SUBJECT: CHEMISTRY

TITLE: Chelating Effect of some Fruits and Vegetables on Heavy Metal Ions Found in the Soil

RESEARCH QUESTION: Which fruit or vegetable (apple, potato, lemon peel, grape, parsley stream) is the most effective as a chelating agent to decontaminate soil from heavy metals (lead, nickel, cadmium, mercury, zinc), when soil is mixed with each of the vegetable or fruit for 4 hours, and the amount of metals determined before and after the treatment by ASS (Atomic Absorption Spectroscopy) method getting results as a wavelength?

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Content

1. Introduction

In chemistry, a heavy metal is a metallic element which is toxic and has a high density, specific gravity or atomic weight. Notably, heavy metals are capable of causing health problems or environmental damage. Hence, they have become a major concern in the twenty-first century. In this study, there is a need to develop techniques that can be employed to reduce or remove heavy metals in the surroundings. The analysis will focus on heavy metals found in soil that may result in soil poisoning.

Soil poison is defined as impurities found in soils that affect soil diversity negatively. Notably, soil poisoning results in both air and water poisoning. Thus, it can be said that soil pollution is the main cause of the other forms of pollution. There are many forms of soil pollutants. However, heavy metals are the main soil pollutants, which are introduced to the soil through processes, such as extraction of valuable minerals, use of fertilizer and pesticides, industrial wastes. Additionally, after the industrialization revolution the industry began to use coal and fuel which causes heavy metal poisoning. Also, the car industry begins to use the fuel which causes heavy metal pollution in the earth. If contaminated soil is used in agriculture all of the plants are also contaminated and this is a risk for the human health. Furthermore, Heavy metals affect the vegetative and also generative organs of the plants. At the end, they affect all the organisms that are alive by the way of food chain. However, living organisms require different amounts of heavy metals. For example, iron, molybdenum and zinc are required by humans. Iron is required as a carrier of oxygen to the tissues from the lungs by red blood cell haemoglobin, as a transport medium for electrons within cells, and as an integrated part of important enzyme systems in various tissues. Lead (Pb), Mercury (Hg), Zinc (Zn), Copper (Cu), Chromium (Cr), Cadmium (Cd) are some of the heavy metals that can be found in polluted soil. People didn't know the effects of heavy metals and they use them as jewellery, water pumps over the past centuries. Thus, heavy metals can be found in the homes, or at the work place. The mentioned heavy metals get transferred to the ecosystems and stay there for a long time and they are toxic at higher concentration.

Therefore, the aim of this experiment is to decontaminate heavy metals which is found in soil with the help of fruits and vegetables, so as to improve the soil efficiency and to decrease the negative effect on human's health.

1.1 Aim

The goal of the research was to identify the chelating effect of some natural chelators, found in fruits and vegetables on heavy metal ions (lead, nickel, cadmium, zinc, mercury) that are common in the soil. Moreover, the study aimed at the determination of the most effective fruits and vegetables can be used for detoxification of various heavy metals present in soil.

2. Background Information

2.1. Heavy Metal being investigated

Lead (Pb)

Figure 1. Picture of lead (Pb)

Lead has an atomic number of 82 and its symbol is Pb. It has a soft, malleable structure.

Nickel (Ni)

Figure 2. Picture of Nickel (Ni)

Nickel has a symbol Ni and its atomic number is 28. It is found in class of transition metals and it has hard and ductile structure.

Cadmium (Cd)

Figure 3. Picture of Cadmium (Cd)

Cadmium is an element which has a symbol of Cd and its atomic number is 48. Cadmium not always considered as a transition metal, because it doesn’t have partly filled d or f electron shells in the elemental form or common oxidation stated structure.

Mercury (Hg)

Figure 4. Picture of Mercury (Hg)

Mercury has a symbol of Hg and its atomic number is 80. Its known as quicksilver. It is the only metallic element that is liquid at room temperature.

Zinc (Zn)

Figure 5. Picture of Zinc (Zn)

Zinc is a B-group metal. It has a brittle structure and crystalized shape at constant temperature.

2.2 Chelating Agents

In chemistry, chelating agents are molecules that have ability to form more than one bond to a metal ion, therefore they increase the stability of the ion complex in a positive way.

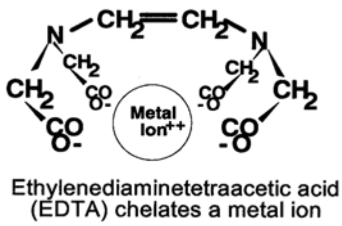


Figure 6. Reaction between a chelator and a metal ion

There are also natural chelators found in fruits and vegetables. By the extract of them or using them completely as chelator is a way to get rid of heavy metals in soil. There are tons of different type of fruits and vegetables grow in different parts of the world. Somehow, there are certain types that you easily find in markets or even local shops. In today's world, we could easily access any type of fruits and vegetables regardless of its climatic growing conditions and areas. In the experiment, the following fruits or vegetables were utilized as chelating agents; apple, potato, lemon, grape, and parsley stream.

Malic Acid (Apple)

Malic acid is an organic compound. Its molecular formula is $C_4H_6O_5$. It is a dicarboxylic acid that is made by all living organisms, give a sour taste of fruits, and used as a food additive.

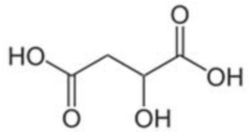


Figure 7. Malic Acid Formulated Structure ($C_4H_6O_5$)

Oxalic Acid (Potato)

Oxalic acid is an organic compound. The chemical formula is $C_2H_2O_4$. It is a crystalline solid occurs as a colourless solution in water. Oxalic acid is a reducing agent and its conjugate base is a chelating agent for metal cations.

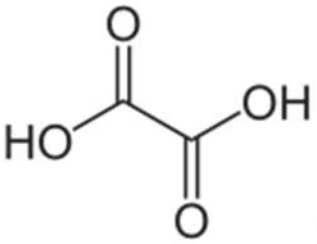


Figure 7. Oxalic Acid Formulated Structure ($C_2H_2O_4$)

Citric Acid (Lemon)

Citric acid is a weak organic tricarboxylic acid. The chemical formula $C_6H_8O_7$. It's found in citrus fruits like lemon and orange.

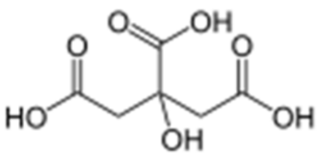


Figure 8. Citric Acid Formulated Structure $C_6H_8O_7$

Tartaric Acid (Grapes)

Tartaric acid is a white crystalline organic acid generally found in plants, like grapes.

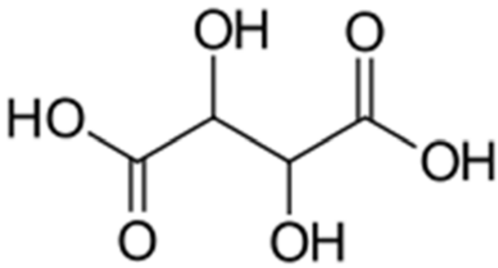


Figure 9. Tartaric Acid Formulated Structure $C_4H_6O_6$

Folic Acid (Parsley Stream)

Parsley stream is a vegetable which is also effective as a chelating agent. It contains folic acid which is also used to treat deficiencies, other than that can cause certain types of anaemia and other diseases.

Folic acid is a food supplement generally use the term folate and in chemistry folate refers to the deprotonated ion, and folic acid to the neutral molecule which both exists in water.

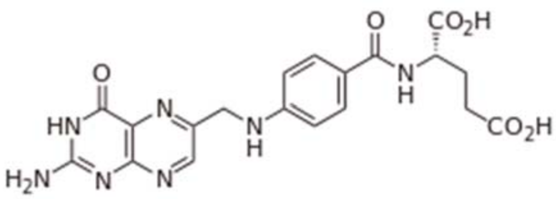


Figure 10. Folic Acid Formulated Structure $C_{19}H_{19}N_7O_6$

To sum up, natural chelating agents found in fruits and vegetables have common property of chelating because they have a stabilization effect on heavy metals found in soil.

2.3. Removal of Heavy Metals from a Contaminated Soil using Organic Chelating Agents

In the past years people also made research and experiments to investigate various techniques for removing toxic heavy metals. At first, it was thought that lifestyle changes and reduced exposure of toxic compounds would get rid of already accumulated toxic elements. However, the most effective way to mobilize the heavy metals from the body is to drink water. If the concentration of water in the body is low it is very difficult to make detoxification as a first step solve for this question.

As a solver, there are many techniques that can be employed to remove heavy metals from soil, which include: soil washing, leaching, flushing with chemical agents or chemical immobilization, stabilization method to reduce the solubility of heavy metals by adding some non-toxic materials into the soil, electro-kinetics known as electro migration, covering up the original polluted soil surface with clean soils, dilution method as mixing polluted soils with surface and subsurface clean soils to reduce the concentration of heavy metals, phytoremediation by plants such as woody trees (Wuana et al, 2010).

Soil washing is also used as soil remediation because it completely removes the contaminants, hence ensures the rapid cleanser of a contaminated site. (Dermont et al, 2008). It meets specific criteria, reduces or eliminates long-term liability, may be the most cost-effective solution and it may produce recyclable material or energy. (Abumaizar et al, 1999). The effectiveness of washing is closely related to the ability of the extracting solution to dissolve the metal contaminants in soils.

Several types of chemicals used for soil washing include surfactants, cosolvents, cyclodextrins, chelating agents and organic acids (Wood et al., 1990; Maturi and Reddy, 2008;

Zvinowanda et al., 2009). All these soil washing extractants have been developed on a case-by-case basis depending on the contaminant type at a particular site. A few studies have indicated that the extraction of heavy metals by washing solutions differs considerably for different soil types. (Yu and Klarup, 1994).

Natural, low-molecular-weight organic acids including oxalic, citric, formic, acetic, malic, succinic, malonic, maleic, lactic, aconitic and fumaric acids are natural products of root exudates, microbial secretions and plant and animal residue decomposition in soils (Naidu and Harter, 1998).

3. Materials and Method

3.1 Research Question

Which fruit or vegetable (apple, potato, lemon peel, grape, parsley stream) is the most effective as a chelating agent to decontaminate soil from heavy metals (lead, nickel, cadmium, mercury, zinc), when soil is mixed with each of the vegetable or fruit for 4 hours, and the amount of metals determined before and after the treatment by ASS (Atomic Absorption Spectroscopy) method getting results as a wavelength?

3.2 Hypothesis

It was hypothesized that natural chelators found in fruits and vegetables can be utilized to remove heavy metals found in the soil.

3.3 Variables

By considering with the aim and the hypothesis of the study, the variables for the analysis are categorized as dependent, independent, and controlled.

1. Independent variable – natural chelators found in fruit and vegetable.
2. Dependent variable – the change in the amount of heavy metals found in soil.
3. Controlled variables – type of soil, type of heavy metal, the amount of fruit and vegetable (1L for total amount of use) , the condition for the experiment (temperature (25^0C) at room conditions, amount of light exist (sunny room))

3.4 Materials and Equipment

The following materials were required for this experiment: soil (all cups had same type of soil which is manufactured soil, 25 kg). The main heavy metals to be investigated were: lead (Pb) , nickel(Ni) , cadmium(Cd) , mercury(Hg) , zinc(Zn). The following chelating agents were utilized: malic acid (apple), oxalic acid (potato), citric acid (lemon), tartaric acid (grapes), and folic acid (parsley stream).

The main equipment utilized was the Atomic Absorption Spectrometry (AAS) that was used for determining change mathematically in heavy metal concentration in soil. Atomic absorption spectrometry (AAS) is an analytical technique that measures the concentrations of elements. Atomic absorption is so sensitive that it can measure down to parts per billion of a gram (µg dm–3) in a sample. The technique makes use of the wavelengths of light specifically absorbed by an element. They correspond to the energies needed to promote electrons from one energy level to another, higher energy level. Atoms of different elements absorb characteristic wavelengths of light. Analysing a sample to see if it contains a particular element means using light from that element. For example with lead, a lamp containing lead emits light from excited lead atoms that produce the right mix of wavelengths to be absorbed by any lead atoms from the sample.

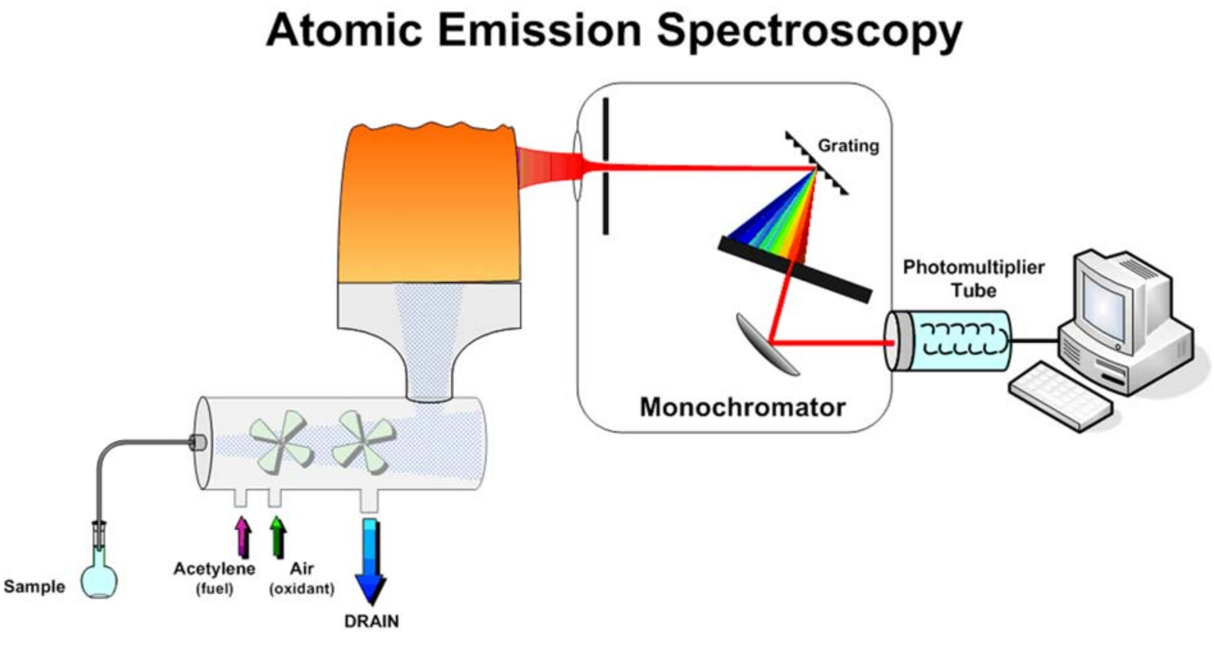


Figure 11. The experiment set-up for Atomic Emission Spectroscopy

3.5 Procedure

The research began by obtaining 25 kg of undeveloped soil from local shops. Then, the following heavy metals (lead, nickel, cadmium, mercury, and zinc) were bought. The following fruit and vegetables (apples, potatoes, lemons, grapes, and parsley stream) were obtained before the start of the study. Using a juice extractor, 100 mL juice was obtained for each cup from the fruits and vegetables. The extracts were divided into five portion, which were placed in 100 mL cups. The 25 kg of extract of fruit and vegetables was divided into 25 equal portions and placed in plastic cups. Five groups of similar soils were created and another group containing one type of fruit/vegetable juice was created. The soil were mixed with the juices and placed under sunlight for four hours. The concentration of heavy metals present in the soils before and after reaction with the chelators was determined by obtaining the absorption of the prepared samples.

4. Safety Information & Precautions

Heavy metal usage during chemical process conducted by hand may result to skin damage. The use of gloves and lab coats should be maintained at all time, while conducting the experiment. I put the soil extracts in chemical waste boxes because it consists also heavy metal particles in it.

5. Results

5.1. Qualitative Data

During the process of the experiment, there is a colour change involved. Like, soil has a dark-brown colour after adding heavy metals there is a little lighten up of the colour.

5.2. Quantitative Data

Table 1. Measurement before adding heavy metals into the soil

FIRST MEASUREMET (SOIL) Wavelength (nm)	201.22

Table 2. Measurement after adding heavy metals into the soil (just after they adedd)

WAVELENGTH (nm) (+/-0.01)	LEAD	NICKEL	CADMIUM	MERCURY	ZINC
FIRST MEASUREMENT	282.90	230.60	227.89	185.0	212.15

Table 3. First results after adding fruit and vegetables into the soil (4 hours later)

WAVELENGTH (nm) (+/-0.01)	LEAD	NICKEL	CADMIUM	MERCURY	ZINC
PARSLEY STREM	282.56	229.53	226.82	184.55	212.00

APPLE	281.35	228.79	226.35	184.43	211.78
GRAPE	281.94	229.46	226.77	183.33	211.53
LEMON PEEL	282.86	230.00	227.66	184.32	211.96
POTATO	281.36	228.73	227.16	184.48	212.04

Table 4. Second results after adding fruit and vegetables into the soil (8 hours later from the whole process started)

WAVELENGTH (nm) (+/-0.01)	LEAD	NICKEL	CADMIUM	MERCURY	ZINC
PARSLEY STEM	281.34	228.92	226.00	184.23	211.95
APPLE	281.11	227.32	225.88	183.89	211.35
GRAPE	280.97	229.31	226.21	181.99	211.00

LEMON PEEL	282.31	229.51	227.13	184.11	211.34
POTATO	280.83	228.34	226.59	184.13	211.21

Table 5. 3rd and last results after adding fruit and vegetables (12 hours later)

WAVLENGTH (nm) (+/-0.01)	LEAD	NICKEL	CADMIUM	MERCURY	ZINC
PARSLEY STEM	280.44	226.30	224.21	182.01	209.11
APPLE	280.21	225.44	223.43	181.22	209.33
GRAPE	280.00	227.55	225.39	182.33	208.77
LEMON PEEL	281.33	228.88	226.44	183.35	209.43
POTATO	279.99	227.99	224.74	183.33	209.33

6. Data Processing

Table 6. (ANOVA results)

FRUIT AND VEGETABLES	HEAVY METALS	MEAN	STANDART DEVIATION	NUMBERS

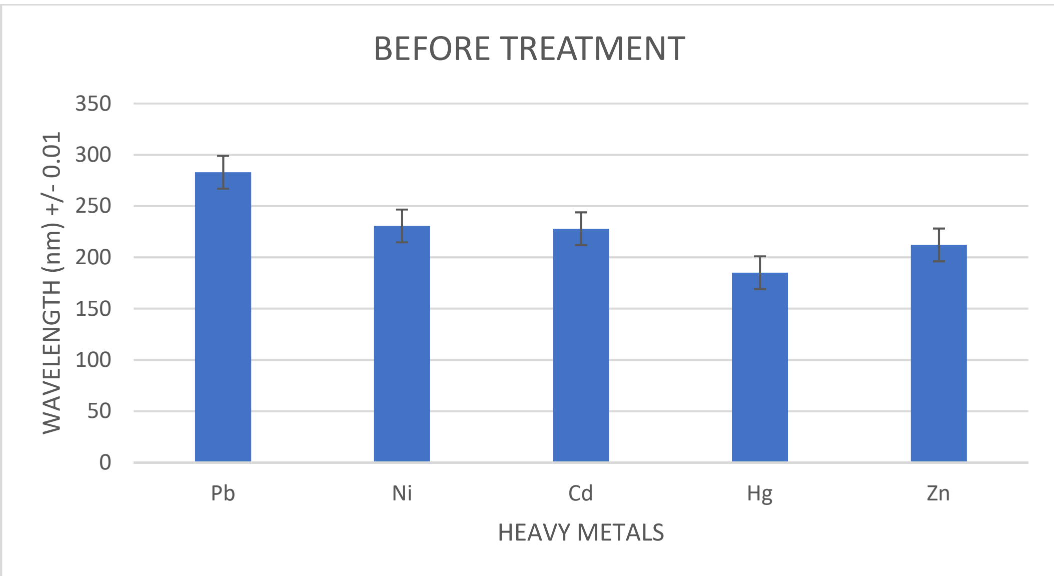
SOIL+ HEAVY METALS	Pb	282,9000	.	1
	Ni	230,6000	.	1
	Cd	227,8900	.	1
	Hg	185,0000	.	1
	Zn	212,1500	.	1
	Total	227,7080	35,77911	5
APPLE	Pb	280,8900	,60100	3
	Ni	227,1833	1,67918	3
	Cd	225,2200	1,56790	3
	Hg	183,1800	1,71875	3
	Zn	210,8200	1,30817	3
	Total	225,4587	33,00750	15
LEMON PEEL	Pb	282,1667	,77501	3
	Ni	229,4633	,56146	3
	Cd	227,0767	,61175	3
	Hg	183,9267	,51033	3
	Zn	210,9100	1,31867	3
	Total	226,7087	33,26969	15
PARSLEY STEM	Pb	281,4467	1,06402	3
	Ni	228,2500	1,71607	3
	Cd	225,6767	1,33470	3
	Hg	183,5967	1,38338	3
	Zn	211,0200	1,65430	3

	Total	225,9980	33,08738	15
POTATO	Pb	280,7267	,69082	3
	Ni	228,3533	,37018	3
	Cd	226,1633	1,26516	3
	Hg	183,9800	,58949	3
	Zn	210,8600	1,38849	3
	Total	226,0167	32,72766	15
GRAPE	Pb	280,9700	,97000	3
	Ni	228,7733	1,06209	3
	Cd	226,1233	,69407	3
	Hg	182,5500	,69656	3
	Zn	210,4333	1,46466	3
	Total	225,7700	33,26137	15
Total	Pb	281,3438	,95529	16
	Ni	228,5419	1,35481	16
	Cd	226,1669	1,21823	16
	Hg	183,5438	1,10819	16
	Zn	210,8925	1,23295	16
	Total	226,0978	32,16000	80

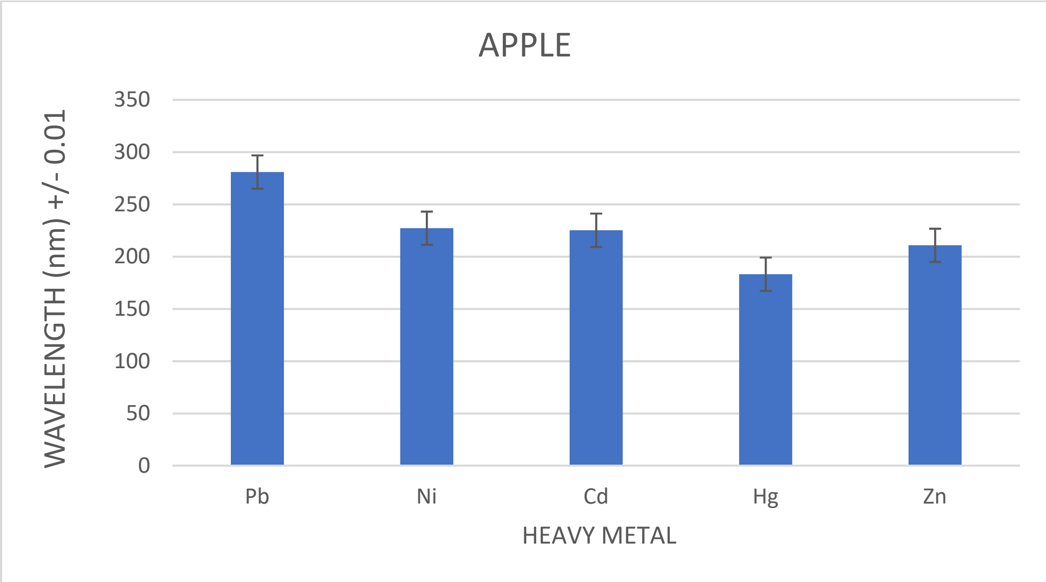
SOURCE	SUM	Df	MEAN	F	Sig.
CORRECTED MODEL	81628,814(a)	9	9069,868	8123,166	,000
INTERCEPT					

	3456076,267	1	3456076,267	3095335,182	,000
SOIL+ HEAVY METALS	26,548	5	5,310	4,755	,001
CUP	81602,265	4	20400,566	18271,180	,000
PERCENTAGE ERROR	78,158	70	1,117		
SUM	4171322,376	80			
CORRECTED SUM	81706,972	79			

7.Graphs

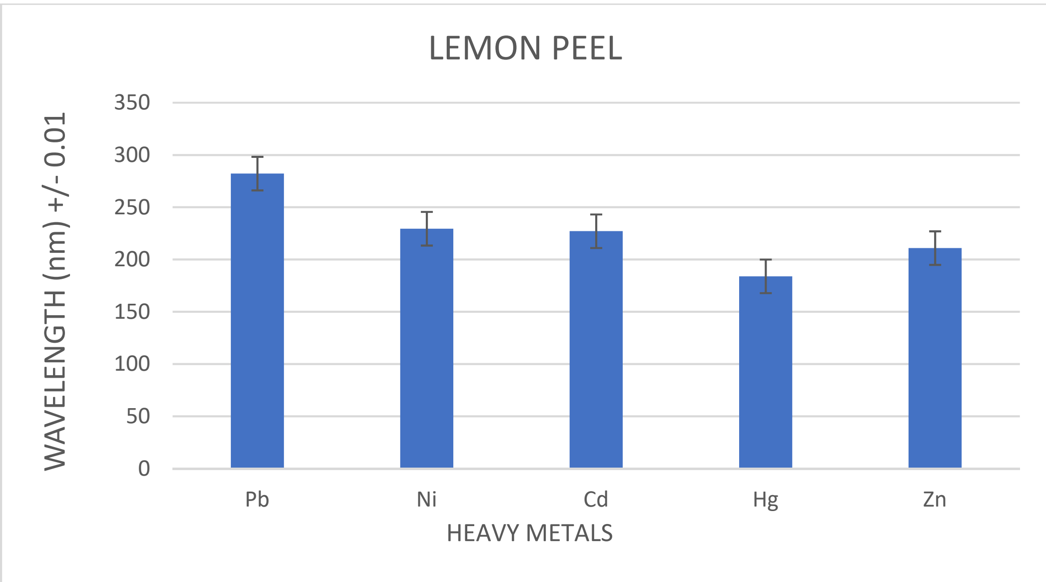


Graph 1. Wavelengths of heavy metals found in soil before adding fruits and vegetables



Metal	Wavelength			Mean difference	Squares	Variance	Average Deviation
Lead	280.44	Average:	224.414	56.026	3138.912676		
Nickel	226.3	std.dev	35.968121	1.886	3.556996	1034.9646	32.17086545
Cadmium	224.21	std.Err	16.085433	-0.204	0.041616		
Mercury	182.01			-42.404	1798.099216		
Zinc	209.11			-15.304	234.212416		

Figure 2. wavelengths of heavy metals which I added apple in cups



Metal	Wavelength			Mean Difference	Squares	Variance	Uncertainity
Lead	281.33	Average:	225.886	55.444	3074.0371		
Nickel	228.88	stdev:	35.928468	2.994	8.964036	1032.6839	32.13539892
Cadmium	226.44	std Err	16.067699	0.554	0.306916		
Mercury	183.35			-42.536	1809.3113		
Zinc	209.43			-16.456	270.79994		

Figure 3. wavelengths of heavy metals which I added lemon peel in cups

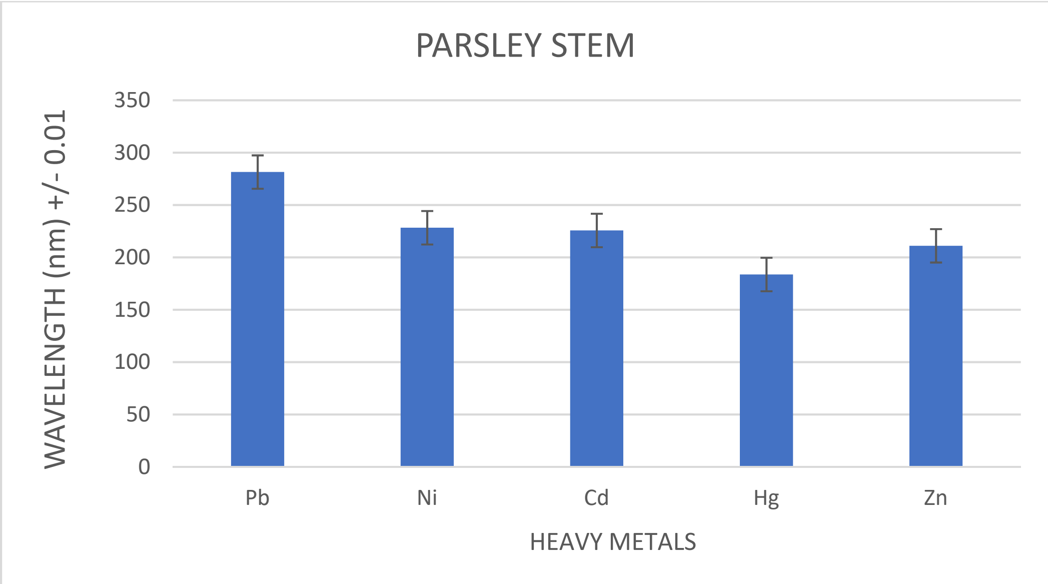
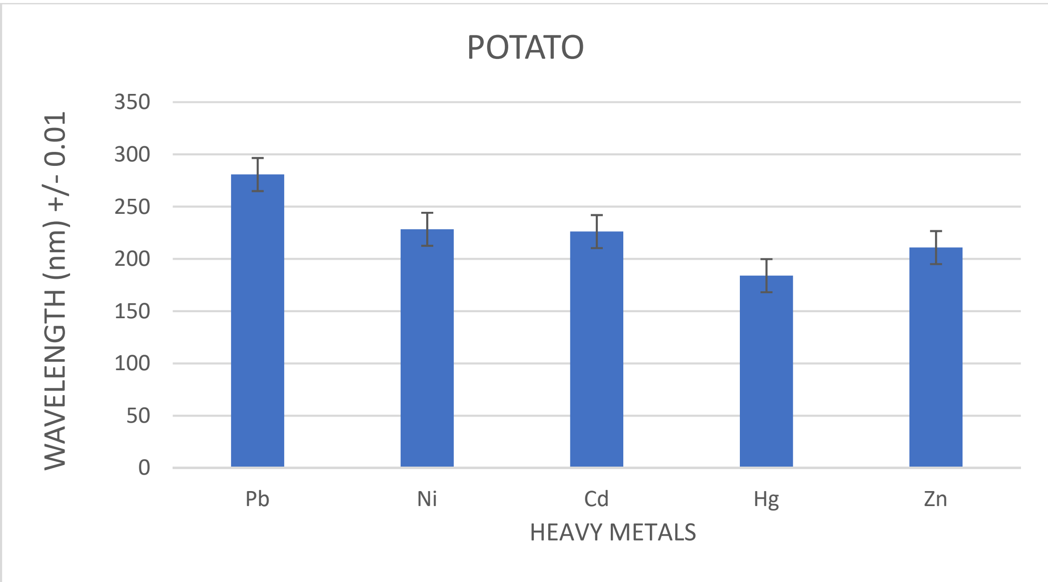


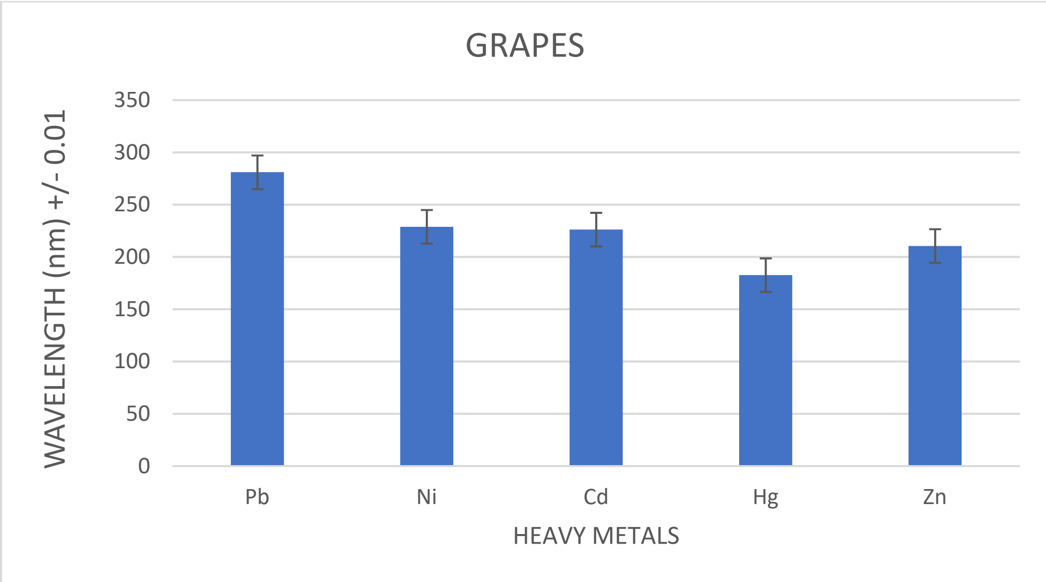
Figure 4. wavelengths of heavy metals which I added parsley stem in cups

Metal	Wavelength				Mean Difference	Squares	Variance	Uncertainity
Lead	280.21	Average:	223.926		56.284	3167.8887		
Nickel	225.44	std.dev	36.080717		1.514	2.292196	1041.4545	32.271574
Cadmium	223.43	std.Err	16.135787		-0.496	0.246016		
Mercury	181.22				-42.706	1823.8024		
Zinc	209.33				-14.596	213.04322		



Metal	Wavelength				Mean Differences	Squares	Variance	Uncertainity
Lead	279.99	Average:	225.076		54.914	3015.5474		
Nickel	227.99	stdev:	35.407685		2.914	8.491396	1002.9633	31.66959652
Cadmium	224.74	std Err;	15.834798		-0.336	0.112896		
Mercury	183.33				-41.746	1742.7285		
Zinc	209.33				-15.746	247.93652		

Figure 5. wavelengths of heavy metals which I added potato in cups



Metal	Wavelength			Mean Difference	Squares	Variance	Uncertainity
Lead	280	Average:	224.808	55.192	3046.1569		
Nickel	227.55	stdev:	35.761754	2.742	7.518564	1023.1224	31.98628481
Cadmium	225.39	std Err	15.993142	0.582	0.338724		
Mercury	182.33			-42.478	1804.3805		
Zinc	208.77			-16.038	257.21744		

Figure 6. wavelengths of heavy metals which I added grapes in cups

8.Experimental Errors

Lab measurements encompasses random error, systematic error, and gross error. Random errors arise from changes in variables that affect the experiment. Random errors are characterized by the positive and negative scattering of data. Similarly, systematic errors arise from instrumental, methodological or human disruptions occurring within the experiment procedure. Gross errors are caused by the experimenter's inaccuracy, carelessness or general failure of equipment. This lab measurement depicts errors occurring in the experimental procedure. For all the fruit species incorporated in chelation, a standard error of an approximate value of 15.8 – 16.5 is observed. The standard error provides a measure in the uncertainties in measurement's average. This values imply that conducting the chelation experiment in another 5 times would result to an average value from the new experiment which is < 1 standard error away from the present study.

Therefore, 3rd and last results after adding fruit and vegetables (12 hours later) incorporates measurements which are reliable and thus can be used in analysis.

Computed values of uncertainty and error portray a disparity in the statistical data. The uncertainty for chelation of all fruit species is quite higher than the error which accounts for the higher standard deviation. For instance, the uncertainty value for grape is ± 31.98628481 Whereas it standard error is 15.99314 which happens in the same manner for all fruits.

Accuracy implicates how close an estimate is to the actual value. Contrary, precision assesses the closeness of two or measurements to each other. The precision is quantified by computing the average deviation. The measurements taken for Parsley stem, apple, lemon, grape and potato show high average deviations implying that the data is widely scattered which translates to a poor precision. However, the accuracy of the measurements is average due to the average standard deviation.

Limitations of the Experiment

Metal leaching in soil profiles poses a great risk in the chelation process. The leaching effect can be attributed to the high persistence of chelators towards biodegradation. Adverse effects including extremely low detoxification rates are observed in the case of leaching. Moreover, the current levels of metal ions in the soil plays a crucial role in determining the chelation procedure. However, sometimes the metal ions may be higher compared to the chelator's ability to absorb them thus making the entire chelation process insignificant.

6.Conclusion, Evaluation and Discussion

6.1.Conclusion

The study sets to identify the chelating effects of certain natural chelators found in plants on heavy metal ions which are common in the soil. Moreover, the study establishes the most effective vegetables and fruits that can help in detoxification of polluted soils through the critical application of the Atomic Absorption Spectroscopy.

After the experiment was successfully done, it was observed that organic chelators cause slight effect on heavy metals. Metal solubilization in this case is extremely low due to the rapid biodegradation of the oxalic, folicitric and tartaric acids in the fruit species. Administration of higher doses of these acids higher than 10 mmol kg^{-1} results to phototoxicity. Hence, they cannot be relied on as the means of elimination of heavy metals. Hence, the first hypothesis, natural chelators found in fruits and vegetables can be utilized to remove heavy metals found in the soil, was taken as true. It was found that the most efficient organic chelator for the heavy metals are:

Lead: Potatoes

Nickel: Apple

Cadmium: Apple

Mercury: Apple

Zinc: Grape

Thus, the hypothesis, apple fruits are the most effective chelating agents compared to potatoes, lemon, grapes, and parsley stream, was rejected. The experiment showed that different chelators react different on various heavy metals.

6.2.Discussion

The statistical analysis was done by using ANOVA. The correlation analysis was used to quantify the association between two continues variables (the dependent and independent variables). Additionally, t - test's statistical significance indicates whether or not the difference between two group's averages most likely reflects a 'real' difference in the groups was sampled. In this article the group is more than two for this reason the correlation coefficient method is used. For the Pearson correlation an absolute value of 1 indicates a perfect linear relationship. A correlation close to 0 indicates no linear relationship between the variables

It was observed that the absorption wavelength of the soil was 201.22 nm. The wavelength increased by addition of the heavy metals except for mercury, which a wavelength of 185.0 nm. The measurements showed that the natural chelators had slight effect on the heavy metals. However, the most efficient organic chelator for the heavy metals are:

Lead: Potatoes

Nickel: Apple

Cadmium: Apple

Mercury: Apple

Zinc: Grape

6.3.Evaluation

The experiment showed that the organic chelators had slight effect on the heavy metals investigated. This might have been due to the contamination of both soil and chelators investigated. Moreover, the natural biodegradation of the chelators plays a crucial role in impacting the heavy metals. The biodegradability of these chelators largely depend on the organic ligand's nature as well as the complex metal ion incorporated in it. Lower biodegradation rate of chelators significantly slows down the chelation process of toxic metal ions therefore would translate to little or no effect on the metal ions. For future experiments, mineral chelators should be investigated to determine the best chelators that can be utilized to reduce presence of heavy metals that cause negative health impacts and environmental pollution.

8. References

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