Research Proposal Draft

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<u>Water waste treatment through the process of coagulation and flocculation with the usage of fruit seeds.</u>

Introduction – Semi Hypothesis

Coagulants are substances employed to encourage the particles in a liquid to clump together, simplifying their separation from the surrounding solution. They find extensive use in water treatment procedures, particularly in eliminating suspended particles and impurities from water. Coagulants come in diverse forms, encompassing inorganic types such as aluminium sulphate (known as alum) and ferric chloride, as well as organic variants like polyacrylamides.

Aluminium Sulphate is the most used chemical coagulant in water treatment however it has some disadvantages that include the likes of not being commercially available to rural communities and that in these communities, very few have the necessary background and understanding of science to make proper use of this coagulant. Researchers have investigated tap water and discovered a potential health hazard related to Alzheimer's disease due to its elevated aluminium content. One drawback worth noting is that, despite its effectiveness in eliminating chemical phosphorus from wastewater, it may not be economically efficient or environmentally friendly, especially for economically disadvantaged rural communities. The need for alternative solutions has prompted this research, which aims to introduce fruit seeds as natural coagulants for water treatment, like the way aluminium sulphate is used in wastewater treatment.

In this study, the seeds from mangos, avocados, papaya and marula will be investigated as bio-coagulant/flocculants. Mangifera indica (MI) aka mangos, Carcia Papaya (CP) aka Papaya, have had research done already although it is not sufficient hence thorough research should be done to have other alternatives from chemical coagulants which may be harmful and are not biodegradable. Nonetheless, limited research has been conducted on Persea americana (PA), commonly known as Avocado, and Sclerocarya birrea (SB), also known as Marula. The scarcity of information has prompted the current research aimed at gathering substantial data for a more effective wastewater treatment solution through coagulation and flocculation, particularly benefiting rural communities.

Literature review

Both ground water and surface water contain dissolved and suspended particles. The process of coagulation and flocculation in drinking and wastewater treatment are used to separate the suspended solids from the water. Suspended particles originating from various sources differ in terms of their origin, charge, particle size, shape, and density. The method of coagulation and flocculation for these particles depends upon the said factors. Suspended solids in water normally have a negative charge. These particles have the same surface charge, and therefore they will repel each other. Hence if the correct method of coagulation and flocculation are not implemented the suspended solids will remain in suspension and will not cluster around [1].

The coagulation process involves three consecutive stages: coagulant formation, particle destabilization, and particle aggregation. During the rapid-mixing stage, treatment chemicals are added and evenly dispersed in the water, achieving coagulant formation and particle destabilization. Subsequently, in the flocculation stage, inter-particle collisions promote floc formation, equivalent to particle aggregation. This leads to the creation of large floc particles that can be easily separated from the treated water. [2].

Aluminium sulphate is one of the most widely used coagulants for water treatment and has proven to be an effective coagulant for the removal of certain contaminants, turbidity and colour. When added into water the aluminium ions hydrolyse rapidly and in an uncontrolled manner, to form a range of metal hydrolysis species. Hydrolysis products may be monomeric or polymeric hydroxyl complexes. Most of them, such as $Al\ (OH)^{2+}$, $Al\ (OH)_2^{+}$, $Al_2(OH)_2^{4+}$, $Al_3(OH)_2^{5+}$ and $Al_{13}O_4(OH)_{24}^{7+}$ (or "Al_{13}"), are positively charged and can interact strongly with the negative colloids, resulting in destabilization and coagulation [2].

The uses of natural plant materials including seeds, sap, bark leaves, fruits and roots of trees and plants for water purification has been well practiced for many centuries. These plant materials can offer several advantages of cost-effectiveness, biodegradability and safe to human health, as opposed to synthetic chemicals such as Alum. Mango (Mangifera indica) seeds has been reportedly used as a water coagulant in traditional water purification system. In addition to the well-documented antimicrobial activities of M. indica, it also possesses numerous health benefits including anti-ulcer, anti-diarrhoea, diuretic, anti-hypertensive, anti-cancer activities and antiparasitic activities. To address the mentioned issue, M. indica could function as a viable natural coagulant, potentially replacing synthetic alum. This substitution could enhance the safety and suitability of water for human consumption. [3]

Carica papaya, commonly known as papaya, is a widely consumed fruit worldwide, typically thriving in tropical or subtropical regions. The consumption of papaya fruits generates a substantial amount of food waste, primarily consisting of discarded papaya peels and seeds, making up approximately 15-20% of its total weight. Therefore, it is imperative to minimize papaya waste by repurposing it, particularly as a bio-coagulant in wastewater treatment. The presence of fat residues associated with protein in this bio-coagulant enhances aggregation by forming clusters, thus promoting the coagulation process. Previous studies on papaya seeds as a bio-coagulant have primarily focused on single-factor effects, such as dosage or pH, in relation to turbidity removal. Understanding the interplay of various parameters is crucial for identifying the optimal conditions for the coagulation process. [4] On the other hand, Marula (Sclerocarya birrea) is an indigenous fruit tree found in Africa and belongs to the Anacardiaceae family. Marula is a deciduous tree, ranging in height from 7 to 18 meters, and it thrives in semi-arid and dry regions in sub-Saharan Africa. It is most abundant in Eastern and Southern Africa, including countries like Kenya, Tanzania, Angola, Botswana, Namibia, Malawi, Mozambique, South Africa, and Swaziland. This tree produces approximately 500 kg of ripe fruits annually, known for their gelatinous and sweetly acidic taste. Marula fruits and seeds have been utilized in the production of cooking oils, jams, jellies, and other parts of the tree are valued for their medicinal properties in disease treatment. However, the extensive utilization of Marula fruit and seeds has led to the disposal of nutshells (seed husks), contributing to agricultural waste that pollutes the environment. [5] The Avocado fruit is one such healthy fruit that contains many macros and micronutrients. The increase in avocado fruit consumption will generate plenty of avocado waste (seed and peel). The utilization of this discarded waste would provide an opportunity to produce an economical and eco-friendly adsorbent material. Rather than simply dumping the solid waste with its simultaneous vaporization. However, plenty of avocado waste is generated worldwide, but it has not yet received adequate attention as an adsorbent and precursor for activated carbon production [6] Active coagulant agent can be extracted using various solvents such as distilled water, alcohol, acid (H_2SO_4) and alkali (NaOH). Different solvents affect the extracted bio-coagulants differently. Among others, the usage of distilled water without additional chemicals is the most preferable as the use of chemicals could alter the initial pH of the treated water or wastewater. Furthermore, chemical-free bio-coagulant produces less sludge. Besides the chemical characterization, there is also lack of knowledge in terms of the interaction effects and optimization among the prevalent operating parameters of the coagulation process. [4]

Experimental Work

Seeds were collected from the fruits of mangos, avocados, papayas and marulas. The seeds were left to dry until they were ready to be crushed into powder form (this is the only way to obtain the correct synthesis of the coagulation and flocculation process).

Fig 1: Sclerocarya birrea (SB), also known as Marula.

Fig 2: Carcia Papaya (CP) aka Papaya

Fig 3: Mangifera indica (MI) aka mangos

Fig 4: Persea americana (PA), commonly known as Avocado.

Coagulation and flocculation process:

Part 1: The reference used for this study was aluminium sulphate (chemical formula), in which 2 g of the powder was dissolved in 20 ml of distilled water. Approximately 2 g of the mango powder and the avocado powder were also dissolved in 20ml of water, these were the stock solution. 20 ml Stock solutions were added to 200 ml of dirty water samples collected at a dam in Bloemfontein. The solutions were then left to settle overnight. 10 ml of the overnight solution was collected. The solutions were left to settle a bit longer and 2 x 50 ml of the solution was collected after a few days and one of the 50 ml and was mixed with approximately 5 g of charcoal ash and was filtered and 10 ml was collected to measure the effects the ash influenced. The remaining solution was also filtered to compare the mass of the starting materials and the flocculated mass.

Step 2: As reference, aluminium sulphate was used by dissolving 1 g in 100 ml distilled water for the stock solution. 100 ml of this stock solution was then added to 150 ml untreated water. The same process was followed to prepare stock solutions of papaya seeds and marula seeds. This was done to see if the seeds would have the same effect as the aluminium sulphate reference. Again 10 ml of the samples were collected after allowing it to flocculate/coagulate overnight, 50 ml was then collected after a few days as well as a separate 50 ml collected that 5 g of charcoal ash was added which was filtered and 10 ml was collected. The rest of the solution was filtered as well to get the mass of the flocs.

Figure 5: Crude water in 250 ml Volumetric flask and stock solution in 100 ml Volumetric flask before the stock solution was added to the crude. Left to right (Papaya, Marula and Aluminium)

Figure 6: Overnight solutions that contains the stock solution and the crude. Left to right (Avo, Mango and Alum)

Characterisation of the powders

The powders were investigated through the FTIR spectrophotometer to determine the presence of functional groups in each sample. A sample portion of the powder were placed on the FTIR spectrophotometer, and the Infrared Spectrum was obtained.

Characterisation of the overnight solutions and ash solutions.

The solutions that were left overnight were investigated with the UV-Vis spectrophotometer to observe the intensity and the concentration of the presence of the coagulants (Powders). The solutions that had ash added were also investigated.

Zeta Potential Investigation

The stability of the powders was investigated through the zeta potential. Dilutions (1, ½, ¼, 1/8, and 1/16) were conducted with 0.01 mg of the powders added into deionised water and were investigated with the Malvern Zetasizer Software.

Investigation into the treatment of water

The treated water was taken to Groundwater Institute for further investigation of whether the water is safe to drink.

Obtained Results and a Brief Discussion

Part 1:

Table 1: Shows the mass collected for the stock solution of mango and avocado and the mass obtained after filtration of the solution that was used for the coagulation and flocculation process.

	Mass weighed (Starting Material – SM)	Mass Obtained (After Filtration – AF)
Mango Powder	2.0060 g	1.5581 g
Avo Powder	2.0015 g	1.6885 g
Aluminium Sulphate	2.0000 g	0.0043 g

Part 2

Table 2: Shows the mass of the seed powders that were collected to make the 100ml stock solution and the mass obtained of the filtered solution for the coagulation and flocculation process.

	Mass weighed (Starting Material – SM)	Mass Obtained (After Filtration – AF)
Papaya Powder	1.0070 g	0.5172 g
Marula Kernel Powder	1.0046 g	0.4669 g
Aluminium Sulphate	1.0009 g	0.0052 g

Sample Characterization (Powder form)

To pinpoint the organic functional groups in the bio-coagulant/flocculants, an ATR FTIR analysis was conducted using powdered samples from all four fruit seeds shown in figures 1a – 1b. Prior investigations have indicated that hydroxyl, carboxyl, esters, and amine groups have a significant impact on coagulation and flocculation processes. The FTIR analysis of the seed samples have confirmed the existence of several of those functional groups, refer to figures 1a – 1b.

The samples that were obtained from the fruits were crushed into a fine powder in order to get the same properties of the aluminum sulphate (alum). The samples were investigated through Fourier-Transform Infrared Spectroscopy to study the chemical composition of the samples. Molecules exhibit distinct vibrational frequencies within the infrared segment of the electromagnetic spectrum. Through the assessment of how a sample absorbs or emits infrared light, FTIR spectroscopy can offer a distinctive signature, aiding in the identification of the specific chemical bonds and functional groups within the sample. Below in figure 1a-1e are the observations of the samples used obtained from the FTIR spectrometer.

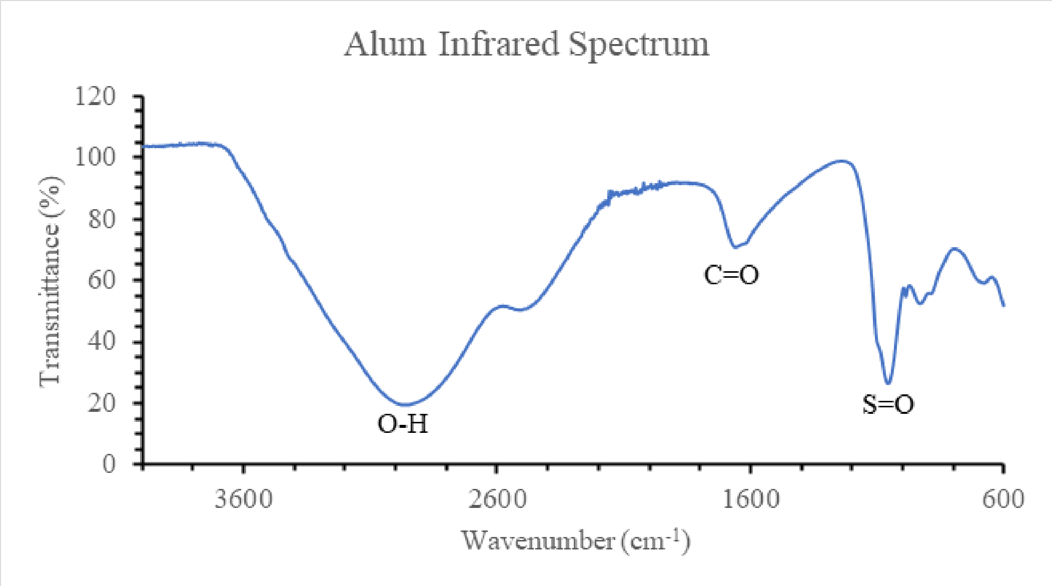

Figure 1a: ATR FTIR spectrum of the powdered alum.

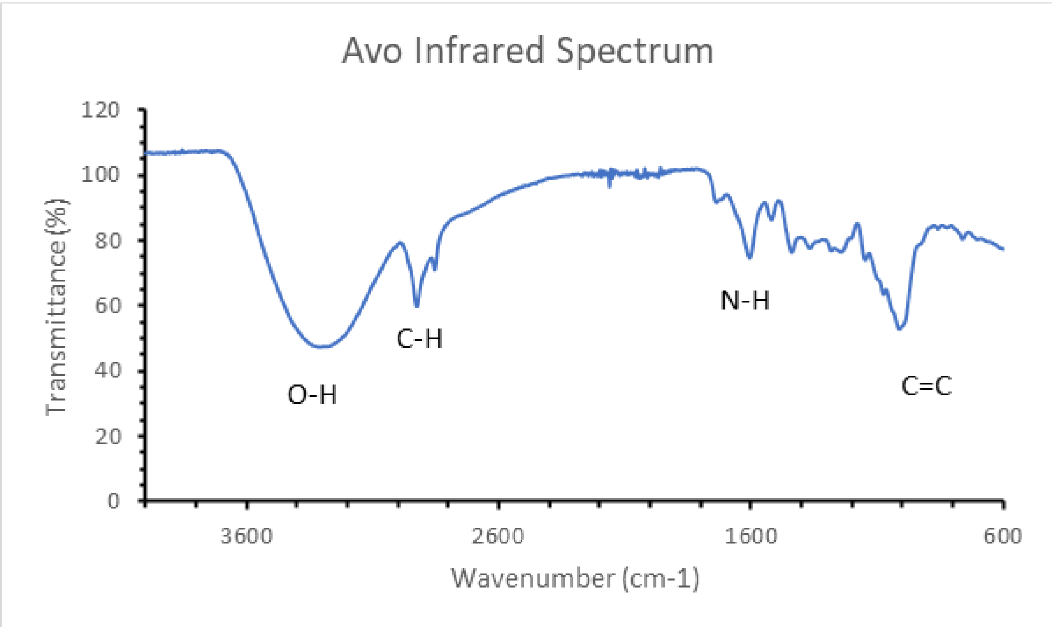

Figure 1b: ATR FTIR of the powdered avocado

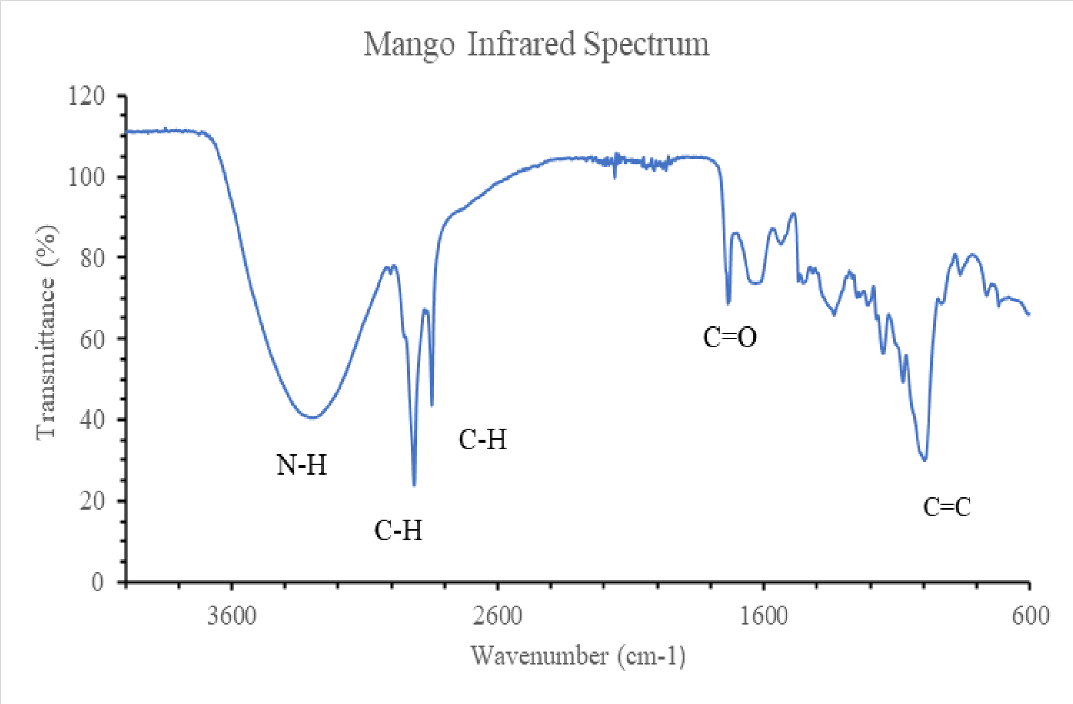

Figure 1c: ATR FTIR of the powdered Mango

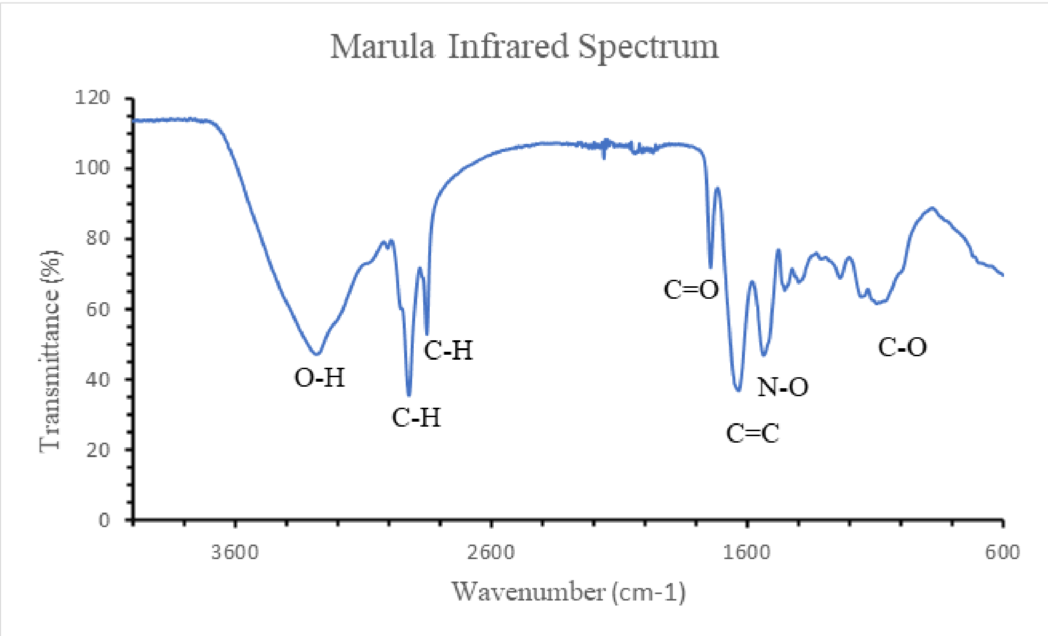

Figure 1d: ATR FTIR of the powdered Marula seed

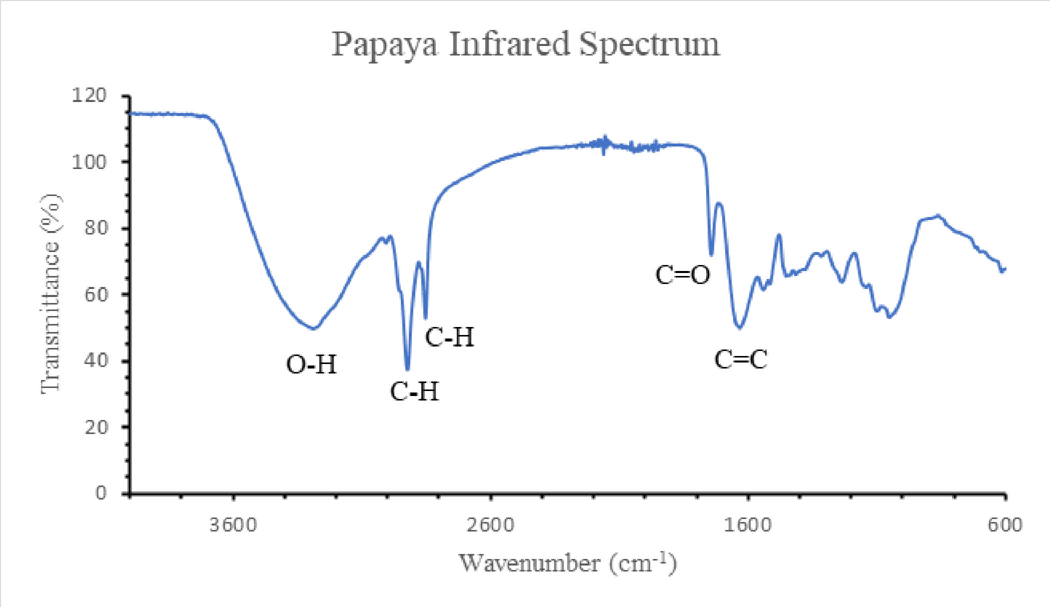

Figure 1e: ATR FTIR of the powdered Papaya seed

Studying the spectrums in figure 1b – 1e similarities and comparisons were observed and were noted down in table 1.

Table 1: Short descriptive of the similarities and comparisons of the presence of functional groups in each sample.

Similarities			
Hydroxyl group	Amine group	Carbonyl group	C double bonds
Fig 1b, 1d & 1e	Fig 1b & 1c	Fig 1c – 1e	Fig 1b – 1e
Comparisons			
• The amine group from fig 1b and 1c were in different positions. • Fig 1d is the only sample with a nitro group.			

Sample Characterization (After filtration)

The samples were poured into the crude to observe and investigate what happened to the crude after the insertion of the coagulants (samples) and these samples that were filtered were weighed and taken for FTIR, the figures 2a-2e are the infrared spectroscopies of the samples after they were filtered from the crude which were interpreted to investigate the chemical properties that were present in the filtered samples. Comparing figure 1e and 2e, there is a slight change in functional groups the carbon double bond that existed in figure 1e was not present anymore after filtration. Possible reasons could be that the papaya seed was soluble in water.

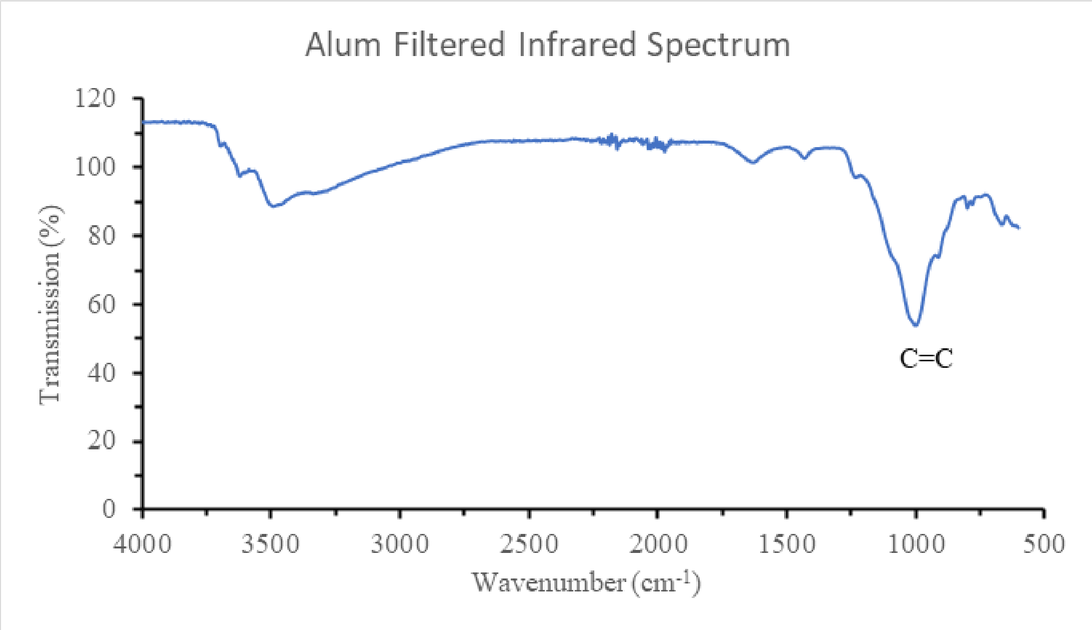

Figure 2a: ATR FTIR spectrum of the alum after filtration.

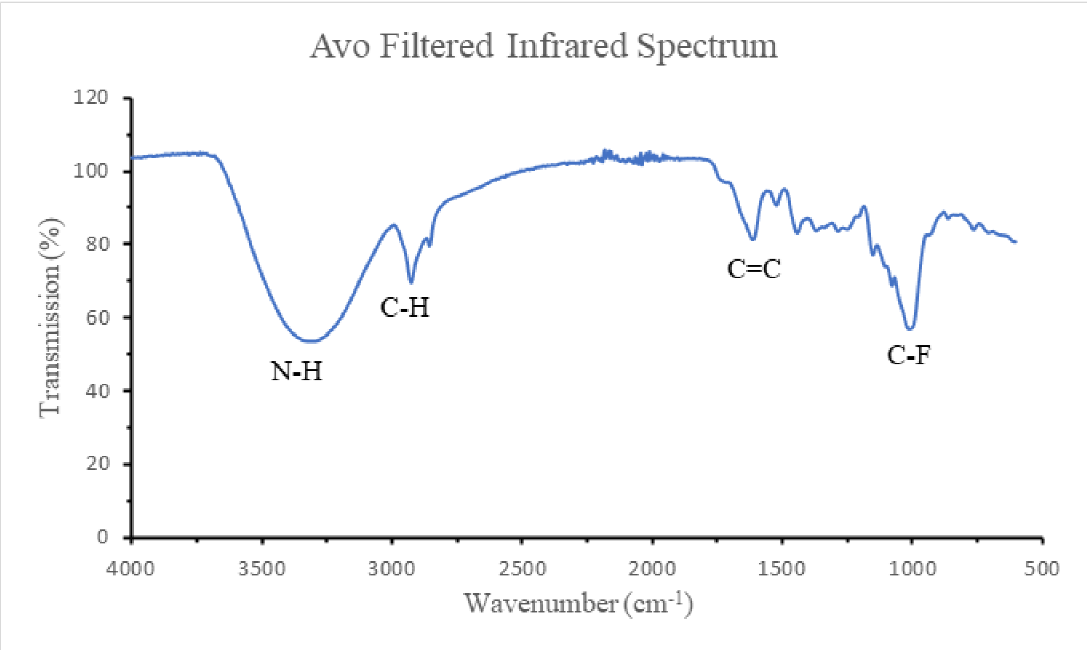

Figure 2b: ATR FTIR Spectrum of the Avocado after filtration.

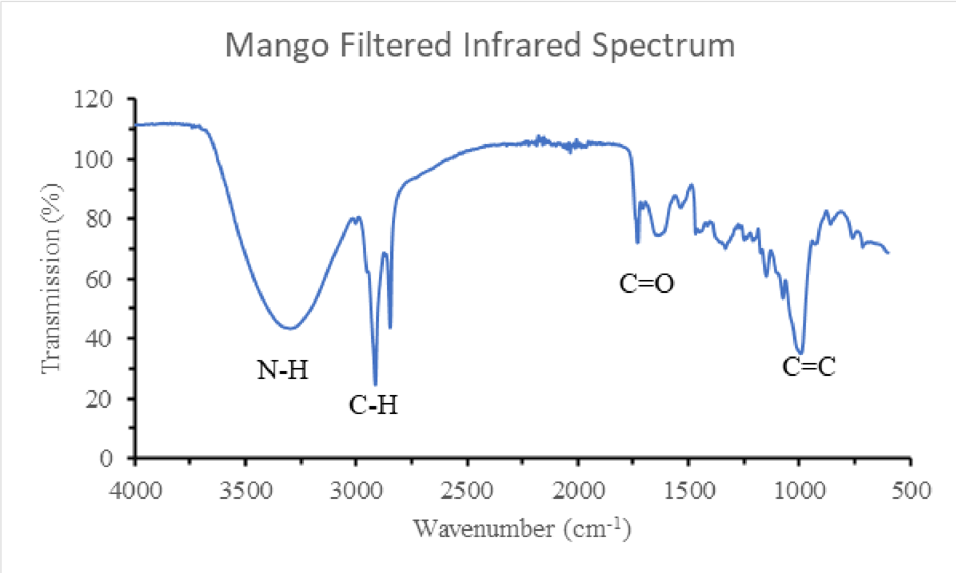

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Figure 2c: ATR FTIR Spectrum of the Mango powder sample after filtration.

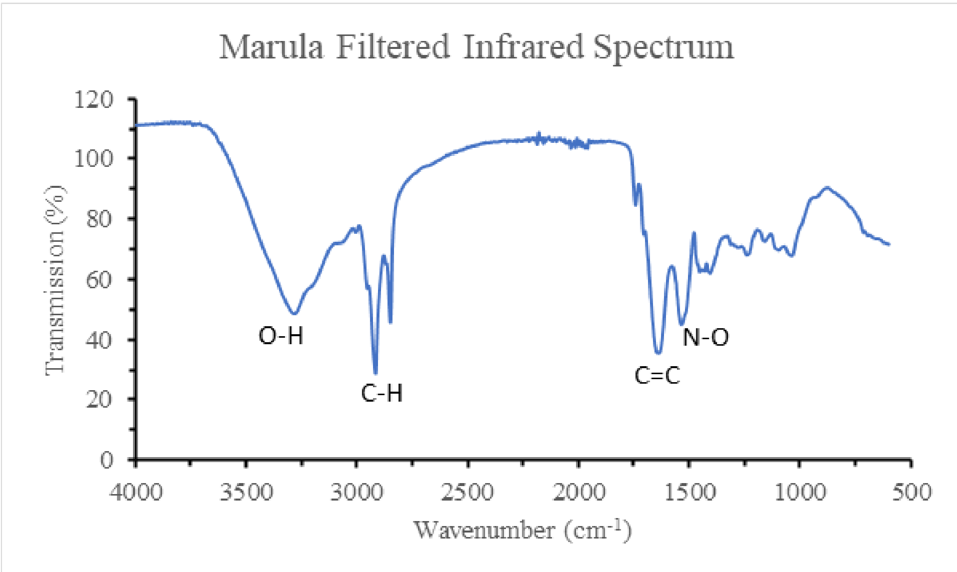

Figure 2d: ATR FTIR Spectrum of the marula powder after filtration.

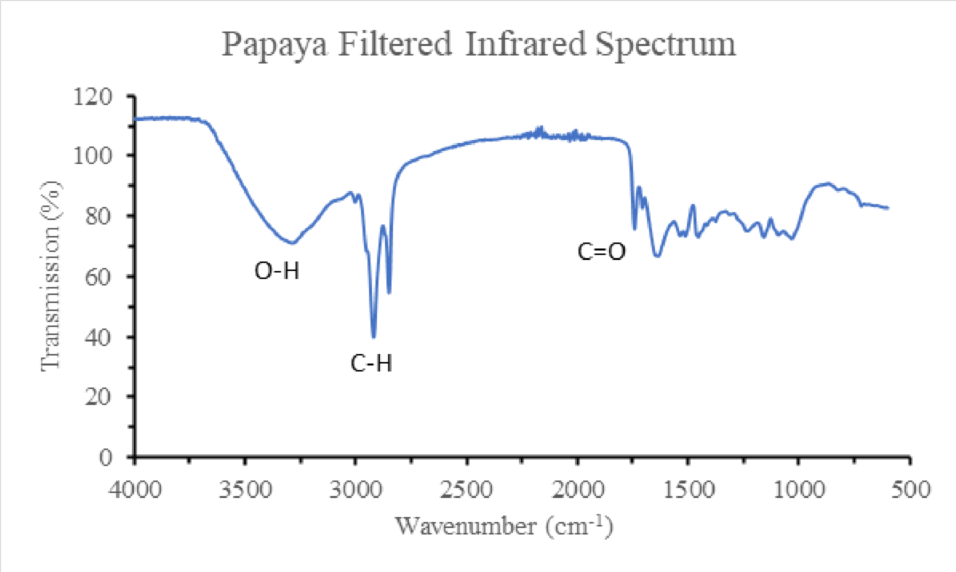

Figure 2e: ATR FTIR Spectrum of the papaya powder after filtration.

Sample Characterization (Overnight and Ash Liquid IR)

The Infrared Spectrum of the solutions were also investigated and figure 3a suggests that Papaya has the highest intensity, which is the furthest apart to the crude. Followed by Marula and Avo which have a similar intensity and mango being the lowest.

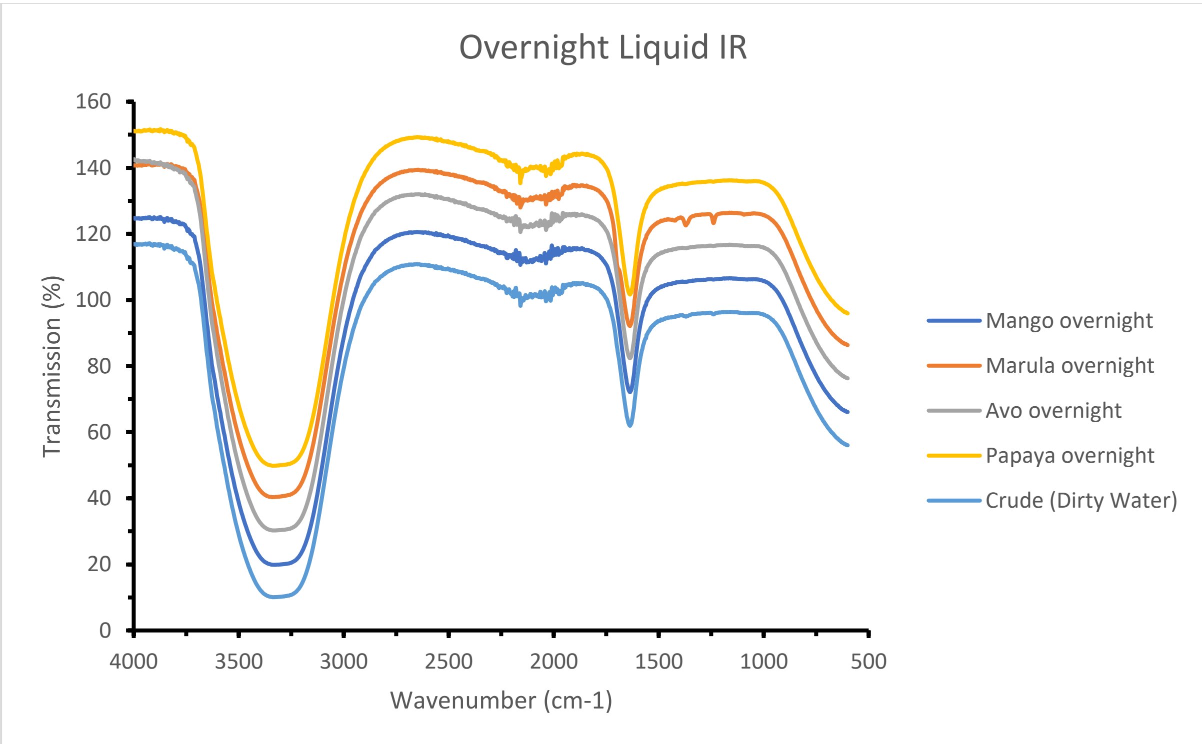

Figure 3a: Infrared Spectroscopy of the overnight solutions

From figure 3b the highest intensity is papaya followed by marula, mango and Avo. The alum solution was also investigated to make comparisons of whether the seeds will have the same characteristics. They all contain hydroxyl and carboxyl groups which are essential for water treatment.

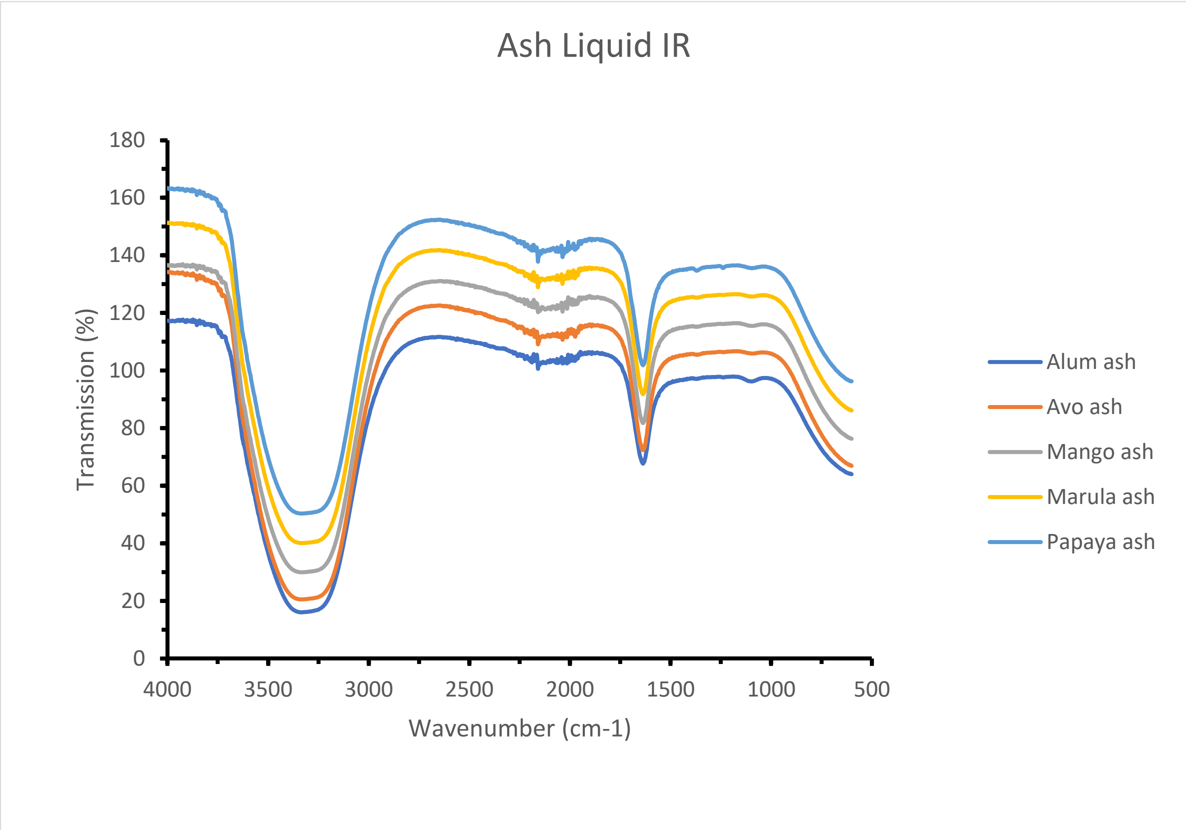

Figure 3b: Infrared spectroscopy for the solutions that were treated with ash.

UV-vis Characterization (Overnight and Ash Filtered Solutions)

The UV-Vis of the solutions that were left to stand overnight were collected and figure 4a-4b are the observed observations of the UV-Vis.

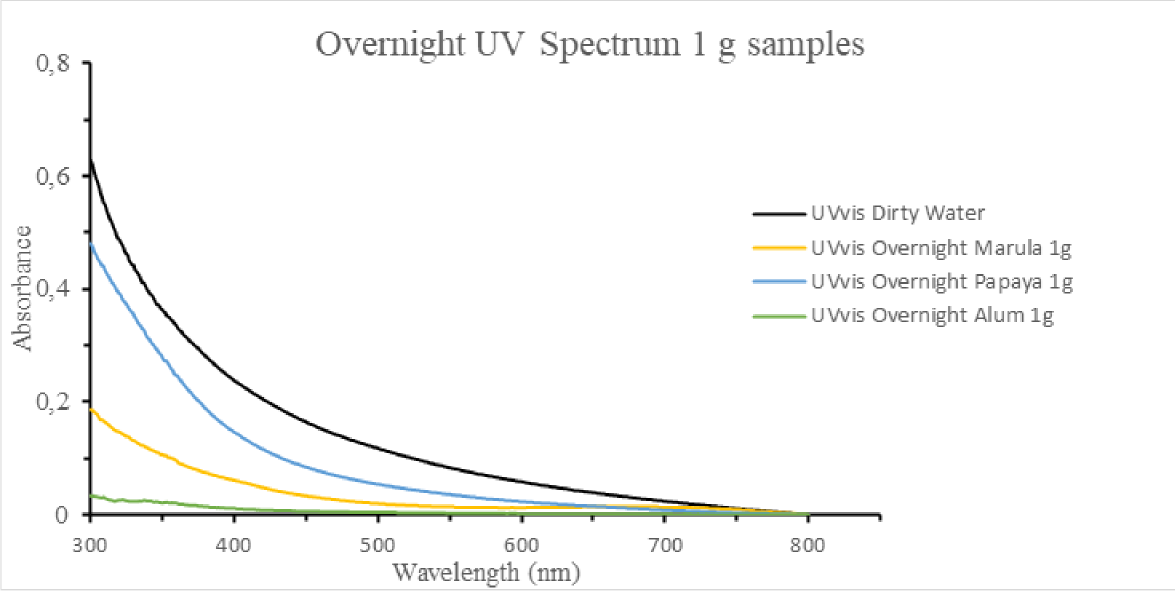

Figure 4a: UV-Vis spectrum of the samples that used 1 g.

The UV-Vis of the solutions that were left overnight after the addition of the powder in the crude that is the dirty water was measured and a graph was plotted. From the graph (fig 4a) indicates that the alum has a low intensity hence it means that the concentration of the alum – the absorbing species has a low concentration. Since literature and previous research, it has confirmed that water treatment through alum works. The crude however has a high intensity and because of the two references, the interpretation of which sample worked best was simple to interpret. Between Marula and Papaya, the one with the high intensity was the marula sample, and the low intensity was the papaya sample. The sample indicates a close relationship between it and the alum. Referring to the FTIR of Papaya in fig 1e it contains the hydroxyl group, and these are important due to the binding of metal ions in water, this can be compared to alum in fig 1a of which it contains an hydroxyl group. Hydroxyl groups assists in removing toxic metals in water. This could suggest that the papaya seed can be a good coagulant for the treatment of water.

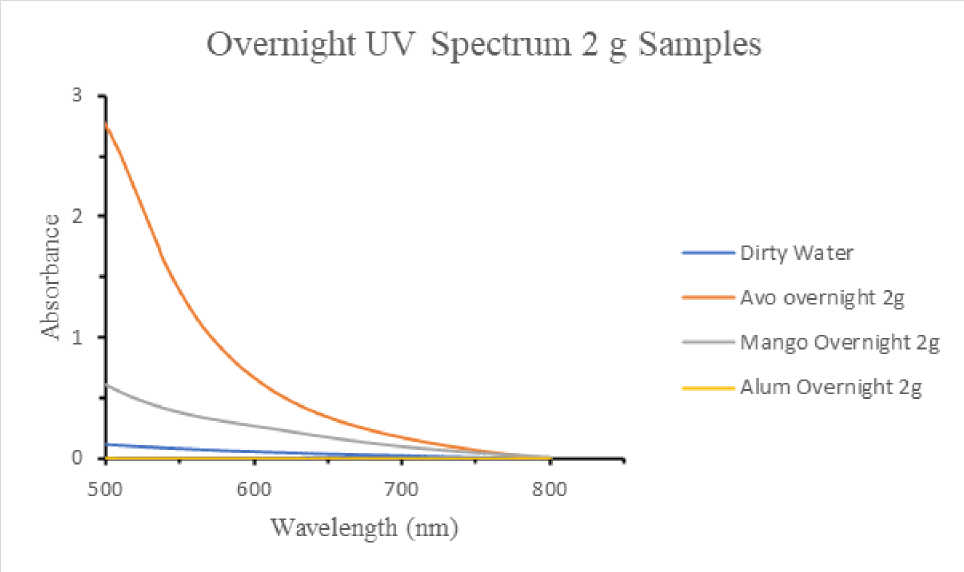

Figure 4b: The UV-Vis of the overnight solutions that used ca. 2 g of the powdered samples.

Once again, the solutions of the 2 g samples were investigated and observed. Avo acquires a high intensity thus a high concentration, which is not good. However, looking at the mango (grey) the intensity of the mango is low and closer to the intensity of the alum. This is a good thing considering that both intensities are low. The intensity of the crude is between the intensity of the Mango and the alum. This is not good because the intensity of clean drinking water should be lower than the intensity of the crude.

Figures 4c-4d show the observed UV-Vis for the solutions that were treated with ash.

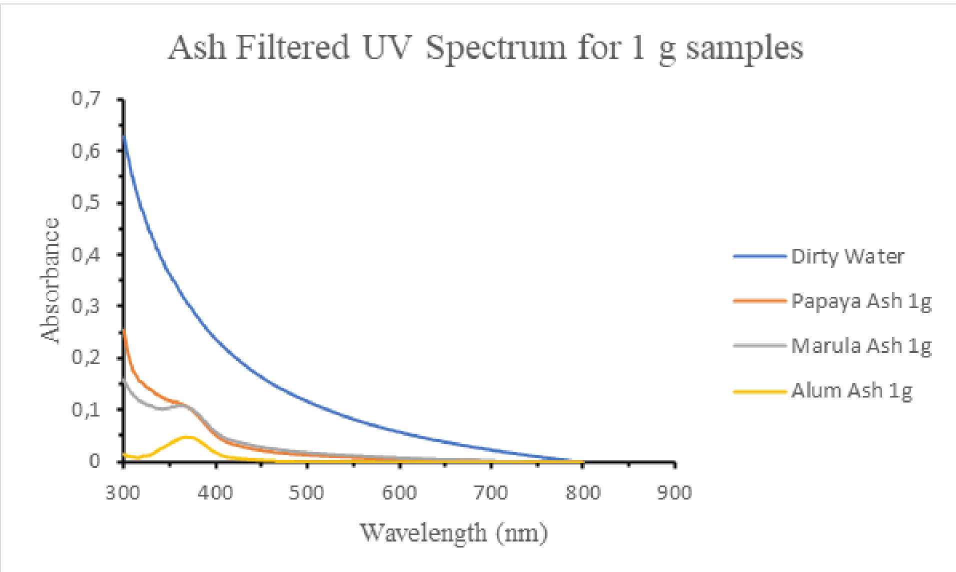

Figure 4c: UV-Vis of the solutions that were treated with 1 g powders.

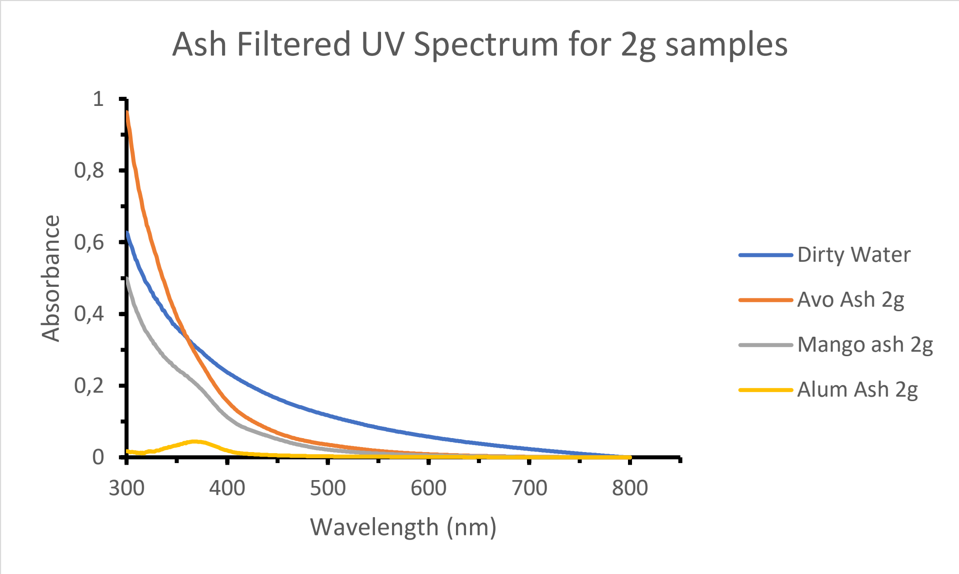

Figure 4d: The UV-Vis of the solutions that were treated with 2 g powder.

Zeta Potential – (Of the powdered samples)

Zeta Potential vs Dilution Graphs

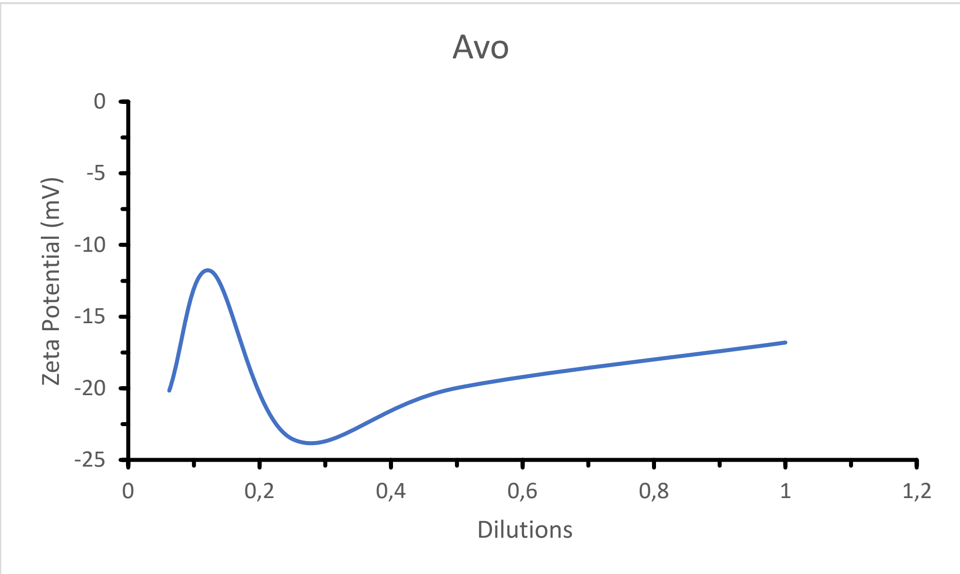

Figure 5a: The zeta potential vs dilution graph of avocado. As the dilution decreases the zeta potential decreases, however there is a limit it reached whereby it increased.

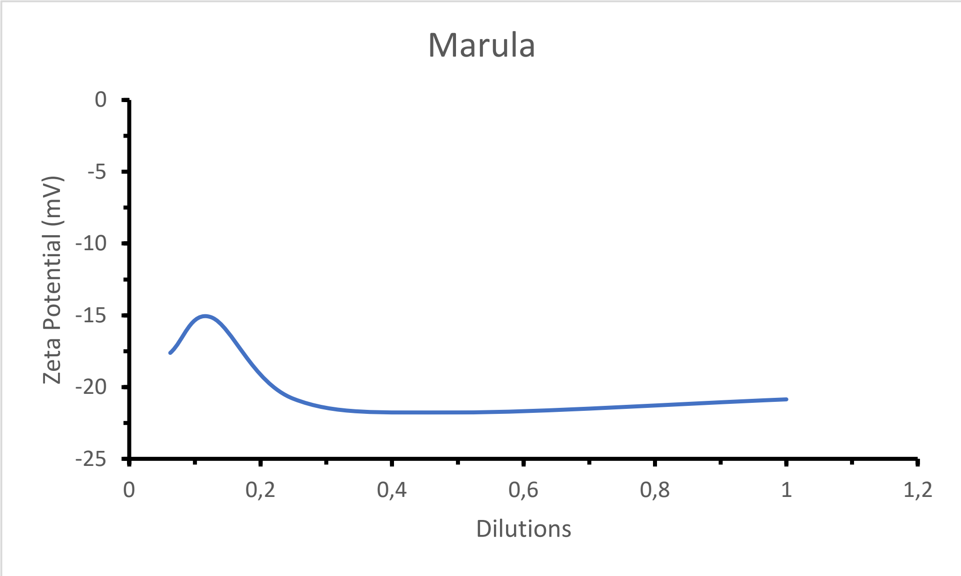

Figure 5b: The zeta potential vs dilution graph of Marula. A decrease in dilution kept the zeta potential constant for some time, followed by an increase.

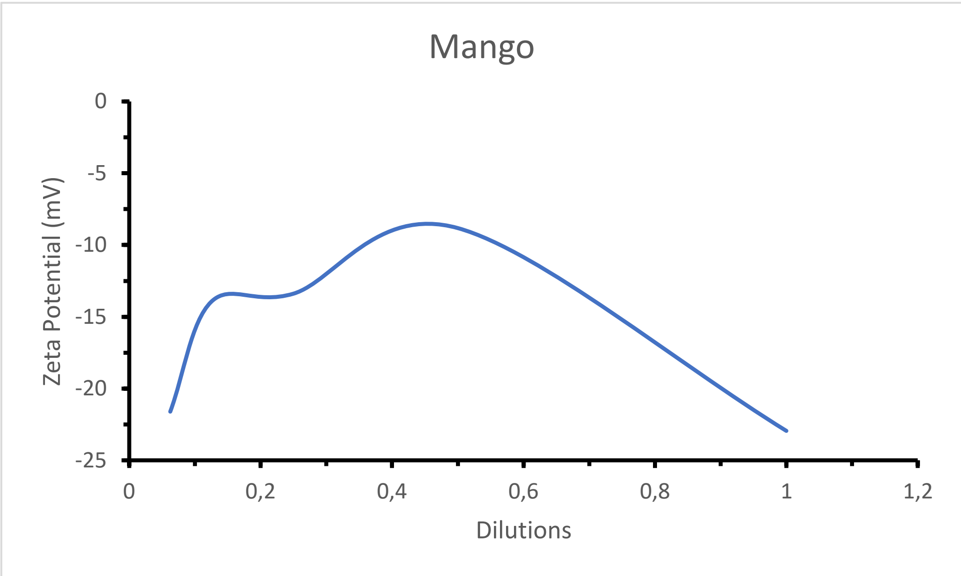

Figure 5c: The zeta potential vs dilution graph of Mango. A decrease in dilution fluctuations the zeta potential by an increase until a certain limit then a decrease.

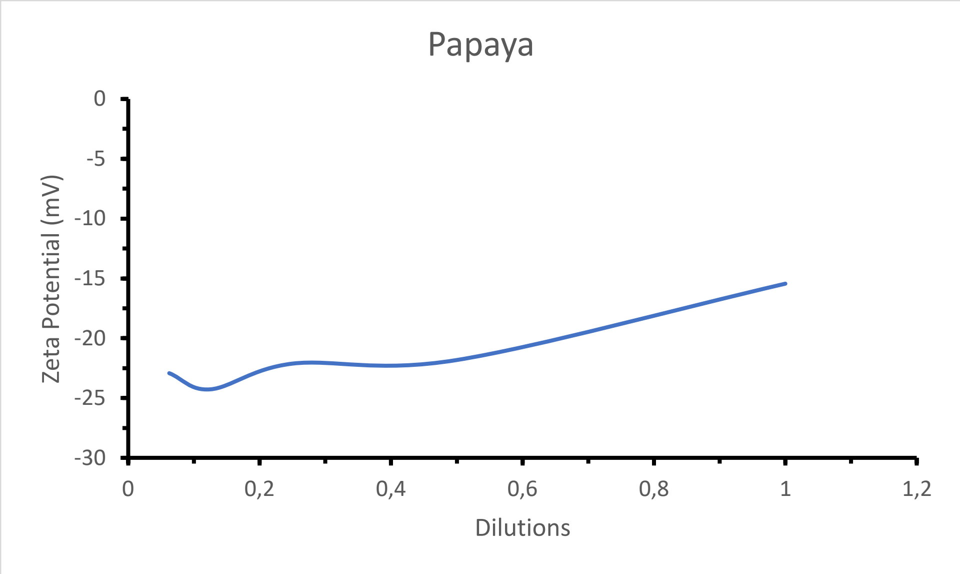

Figure 5d: The zeta potential vs dilution graph of Papaya. A decrease in dilution decreases the zeta potential.

Dilution involves decreasing the solute concentration in a solution by adding additional solvent. When applied to colloidal suspensions, it entails introducing more liquid into the mixture, thereby diminishing the concentration of the colloidal particles in the system. Zeta potential (ζ-potential) is a measure of the electrostatic potential on the surface of colloidal particles. It indicates the degree of repulsion between adjacent, similarly charged particles in a dispersion. Zeta potential is a key parameter in understanding the stability of colloidal suspensions.

Table 5a: Results obtained with the Malvern Zetasizer Software.

	Avo	Mango	Marula	Papaya
Size (nm)	1442	717.8	981.7	1495
pH	6.24	6.29	6.22	6.45
Electrical Conductivity (mS/m)	1.34	1.06	1.30	1.22
Zeta Potential (mV)	-18.46	-16.14	-19.24	-21.31

Comparing the difference between table 5a and table 5b the electrical conductivity and the pH of table 5a are lower compared to the values in table 5b.

Table 5b: Results obtained from the Institute of Groundwaters

	Crude	Ash	Alum	Avo	Mango	Marula	Papaya
pH	8.63	12.07	3.71	12.39	12.62	12.64	12.60
Electrical Conductivity (mS/m)	31.65	649.37	308.49	1476.02	1298.40	1495.55	1345.22

CONCLUSION

The study and investigation of the four powders have been conducted, the characteristics of the powder were obtained and well as the absorbances. From all the samples it been concluded that papaya was seen as a better coagulant to be used for coagulation/flocculation for water treatment. The zeta potential of papaya was found to be -21.31 mV which was the highest negative amongst all four samples and that makes it most stable. The disappearance of the carbon double bond in figure 2e played are role in that as much as the hydroxyl and carboxyl groups are presents the absence of the C=C suggests possibilities of the papaya seed being an alternative for a natural coagulant. The pH of the papaya is the highest and closer to 7, another possibility because clean drinking ranges around 7.

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