples were filtered using 150 mm filter paper and the filtrate was analyzed for the metals of interest.

3.4.9.2 Effect of contact time

The effect of contact time was investigated at optimum adsorbent mass, pH, concentration, and temperature for varying contact times between 15 and 240 min. The samples were filtered using 150 mm filter paper and the filtrate was analyzed for the metals of interest.

3.4.9.3 Effect of pH

The study of the effect of pH on adsorption was performed in the pH range of 4 - 9. The pH was adjusted using 0.1 M NaOH and 0.1 M HCl solutions using a pH meter. The samples were filtered using 150 mm filter paper and the filtrate was analyzed for the metals of interest.

3.4.10 Method performance and method validation

3.4.10.1 Precision

The precision of an analytical procedure expresses the closeness or agreement (degree of scattering) between a series of measurements obtained under the specified conditions from multiple sampling of the same homogenous sample. Precision always follows accuracy but a high degree of accuracy does not imply precision. The precision of an analytical method is usually expressed as the variance, standard deviation or coefficient of variance of a sequence of measurements (EMEA 2006).

3.4.10.2 Accuracy

The accuracy of an analytical method is to what extent the method generated test results agree with the true value. Accuracy can also be defined as the closeness or agreement between a measurement value and true value. The percentage recovery or the difference between the mean and the accepted true value together with the confidence intervals are recommended. (Lopez et al. 2011).

4 RESULTS AND DISCUSSION

4.1 Determination of heavy metals in wastewater

The concentrations of the three elements (Cr^{3+}, Cd^{2+} and Ni^{2+}) in the digested wastewater, groundnut shell, lentil husk and orange peel were analyzed by FAAS. Among the analyzed metals, only Cr^{3+} was detected in the wastewater sample but Cd^{2+} and Ni^{2+} were below detection limit. All the three elements (Cr^{3+}, Cd^{2+} and Ni^{2+}) were not found in the groundnut shell, lentil husk and orange peel and the level of metals in the wastewater are shown in the table below.

Table 9: Average concentration and relative standard deviation of the selected heavy metals in wastewater

Metals	Mean± SD	RSD %
Cr	30.8±1.1	3.64 %
Ni	BDL	BDL
Cd	BDL	BDL

4.1.1 Determination of heavy metals in adsorbents

The adsorbents collected from different areas were not found to contain detectable heavy metal content. Since these adsorbents did not contain any of the selected heavy metals, we can conclude that there will be no flow of metals from the adsorbents to the wastewater and standard solutions. Additionally, the transfer of the selected heavy metals was checked by soaking 2 g each of the adsorbents in 100 mL distilled water for 3 hrs and were found free of those selected heavy metals.

4.2 Effect of adsorbent mass

The effects of adsorbent mass were studied by varying the masses of GS, LH and OP from 0.2 to 3.5 g. Figure 10 indicates the effect of the mass of GS, LH and OP on the amount of Cr^{3+} ions removed from wastewater. The results show that as the adsorbent mass increased from 0.2 to 3.5, 0.025 to 1.2 and 0.2 to 1.2, the Cr^{3+} removal increased from 7.66 to 71.28%, 0.55 to 76.45%, and 13.57 to 55.52%, respectively, for GS, LH and OP. Adsorption percentage increased with adsorbent surface area and due to more adsorption sites are available. Therefore, for further experiments 3 g, 3 g and 2.5 g of GS, LH and OP, respectively were used as optimized masses.

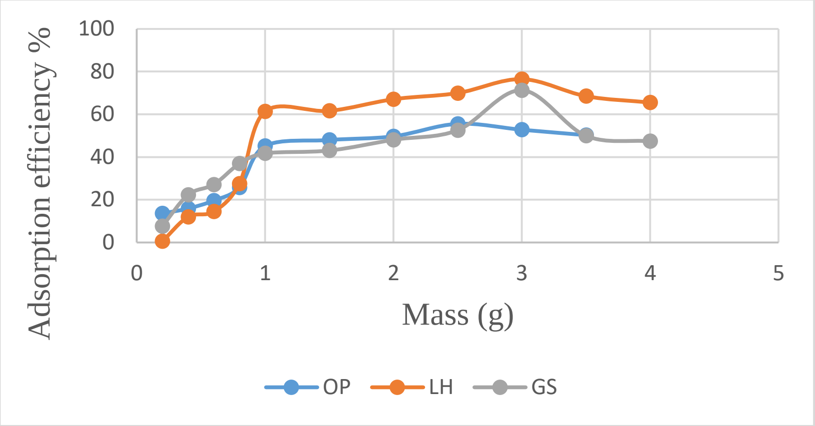


Figure 10: Effect of adsorbent mass on the adsorption efficiency of GS, LH and OP for Cr $^{3+}$

Figure 11 shows the effect of adsorbent mass on adsorption of Cd $^{2+}$ on GS, LH, and OP. As shown in the Figure, as the contact surface for adsorbate increased, the efficiency of Cd $^{2+}$ adsorption increased with increase in the adsorbent mass. Increasing mass increased the availability of more active sites for adsorption, making it easier for metal ions to reach the adsorption sites. As in Figure 11, Cd $^{2+}$ adsorption efficiency increased from 85.08 to 100%, 84.69 to 100%, and 94.03 to 96.67%, respectively, for GS, LH and OP. At adsorbent mass of 0.2 g for GS and LH, a maximum adsorption of 100% was observed. Therefore, the use of 0.15 g for GS and LH, and 0.8 g for OP is justified for economic purposes.

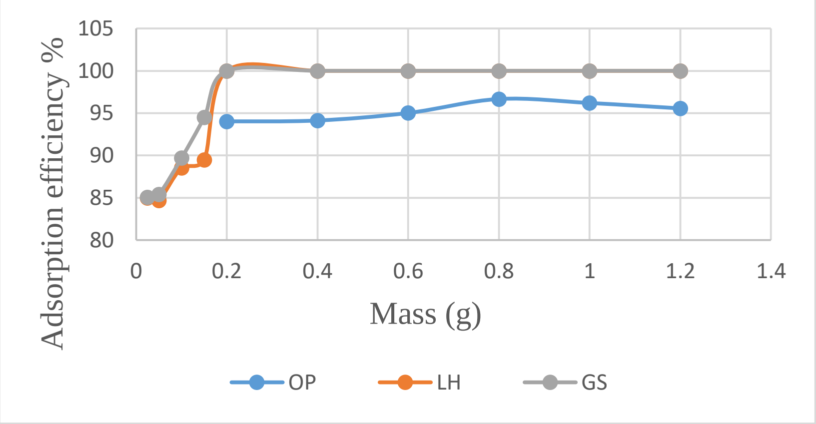


Figure 11: Effect of adsorbent mass on the adsorption efficiency of GS, LH and OP for Cd $^{2+}$

The mass of adsorbents is a critical parameter in batch experiments, because it determines the adsorption efficiency of adsorbents. The effect of various amounts of GS, LH and OP was studied for their adsorption efficiency for Ni $^{2+}$. The percentage of adsorption increased as the mass of the adsorbent increased as shown in Figure 12. The increase in adsorption might be due to the increase in the number of sites available for adsorption as the adsorbent surface area and functional groups on the surface increase as the mass is increased. The adsorption percentage for GS, LH and OP increased from 78.77 to 86.91%, 67.5 to 76.12%, and 39.24 to 53.37% respectively. Accordingly, the maximum adsorption of Ni^{2+} by GS, LH, and OP obtained were 86.91%, 76.12% and 53.37%. Therefore it was justified to use 0.8 g, 0.8 g, and 0.4 g of GS, LH, and OP respectively.

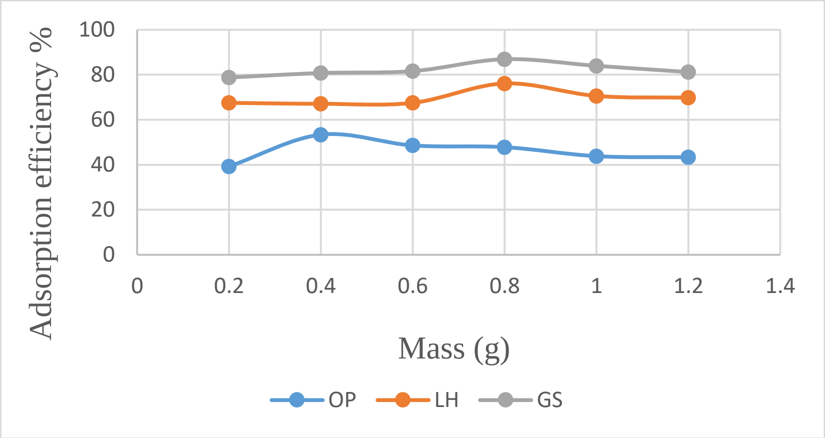


Figure 12: Effect of adsorbent mass on the adsorption efficiency of GS, LH and OP for Ni^{2+}

The detailed optimization of the effect of adsorbent dosage could not be performed due to some practical inconveniences. Hence in our preliminary work for adsorption of Cr^{3+} the optimized adsorbent masses taken were 3 g, 3 g and 2.5 g for GS, LH and OP respectively. Similarly for Cd^{2+} 0.15 g of GS and LH and 0.8 g of OP were used. Further 0.8 g of GS and LH and 0.4 g of OP were used for Ni^{2+}. The masses of adsorbents taken are comparable to the masses taken in similar adsorption studies. Gupta and Sen have used 0.1-2.5 g of chemically modified Groundnut husk for the removal of Cr^{3+} (Gupta and Sen 2017) and Trivedi et al used 1 to 6 g of groundnut shell ash for the removal of 2,4- dichlorophenoxy acetic acid (Trivedi et al. 2019).

4.3 Effect of contact time

In removing the selected heavy metals, the contact time between adsorbent and adsorbed species plays an important role. To study the effect of contact time of Cr^{3+}, batch adsorption studies were performed in separate flasks and the samples were withdrawn at a time interval between 30 and 240 min. Figure 13 demonstrates the adsorption efficiency for Cr^{3+} ions versus contact time of GS, LH and OP. The adsorption efficiency increased from 14.09 to 71.38%, 73.27 to 87.82% and 47.62 to 76.46% for GS, LH and OP respectively. The adsorption rate of Cr^{3+} ions on the adsorbents was rapid, with maximum adsorption for LH and OP being observed within 120 min while maximum adsorption for GS occurred at 180 min.

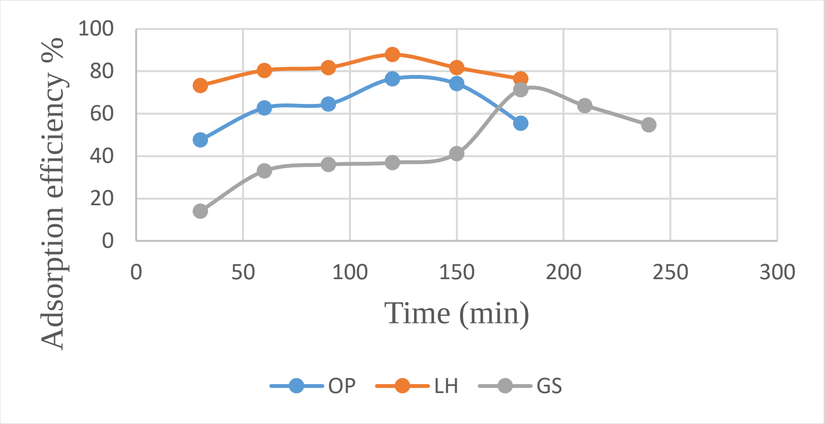


Figure 13: Effect of contact time on the adsorption efficiency of GS, LH and OP for Cr $^{3+}$

One of the important factors in the process of batch adsorption is contact time. As shown in Figure 14, the adsorption efficiency for Cd $^{2+}$ increased rapidly and the optimal removal efficiency was achieved for GS, LH and OP with in about 30, 60 and 120 min respectively. The adsorption was initially rapid when the number of available sites was much higher than the number of adsorbable metal species. The adsorption efficiency of GS, LH and OP increased from 95.9 to 100%, 93.27 to 100%, and 93.95 to 96.67% respectively. Thus, the contact time for GS, LH and OP was selected to be 60, 60 and 120 min respectively.

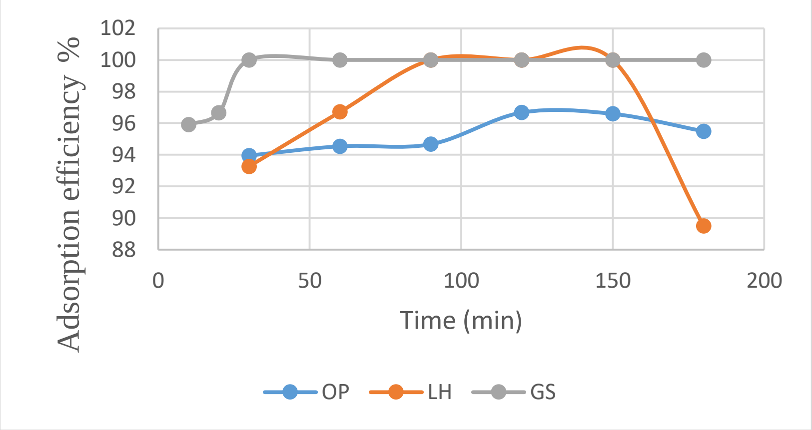


Figure 14: Effect of contact time on the adsorption efficiency of GS, LH and OP for Cd $^{2+}$

The effect of the adsorption contact time on Ni $^{2+}$ adsorption was studied from 30 to 180 min. The results are shown in Figure 15. As can be seen from Figure 14, adsorption efficiency of 74.36% was observed for OP during the first 30 minutes of the experiment but was observed to decrease in the adsorption efficiency beyond 30 minutes. Initially, the adsorption efficiency for GS and LH increased from 95.95 to 100% and 63.69 to 76.12% respectively, and the optimum removal efficiency was achieved within around 30, 120 and 60 min for GS, LH and

OP. Further increase in contact time showed no substantial improvement, though the percentage of adsorption was increasing.

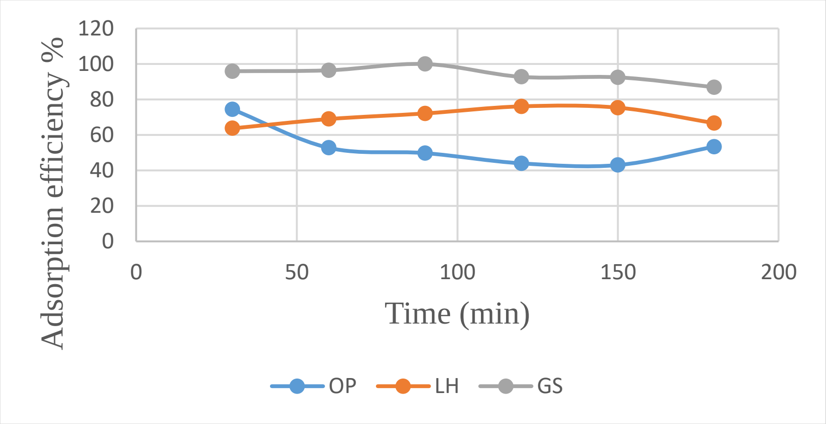


Figure 15: Effect of contact time on the adsorption efficiency of GS, LH and OP for Ni $^{2+}$

4.4 Effect of pH

It is well known that the pH value affects the protonation of the functional groups on the biomass as well as the metal chemistry. The effect of pH on Cr $^{3+}$ ions adsorption efficiency on GS, LH and OP is shown in Figure16. At low pH value, the amount of Cr $^{3+}$ adsorbed is low for GS but high for LH and OP. Increase in Cr $^{3+}$ adsorption was observed with pH value increasing from 4 to 7 for GS and LH but decreased for OP. The highest adsorption efficiency was observed at 7, 7 and 5 for GH, LH and OP respectively.

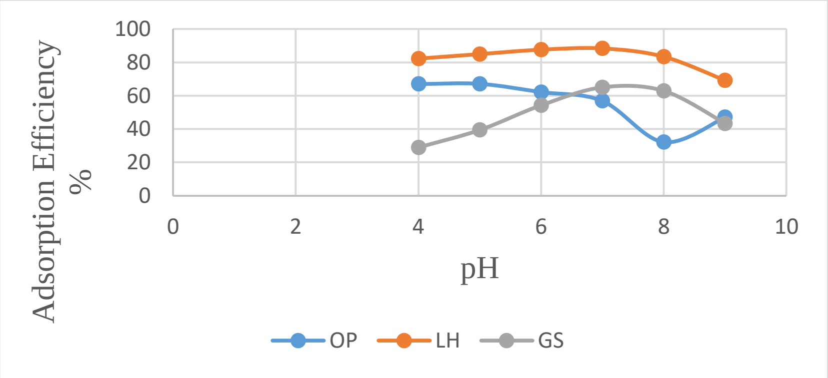


Figure 16: Adsorption efficiency of Cr $^{3+}$ on GS, LH and OP as a function of pH

The effect of pH for Cd $^{2+}$ adsorption was investigated by carrying onto the batch adsorption procedure in the pH range from 4 to 9 and is shown in Figure 17. The adsorption efficiency of Cd $^{2+}$ on OP showed an increasing trend from 91.71 to 99.34% with increasing pH from 4 to 7. Adsorption efficiencies of GS and LH decreased with increase in pH from 5 to 9. Highest adsorption efficiencies were 88.93%, 88.61% and 99.34% in solutions of pH 6, 7 and 5 for GS, LH and OP respectively. Therefore, pH 5, 5 and 7 were selected optimum solution pHs.

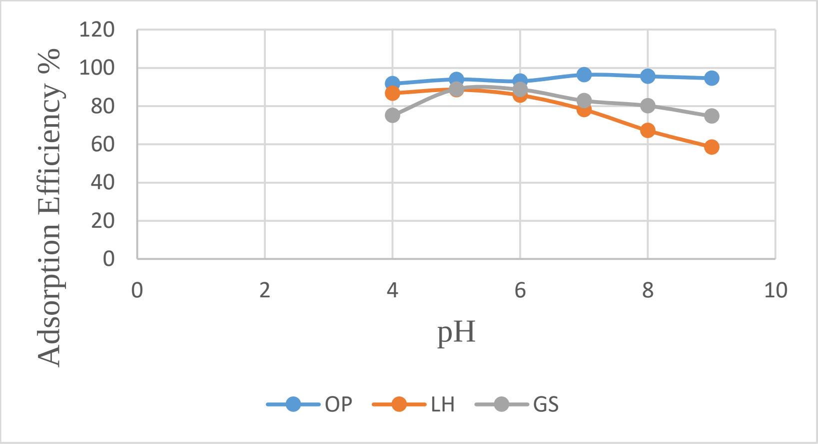


Figure 17: Adsorption efficiency of Cd $^{2+}$ on GS, LH and OP as a function of pH

The pH values of solutions have a significant influence on the adsorption process. Figure 18 gives the effect of pH on adsorption of Ni $^{2+}$ on GS, LH and OP. GS showed higher adsorption efficiency for Ni $^{2+}$ than LH and OP. From this Figure it can be seen that at low pH value of 4, the adsorption efficiency was 93.47%, 66.45% and 36.36% for GS, LH and OP respectively. When the pH of the solution was raised from 4 to 7, the adsorption efficiency increased sharply first and then decreased slightly for OP and LH. It however, remained constant for GS. The maximum adsorption observed at pH 7 with adsorption efficiency about 100%, 92.61% and 78.99% for GS, LH and OP respectively. GS and LH showed better adsorption ability for Ni $^{2+}$ than OP. At the lower pH values, H^+ in the solution will compete strongly with Ni $^{2+}$ for the active sites. However, at higher pH values, Ni $^{2+}$ will be precipitated, so the experimental pH values was controlled at 7.

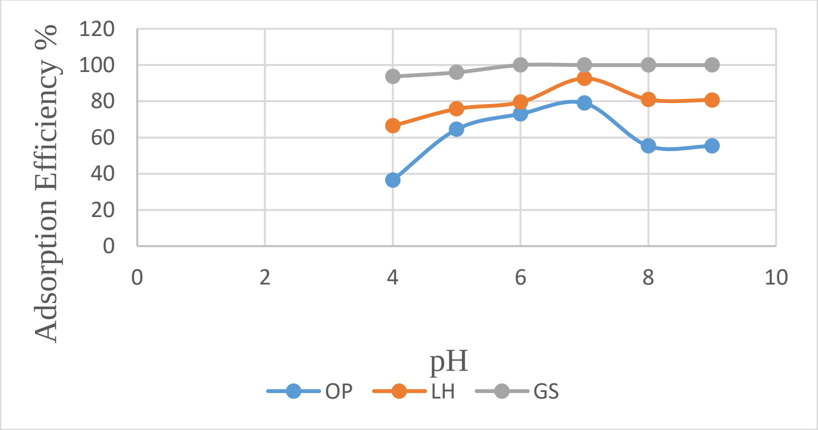


Figure 18: Adsorption efficiency of Ni $^{2+}$ on GS, LH and OP as a function of pH

The selected heavy metal concentrations in the wastewater and standard solutions are shown in Table 10. The experiment conducted showed that the adsorption efficiencies of selected heavy metals in the different adsorbents of different metals processing were in the following order: Cd(OP) > Cd(LH) > Cd(GS) > Ni(GS) > Cr(OP) > Ni(LH) > Ni(OP) > Cr(GS) > Cr(LH).

Table 10: Level of selected heavy metals in wastewater and standard solutions

Adsorbent	Metals	Initial Conc. (ppm)	After Adsorption (ppm)	Optimum pH	Adsorbent mass (g)	Contact Time (min)	Adsorbed amount (mg g^{-1})	Adsorption efficiencies (%)
GS	Cr	30.8	3.08	7	3	180	0.92	90.01
	Cd	10	0.22	5	0.15	60	6.51	97.62
	Ni	10	0.32	7	0.8	60	1.21	96.79
LH	Cr	30.8	3.44	7	3	120	0.91	88.83
	Cd	10	0.18	5	0.15	60	6.54	98.17
	Ni	10	0.48	7	0.8	120	1.19	95.17
OP	Cr	30.8	1.45	5	2.5	120	1.17	95.29
	Cd	10	0.17	7	0.8	120	1.23	98.26
	Ni	10	0.72	7	0.4	30	2.32	92.75

4.5 Comparison of removal efficiency of adsorbent with literature

The results obtained in this study were compared with the removal efficiencies of various other adsorbents reported in the literature and are shown in the Table 11. It should be noted that the removal percentage varies widely due to various parameters and characteristics of individual adsorbents. Like GS, LH and OP, other adsorbents such as activated carbon, corncob biochar, rice husk and cucumis melopeel are practical adsorbents which were used to remove heavy metals. Comparison of their removal percentage is very essential to know their adsorption efficiencies. There is a report on the adsorption level of chromium [Tomul et al. 2017], Cadmium [Mahvi et al. 2005, Manjuladevi & Oviyaa 2017] and Nickel [Jiang et al 2019, Wu et al 2016, Manjuladevi & Oviyaa 2017] on GS, LH and OP respectively. Most of the removal efficiency of adsorbents mentioned in the literature is lower than in this study and this indicates that these adsorbents have higher removal efficiency. The removal percentage of Cd^{2+} and Ni^{2+} reported in [Mahvi et al. 2005, Manjuladevi & Oviyaa 2017 and [Jiang et al 2019, Wu et al 2016, Manjuladevi & Oviyaa 2017](72.39-93% and 54-92.64%) respectively are much lower than the value obtained in this study (97.50-98.27% and 92.67-96.79%). The Cr^{3+} adsorption level reported in [Tomul et al. 2017] (80%) is relatively in good agreement with the values in this study (88.82-96.13).

Table 11: Comparison of removal percentage of the selected heavy metals with literature

Adsorbent	Metal	pH	Initial Conc. (ppm)	% removal	References
Orange peel activated with potassium carbonate	Cr	3	30	80	Tomul et al. 2017
Rice husk	Cd	6	10	97.2	Mahvi et al. 2005
Cucumis melopeel		3	100	72.39	Manjuladevi & Oviyaa 2017
Rice polish		9	125	85.29	Manjuladevi & Oviyaa 2017
Flower globular $Mg(OH)_2$	Ni	6.07 - 7.71	80	92.64	Jiang et al. 2019
Modified rice husk		7	600	54	Wu et al. 2016
Cucumis melopeel		3	100	73.40	Manjuladevi & Oviyaa 2017
GS, LH & OP	Cr	7,7 & 4	30.8	90.01, 88.82 & 96.13	This study
GS, LH & OP	Cd	5,5 & 7	10	97.50, 98.15 & 98.27	This study
GS, LH & OP	Ni	7, 7 & 7	10	96.79, 95.2 & 92.67	This study

4.6 Statistical analysis of variance (ANOVA)

Statistical analysis involves arranging and analyzing data in accordance with well-defined, systematic and mathematical procedures and rules. The term "data” refers to information gathered through data collection to answer questions such as “How much?” “How many?” “How long?” “How fast?” and “How related?”. Data is represented by numbers in statistical analysis. The value of numerical representation lies largely in the clarity of numbers asserted. This property cannot always be expressed in words (Gould and Ryan 2014). The ANOVA "one-way," or "single-factor" ANOVA, has the same purpose as t-testing. It is designed to compare sample group means to determine whether a significant difference in population can be inferred. But, one-way ANOVA, also known as the "F-test," can manage two or more groups. It is an extension of the t-test to a situation involving two or more classes. As in t-test, the null hypothesis for an ANOVA states that there is no difference between the means of two or more populations (Depoy and Gitlin 2016).

Table 12 presents a one-way analysis of variance (ANOVA) statistical comparison of the selected heavy metal contaminants on different adsorbents. The results indicate that adsorbents are individually different from each other and are thus not the same. The ANOVA results (Table 12) showed that no statistically significant differences exist at 95% confidence level in mean concentrations of Cr^{3+} and Ni^{2+} but there is significant difference in concentration of Cd^{2+}. Variations in this regard probably arise from different composition of adsorbents and slight variation in net effect of pH dependent processes.

Table 12: One-way ANOVA comparison of detected heavy metals between and within adsorbents at 95% confidence level

Metal	Comparison	SS	Df	MS	F_{calc}	F_{crit}	Remark
Cr	between samples	1.2106	2	0.6054	0.268	9.55	No significant difference between sample mean
	within samples	6.7864	3	2.2621			
Cd	between samples	0.0058	2	0.0029	28.32	9.55	Significant difference between sample mean
	within samples	0.0003	3	0.0001			
Ni	between samples	0.0757	2	0.0378	0.47	9.55	No significant difference between sample mean
	within samples	0.2423	3	0.0807			

4.7 Pearson’s correlation of metals

Pearson's coefficient of correlation (r) is a measure of the linear relationship between two variables. Typically, the correlation analysis starts with a graphical representation using a scatter diagram of the data pair relation. The correlation coefficient values vary between -1 and +1. Positive values of the coefficient of correlation indicate a tendency for one variable to increase or decrease along with another. Negative values of the correlation coefficient indicate a tendency to associate the increase of values of one variable with the decrease of values of the other variable and vice versa. Values of the near-zero correlation coefficient indicate a weak low relationship between variables, and those close to – 1 or +1 indicate a strong linear association between the two variables. The square of the correlation coefficient is the coefficient determination which gives the proportion of the variation in one variable which can be explained from the other variable's variation. The requirements for applying Pearson's coefficient of correlation are (a) linear relationship between variables, (b) continuous random variables, (c) variables must be normally distributed, and (d) variables must be independent of each other (PCC 2008).

Table 13 presents the results of the Pearson's correlation analysis for the selected heavy metals in groundnut. The obtained results indicate the presence of strong correlation between selected heavy metals. It can be assumed that statistically significant correlations among the heavy metals may prove that they possibly have a similar accumulation behavior.

Table 13: Pearson's correlation coefficients of the selected heavy metals in groundnuts

	Cr	Cd	Ni
Cr	1		
Cd	-0.9723	1	
Ni	-0.9956	0.9470	1

The correlation coefficients between the selected heavy metals for lentil husk reflected very strong associations between Cd-Ni as shown in Table 14. The weakest correlation coefficients were between Cr-Cd and Cr-Ni.

Table 14: Pearson's correlation coefficients of the selected heavy metals in lentil husk

	Cr	Cd	Ni
Cr	1		
Cd	0.3827	1	
Ni	0.2616	-0.7915	1

The Pearson's correlation coefficients for orange peel, in Table 15, show strong and weak correlation relationships. Cr-Ni has negative strong correlation and Cr-Cd and Cd-Ni have weak positive and negative correlations.

Table 15: Pearson's correlation coefficients of the selected heavy metals in orange peel

	Cr	Cd	Ni
Cr	1		
Cd	0.2915	1	
Ni	-0.9661	-0.0348	1

5 CONCLUSION

In this study, GS, LH and OP were used for the removal of Cr^{3+}, Cd^{2+} and Ni^{2+} from wastewater. The adsorption performance of Cr^{3+}, Cd^{2+} and Ni^{2+} are significantly affected by adsorbent mass, contact time and pH. In general OP showed greater adsorption efficiencies than LH and GS. The maximum adsorption efficiencies for Cr^{3+}, Cd^{2+} and Ni^{2+} on GS, LH and OP are found to be 96.13% (OP), 98.27% (OP), and 96.79% (GS) respectively. The level of adsorption efficiencies in this study are in the following order Cd(OP) > Cd(LH) > Cd(GS) > Ni(GS) > Cr(OP) > Ni(LH) > Ni(OP) > Cr(GS) > Cr(LH). The ANOVA results at 95% confidence level suggest that there were no significant differences in the mean concentration of the two metals Cr^{3+} and Ni^{2+}, but there was significant difference for Cd^{2+}. Adsorption of Cd^{2+} on OP, LH and GS was very fast and more efficient than Ni^{2+} and Cr^{3+}. GS and LH showed better adsorption ability for Ni^{2+} and Cd^{2+} than Cr^{3+}. This study showed high adsorption efficiency of the heavy metals using easy and simple water treatment process by utilizing inexpensive adsorbents. However, since this is a preliminary work further systematic study is required. The method developed has shown the application of groundnut shell, lentil husk and orange peel for the removal of Cr^{3+}, Cd^{2+} and Ni^{2+} from water. However further study is required with respect to the effect of initial metal ion concentration and specific site sampling and investigation.

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APPENDIX

APPENDIX A

Table A 1: Optimization of reagent volume for the digestion of 0.25 g samples of the groundnut shell at constant temperature and time

Volume ratio (HNO_3: $HClO_4$)	Temperature (℃)	Digestion time (hr)	Observation
1:2	300	2:30	Not clear and colorless
2:1	300	2:30	Not clear and colorless
3:2	300	2:30	Not clear and colorless
4:2	300	2:30	Not clear and colorless
2:3	300	2:30	Not clear and colorless
2:4	300	2:30	**Clear and colorless**
2:5	300	2:30	Light yellow

Table A 2: Optimization of time for the digestion of 0.25 g samples of the groundnut shell at constant volume and temperature

Digestion time (hrs)	Volume ratio (HNO_3: $HClO_4$)	Temperature (℃)	Observation
0:30	2:4	300	Light yellow
1:00	2:4	300	Light yellow
1:30	2:4	300	Not clear and colorless
2:00	2:4	300	Not clear and colorless
2:30	2:4	300	**Clear and colorless**
3:00	2:4	300	Not clear and colorless

Table A 3: Optimization of temperature for the digestion of 0.25 g samples of groundnut shell at constant volume and time

Temperature (℃)	Volume ratio (HNO_3: $HClO_4$)	Digestion time (hrs)	Observation
30	2:4	2:30	Yellow
60	2:4	2:30	Yellow
90	2:4	2:30	Yellow
120	2:4	2:30	Yellow
150	2:4	2:30	Yellow
180	2:4	2:30	Light yellow
210	2:4	2:30	Light yellow
240	2:4	2:30	Light yellow
270	2:4	2:30	**Clear and colorless**
300	2:4	2:30	Not clear and colorless

Table A 4: Optimization of reagent volume for the digestion of 0.25 g samples of the lentil husk at constant temperature and time

Volume ratio (HNO_3: $HClO_4$)	Temperature (℃)	Digestion time (hrs)	Observation
2:1	300	2:30	Not clear and suspension
3:1	300	2:30	Not clear and suspension
4:2	300	2:30	**Clear and colorless**
4:3	300	2:30	Not clear and colorless
4:4	300	2:30	Yellow
4:5	300	2:30	Yellow

Table A 5: Optimization of time for the digestion of 0.25 g samples of the lentil husk at constant volume and temperature

Digestion time (hrs)	Volume ratio (HNO_3: $HClO_4$)	Temperature (℃)	Observation
0:30	4:2	300	Light yellow
1:00	4:2	300	Yellow
1:30	4:2	300	**Clear and colorless**
2:00	4:2	300	Not clear and colorless
2:30	4:2	300	Not clear and colorless
3:00	4:2	300	Not clear and colorless

Table A 6: Optimization of temperature for the digestion of 0.25 g samples of lentil husk at constant volume and time

Temperature (℃)	Volume ratio (HNO_3: $HClO_4$)	Digestion time (hrs)	Observation
30	4:2	1:30	Yellow
60	4:2	1:30	Yellow
90	4:2	1:30	Yellow
120	4:2	1:30	Light yellow
150	4:2	1:30	Not clear and colorless
180	4:2	1:30	Not clear and colorless
210	4:2	1:30	Not clear and colorless
240	4:2	1:30	**Clear and colorless**
270	4:2	1:30	Light yellow
300	4:2	1:30	Yellow

Table A 7: Optimization of reagent volume for the digestion of 0.25 g samples of the orange peel at constant temperature and time

Volume ratio (HNO_3: $HClO_4$)	Temperature (℃)	Digestion time (hrs)	Observation
1:2	300	2:30	Not clear and colorless
2:2	300	2:30	Not clear and colorless
3:2	300	2:30	Not clear and colorless
4:1	300	2:30	Not clear and colorless
4:2	300	2:30	Not clear and colorless
4:3	300	2:30	**Clear and colorless**
4:4	300	2:30	Not clear

Table A 8: Optimization of time for the digestion of 0.25 g samples of the orange peel at constant volume and temperature

Digestion time (hrs)	Volume ratio (HNO_3: $HClO_4$)	Temperature (℃)	Observation
0:30	4:3	300	Yellow
1:00	4:3	300	Light yellow
1:30	4:3	300	Light yellow
2:00	4:3	300	Not clear and suspension
2:30	4:3	300	**Clear and colorless**
3:00	4:3	300	Not clear and colorless

Table A 9: Optimization of temperature for the digestion of 0.25 g samples of orange peel at constant volume and time

Temperature (℃)	Volume ratio (HNO_3: $HClO_4$)	Digestion time (hrs)	Observation
30	4:3	2:30	Dark red
60	4:3	2:30	Red
90	4:3	2:30	Orange
120	4:3	2:30	Yellow
150	4:3	2:30	Yellow
180	4:3	2:30	Yellow
210	4:3	2:30	Yellow
240	4:3	2:30	Light yellow
270	4:3	2:30	Not clear and colorless
300	4:3	2:30	**Clear and colorless**

APPENDIX B

Table B 1: Optimization of adsorbent mass of Cr $^{3+}$ (Co = 30.8 ppm)

Mass(g)	GS	LH	OP
0.2	28.44	30.63	26.62
0.4	23.93	27.101	25.91
0.6	22.5	26.35	24.76
0.8	19.441	22.31	22.86
1	17.959	11.91	16.903
1.5	17.56	11.83	16.03
2	15.997	10.148	14.502
2.5	14.62	9.26	**13.69**
3	**8.846**	**7.253**	14.55
3.5	15.431	9.71	15.33
4	16.216	10.626	

Table B 2: Optimization of adsorbent mass of Cd $^{2+}$ (Co = 10 ppm)

Mass(g)	GS	LH	OP
0.025	1.492	1.501	
0.05	1.459	1.531	
0.1	1.031	1.145	
0.15	**0.551**	**1.05**	
0.2	BDL	BDL	0.597
0.4	BDL	BDL	0.587
0.6	BDL	BDL	0.498
0.8	BDL	BDL	**0.333**
1	BDL	BDL	0.38
1.2	BDL	BDL	0.444

Table B 3: Optimization of adsorbent mass of Ni $^{2+}$ (Co = 10 ppm)

Mass(g)	GS	LH	OP
0.2	2.123	3.25	6.076
0.4	1.924	3.291	**4.663**
0.6	1.84	3.25	5.142
0.8	**1.309**	**2.388**	5.218
1	1.604	2.943	5.618
1.2	1.881	3.02	5.665

Table B 4: Optimization of contact time of Cr $^{3+}$ (Co = 30.8 ppm)

Time(min)	GS	LH	OP
30	26.46	8.23	16.13
60	20.63	6.027	11.48
90	19.7	5.608	10.94
120	19.43	**3.75**	**7.25**
150	18.12	5.636	7.965
180	**8.8**	7.25	13.69
210	11.15		
240	13.94		

Table B 5: Optimization of contact time of Cd $^{+2}$ (Co = 10 ppm)

Time(min)	GS	LH	OP
10	0.41		
20	0.335		
30	BDL	0.673	0.605
60	**BDL**	**0.329**	0.546
90	BDL	BDL	0.533
120	BDL	BDL	**0.333**
150	BDL	BDL	0.341
180	BDL	1.05	0.451

Table B 6: Optimization of contact time of Ni $^{2+}$ (Co = 10 ppm)

Time(min)	GS	LH	OP
30	0.405	3.631	**2.564**
60	**0.354**	3.105	4.731
90	BDL	2.788	5.029
120	0.727	**2.388**	5.606
150	0.751	2.462	5.702
180	1.307	3.334	4.663

Table B 7: Optimization of pH of Cr $^{3+}$ (Co = 30.8 ppm)

pH	GS	LH	OP
4	21.88	5.467	10.164
5	18.66	4.6354	**10.13**
6	14.1	3.813	11.65
7	**10.771**	**3.579**	13.29
8	11.42	5.113	20.9
9	17.44	9.49	16.31

Table B 8: Optimization of pH of Cd^{2+} (Co = 10 ppm)

pH	GS	LH	OP
4	2.487	1.324	0.829
5	**1.107**	**1.139**	0.603
6	1.134	1.432	0.698
7	1.718	2.184	**0.366**
8	1.983	3.279	0.442
9	2.528	4.14	0.544

Table B 9: Optimization of pH of Ni^{2+} (Co = 10 ppm)

pH	GS	LH	OP
4	0.633	3.355	6.364
5	0.405	2.423	3.553
6	BDL	2.05	2.7
7	**BDL**	**0.739**	**2.1**
8	BDL	1.9	4.469
9	BDL	1.931	4.477