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COMPARATIVE STUDY OF ACHYRANTHUS ASPERA AND PHYLLANTHUS AMARUS FOR THE REMOVAL OF LEAD FROM POLLUTED WATER BY USING THEIR BIOSORBENTS POWDER

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ABSTRACT

Lead metal is highly inert metal used widely because of its mechanical properties like high density, low melting point and ductility. Half of the lead produced is used as electrodes in lead acid car batteries, construction of buildings and pipes. Lead is poisonous to human beings if inhaled or swallowed. Achyranthus aspera and Phyllanthus amarus both the plants are widely available as weeds and they have excellent medicinal values. These plants are extensively used in folk, Ayurveda and Unani medicines. The leaves, stems, fruits, flowers and seeds cut from both the plants were washed with distilled water and dried in sun light. The dried materials were crushed and meshed to reduce the size of the particles below75µ and activated at $100^0{}_C$ *using hot air oven. At pH 6, at the period of 7 days with maximum adsorbent dose seed ash and dry powders of P.amarus plant shown highest adsorption of lead 88.54% and 86.75% respectively. At the same conditions A.aspera's flowers ash and dry powders has shown 84.69% and 80.61% of lead adsorption from polluted water. The Bio sorbent powders are structurally analyzed with FT-IR spectroscopy before and after adsorption.*

Keywords: Achyranthus aspera, adsorption, biosorbent powders, FT-IR, Lead, Phyllanthus amarus and removal.

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1. INTRODUCTION

1.1. Lead

Lead (Pb) belongs to 14th group element of the periodic table having atomic number 82. It is a heavy and stable metal with silvery white or grayish colour[1]. When freshly cut, lead is bluish-white; it tarnishes to a dull gray color when exposed to air. Lead is soft, malleable, and has relatively low melting point. Lead metal is highly corrosive resistant that's why it is durable[2]. Lead is extensively used in construction, plumbing, batteries, bullets and shot, weights, solders, pewters, fusible alloys, white paints, leaded gasoline, and radiation shielding due to its high density, low melting point, relative inertness to oxidation, its relative abundance and low cost[3-7]. Lead widely used to make statues and sculptures[8]. It is also use in radiation shields around X-ray equipment[9]. Lead has been used as a paint additive, in face whitening make-up, in water pipes, preservative for food and drinks, pesticide, and in paint used on children's toys.

Lead element is poisonous to human beings if inhaled or swallowed. Lead poisoning can cause various health disorders which vary depending on the individual and the duration of lead exposure. Exposure to organic Lead is probably more toxic than inorganic Lead due to its rapid lipid solubility. Poisoning by organic Lead compounds has symptoms predominantly in the central nervous system[10]. It can damage the body's organs and can cause weakness in the body's joints. Some symptoms of lead poisoning include nausea, vomiting, extreme tiredness, high blood pressure, and convulsions (spasms). Over a long period of time, children often suffer brain damage. They lose the ability to carry out normal mental functions. Lead poisoning occurs due to contamination of soil and water nearby industries, usage of lead pipes, lead paint and residual emissions from leaded gasoline[11].

It is very essential to remove Lead from the polluted water because of above adverse effects, to prevent environmental pollution and human beings. Few research articles are available for the removal of Lead from the polluted water by using Achyranthus aspera and Phyllanthus amarus plants. Chandrakant D. Shendkar[12] et al have developed efficient adsorption of Pb^{+2} and Cd^{+2} from polluted water by using A. Aspera adsorbents. Marques P. Rosa[13] et al have experimented on the effect of pH on the removal of Pb^{+2}, Cd^{+2} and Cu^{+2}. Genevieve Etomam Adukpo[14] et al have done heavy metal analysis in Ghana area using P. Amarus biosorbents. Extensive research work is not done on the selected plants for the removal lead from polluted water.

2. PLANTS DESCRIPTION

2.1. Achyranthus Aspera

Achyranthes aspera commonly named as Uttareni, chaff-flower, prickly chaff flower, devil's horsewhip, is a species of plant in the Amaranthaceae family[15-17]. It is widely distributed on road sides, gardens, crops, grasslands, savanna and forest margins. *Achyranthes aspera* is an erect long-lived perennial herb which can grow up to 2 m tall. It stems become woody at the base, leaves are dark green above and paler below. They are opposite, simple and egg-shaped with broad end at base (ovate) up to 10 cm long by 8 cm wide, densely to sparsely hairy tapering to a point at both ends and shortly stalked[18]. The small greenish-white flowers have shown form narrow, elongated terminal spikes. As the flowers age, they bend downwards and become pressed closely against the stem. The bracts surrounding the flowers in the fruiting stage have sharp, pointed tips making the heads spiny to the touch[19]. The sharp-pointed fruits are orange to reddish purple or straw-brown capsules.

Achyranthes aspera contains triterpenoid saponins which possess oleanolic acid as the aglycone. ecdysterone, an insect moulting hormone, and long chain alcohols are also found in.

Other chemical constituents such as achyranthine, betaine, pentatriaontane, 6-pentatriacontanone, hexatriacontane, and tritriacontane[20] are also present. Achyranthes aspera has occupied a pivotal position in Indian culture and folk medicine[21,22]. The tribal and rural people of India commonly use this herb in various disorders. In Uttar Pradesh, the plant is used for medicinal purposes, especially in obstetrics and gynecology, including abortion, induction of labor, and cessation of postpartum bleeding. The seeds are given in cases of snake-bites, as well as in ophthalmia and cutaneous diseases. The flowering spikes, rubbed with a little sugar, are made into pills, and given internally to people bitten by mad dogs. The leaves, taken fresh and reduced to a pulp, are considered a good remedy when applied externally to the bites of scorpions[23].

2.2. Phyllanthus Amarus

Bhumi amla or Nelausiri or Bhuiamla botanically named as Phyllanthus amarus is an annual herb mainly growing in rainy season. The plant grows as weed in many places of America, Australia, South Africa and Asia[24,25]. It can be survives under tropical and high rainfall conditions and tolerates temporary water logging[26]. During rainy season, it grows abundantly in cultivated lands, waste lands, along roadsides and open areas[27]. The plant grows 20-75 cm height, branching profuse towards upper region bearing 5-10 pairs of leaves. Fruits are distributed underneath the leaves small smooth capsules which look like amla[28]. The plant extract has been found to contain high levels of saponins, tannins, flavonoids and alkaloids Phyllanthus amarus is an important herbaceous medicinal plant used in the traditional and folk medicines for the treatment of several diseases like jaundice, asthma, hepatitis, tuberculosis, ulcer and urinary diseases. It is also used in stomach ailments like dyspepsia, colic, diarrhea, dysentery, dropsy, urinogenital problems and for external application in case of swelling and inflammation[29]. This medicinal herb is widely used in Ayurveda and Unani medicins to treat various health problems. For medicinal purpose whole plant and roots are used. The plant is very rich in potassium due to which it is powerful diuretic. Therefore the authors selected these medicinal plants for this comparative study due to their high medicinal values and availability as weed. The developed method is novel, simple, eco-friendly.

Figure 1. Achyranthus aspera and Phyllanthus amarus plants

2.3. Objective of this method

- Stems, fruits, leaves, seeds and flowers of the Achyranthus aspera and Phyllanthus amarus plants in dry and ash powders were used as bio-sorbents to remove Lead from the polluted water.
- To calculate the pH verses percentage of removal of Lead.

- To calculate the time verses percentage of removal of Lead.
- To calculate the adsorbent doses verses percentage of removal of Lead.
- The effect of temperature verses percentage of removal of Lead
- To determine the structural analysis of bio-sorbents before and after adsorption by using FT-IR spectroscopy.

3. EXPERIMENT

Apparatus: Analytical balance, reagent bottles, volumetric flasks, conical flasks, pipettes, burettes, measuring jars, burette stand and Hot air oven.

Chemicals: Lead nitrate, potassium chromate, acetic acid, sodium acetate, sodium thiosulphate, hydro chloric acid (HCl) and starch powder.

3.1. Preparation of biosorbents powder

The leaves, stems, fruits, seeds and flowers cut from Achyranthus aspera and Phyllanthus amarus plants were washed with distilled water and dried in sun light. The dried materials were crushed and meshed to reduce the size of the particles below75µ and activated at 100^0C using oven. Ash adsorbents were prepared by burning the plant materials as discussed above.

3.2. Preparation of solutions

1.0 gram of Lead nitrate is dissolved 1000mL of distilled water to make the concentration of 1000 ppm.

3.2.1. Preparation of Potassium chromate solution

1.0 gram of Potassium chromate is dissolved in 1000 mL of water to get the concentration of 1000 ppm.

3.2.2. Preparation of acidic buffer:

50 mL of Acidic acid is dissolved 70mL of water contains 4 grams of sodium acetate.

3.2.3. Preparation of hypo solution:

15 grams of Sodium thio sulphate (hypo) is dissolved in 1000mL of distilled water.

3.2.4. Preparation of starch solution

1.0 gram of starch powder is dissolved in 2 to 3mL of distilled water and poured this content into 100 mL boiling water. Stirred the contents with glass rod and made into a uniform solution and cool to room temperature.

3.2.5. Preparation of stock solution

500 mL reagent bottles were thoroughly washed and rinsed with distilled water and each bottle is filled with 250 mL of 1000 ppm Lead nitrate solution. In reagent bottles different doses of bio-sorbents (dry and ash powders) are added and shaken well with frequent times and kept it for better adsorption of Lead. The contents are thoroughly shaken and filtered through Wattmann filter paper through funnel into a cleaned reagent bottle. The filtrate is stored in cold and dry place for further experiment. The powders of bio-sorbents before and after absorption were examined with FT-IR spectrophotometer to determine the change of the spectra due to absorption of Lead.

3.3. Procedure

20mL biosorbent solution is of is pipetted out into a clean conical flask. To this same quantity of potassium chromate solution is added yellow color precipitate is formed. The precipitate is dissolved with concentrated HCl and 2mL of acidic buffer is added. To this one gram of potassium iodide is added and closed the conical flask and kept in dark place for 5 minutes. After 5 minutes the contents are titrated against hypo until pale yellow color is reached. To this 1mLof starch indicator is added and titrated against hypo solution till the contents in the flask turns to pale green color. The end point is noted from the burette reading. The same procedure is repeated with blank and as well as with stock solutions of various bio sorbents.

4. RESULTS AND DISCUSSIONS

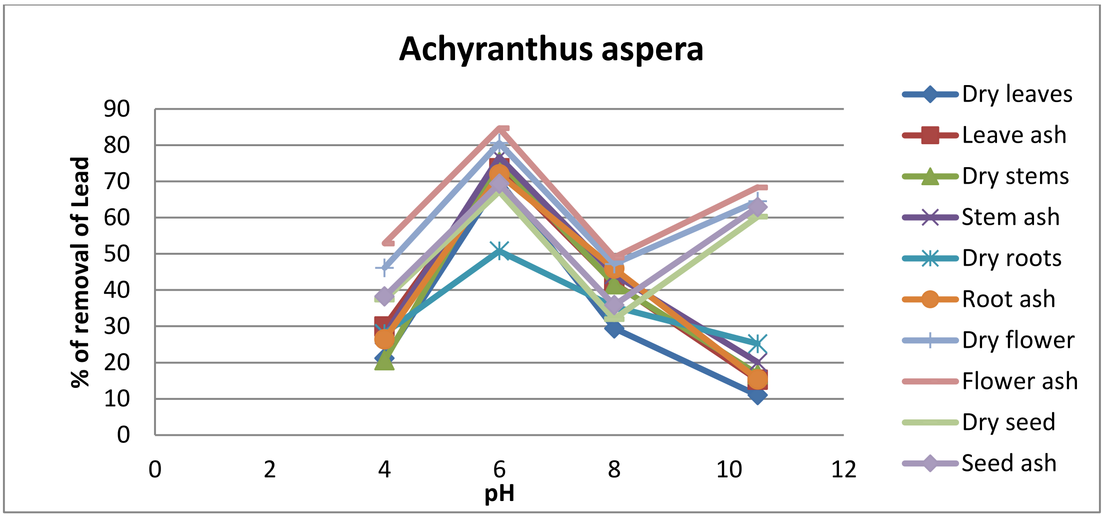
The removal of Lead from polluted water was investigated by changing the various physicochemical parameters like pH, time, adsorbent doses and temperature.

4.1. Effect of pH on adsorption of Lead

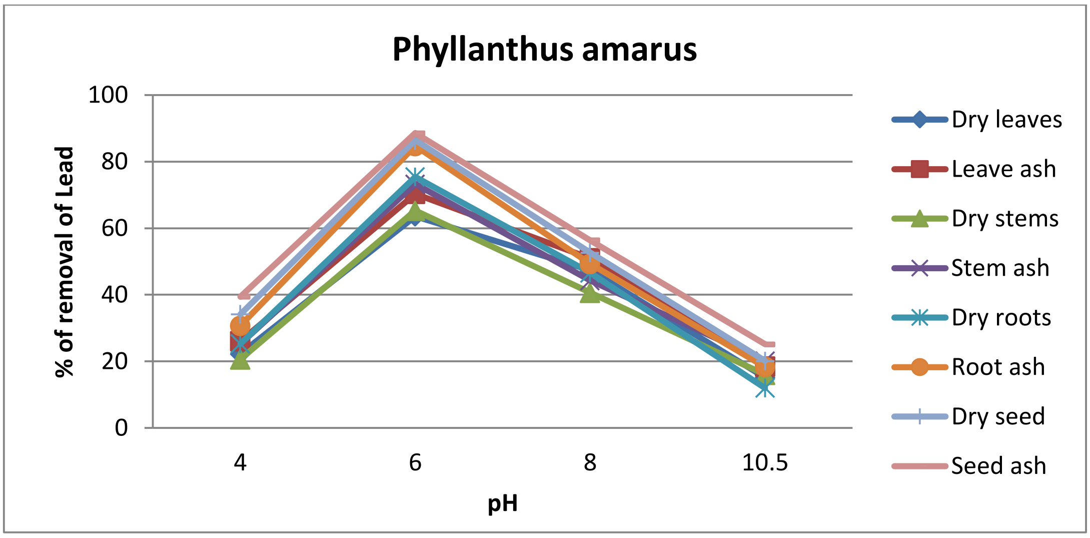
The adsorption of Lead is observed with dry leaves, leaves ash, dry stems, stems ash, dry roots and roots ash for both the plants. A. aspera has flowers therefore flowers dry and ash powders are also taken. Both the plants are shown maximum adsorption of Lead at pH 6 and falls gradually from 6 to 10.5 pH. Among these two plants P. amarus dry fruits and fruit ash powders were shown maximum adsorption at pH 6. The highest adsorption of Lead was shown by P. amarus plant fruit ash, dry fruits and root ash of 88.54%, 86.75% and 84.70% respectively. A. aspera flower ash has highest 84.69% of adsorption where as dry flowers have 80.61% of adsorption and stem ash have 76.66% adsorption of Lead. The least adsorption was shown by dry leaves of A. aspera dry leaves 11.02% and P. amarus dry roots 12% at 10.5%. The percentage of removal of Lead by biosorbents powders of two plants were presented in theTable-1. The adsorption isotherms were shown in the Graph-1 and 2.

Table 1 Effect of pH on % of removal of Lead by Achyranthus aspera and Phyllanthus amarus

pH	dry leaves	leave ash	dry stems	stem ash	Dry roots	Root ash	Dry Flower	Flower ash	Dry seed	Seed ash
4	21.20 22.29	29.96 26.09	20.65 20.61	27.62 25.32	28.01 25.29	26.45 30.73	46.15	52.89	37.36 34.17	38.25 39.45
6	70.17 63.58	73.68 70.31	75.43 65.27	76.66 73.25	50.8 75.43	71.92 84.70	80.61	84.69	67.2 86.75	69.38 88.54
8	29.45 47.36	41.97 50.97	41.65 40.65	44.32 44	35.42 46.62	45.92 49.32	47.23	48.98	32 52.69	35.85 56.37
10.5	11.02 15.13	15.24 18.54	16.81 16.0	20.09 20.13	25.20 12	15.40 18.36	64.52	68.35	60.28 20.15	62.93 25.14



Graph-1 Effect of pH on % of removal of Lead by Achyranthus aspera



Graph-2 Effect of pH on % of removal of Lead by Phyllanthus amarus

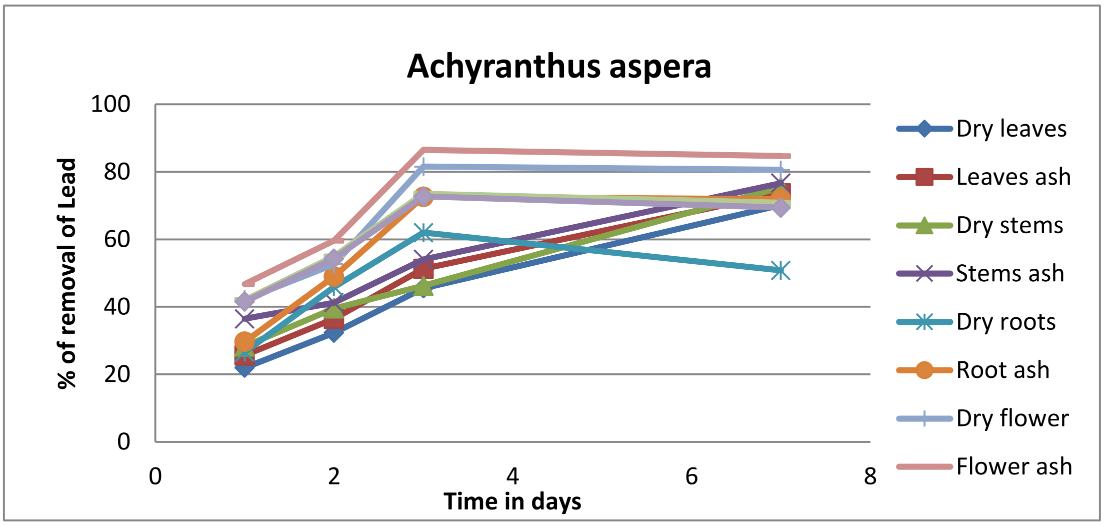
4.2. Effect of time on adsorption of Lead

By increasing the time from 1 to 7 days by frequent shaking, flower ash of A. asper has shown highest 86.53% adsorption on 5th day and 84.69% on 7th day. Followed by dry flowers have shown 81.54% on 5th day and 80.61% on 7th day of adsorption of Lead. It has been observed that by increasing the time from 1to 5 days with different bio-sorbents, the removal of Lead has increased gradually from dry roots to seed ash. P.amarus has shown maximum adsorption of Lead in 7th day. The maximum absorption of Lead was shown by fruit ash 88.54% and dry fruits 86.75%. The least adsorption was shown by dry roots 50.8% of A. aspera and dry leaves 62.31% of P. amarus. The % of removal of Lead by bio sorbent powders of two plants were shown in theTable-2. The absorption isotherms are shown in the Graph-3 and 4.

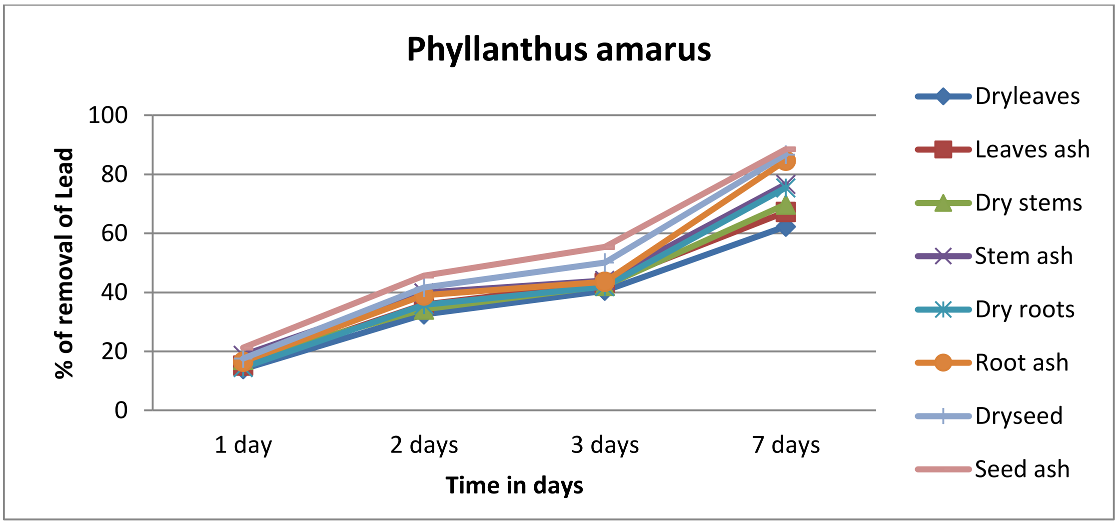
Table 2 Effect of Time on % of removal of Lead by Achyranthus aspera and Phyllanthus amarus

Time in days	dry leaves	leaves ash	dry stems	stems ash	dry roots	Root ash	Dry Flower	Flower ash	Dry seeds	Seed ash
1	22.01 14.01	25.64 15.25	28.29 17.21	36.48 18.72	26.57 14.57	29.68 16.56	42.15	46.78	42.0 17.59	41.53 21.25

3	32.34 32.58	36.45 35.94	39.54 34.25	41.25 39.89	45.89 35.82	49.01 39.01	52.65	59.63	54.97 41.59	54.29 45.66
5	45.52 40.57	51.25 43.25	46.25 42.18	54.05 44.05	61.97 41.97	72.63 43.62	81.54	86.53	73.51 50.14	72.69 55.39
7	70.17 62.31	73.68 67.24	75.43 69.82	76.66 76.66	50.8 75.43	71.92 84.70	80.61	84.69	70.81 86.75	69.38 88.54



. **Graph-3** Effect of Time on % of removal of Lead by Achyranthus aspera



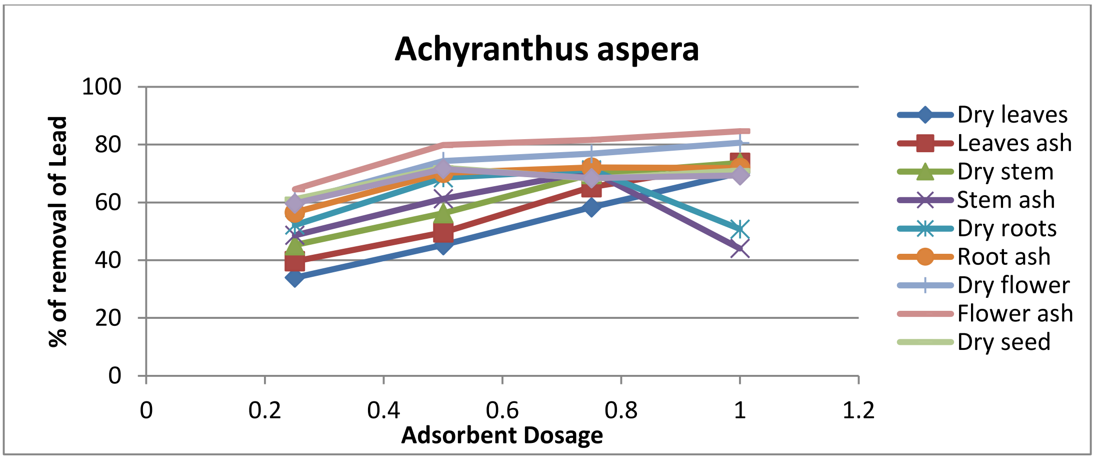
Graph-4 Effect of Time on % of removal of Lead by Phyllanthus amarus

4.3. Effect of adsorbent doses on adsorption of Lead

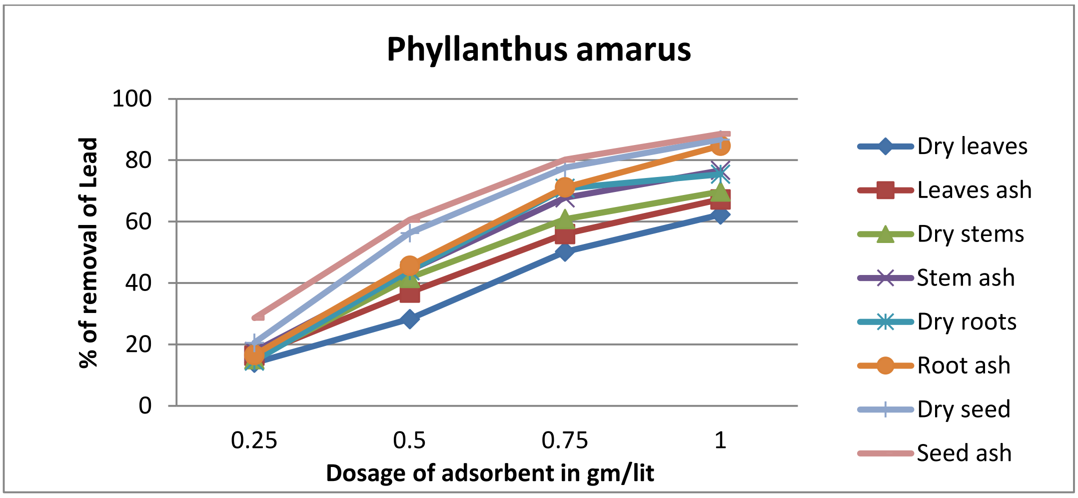
The doses of adsorbent powders were increasing from 0.25gm to 1gm, the elimination of Lead has also increased gradually. A. aspera flowers ash has maximum adsorption of 84.69% and 81.65% at 1g and 0.75g doses. At 1 g of adsorbent dose P.amarus fruit ashes 88.54% and dry fruits 86.75% has shown highest adsorption of Lead. Dry leaves of P.amarus have shown 14.01% of least adsorption at 0.25g doses of biosorbent powder. The % of removal of Lead by bio sorbent powders of two plants were presented in theTable-3. The adsorption isotherms are shown in the graph-5 and 6.

Table 3 Effect of absorbent doses on % of removal of Lead by Achyranthus aspera and Phyllanthus amarus

Absorbent doses	dry leaves	leaves ash	dry stem	stem ash	dry roots	Root ash	Dry Flower	Flower ash	Dry seed	Seed ash
0.25	34.01 14.01	39.64 16.34	45.23 15.21	48.65 17.73	52.16 14.57	56.56 16.56	60.25	64.53	61.09 20.54	59.65 28.59
0.5	45.26 28.24	49.65 36.89	56.28 41.69	61.27 44.07	68.53 43.99	70.25 45.62	74.28	79.86	71.99 56.27	71.56 60.58
0.75	58.36 50.19	65.34 55.97	69.81 60.81	70.76 67.76	71.32 70.83	72.08 71.14	76.85	81.65	68.21 77.58	68.45 80.15
1	70.17 62.31	73.68 67.24	73.68 69.82	44.07 76.66	50.8 75.43	71.92 84.70	80.61	84.69	71.0 86.75	69.38 88.54



Graph-5 Effect of Doses on % of removal of Lead by Achyranthus aspera



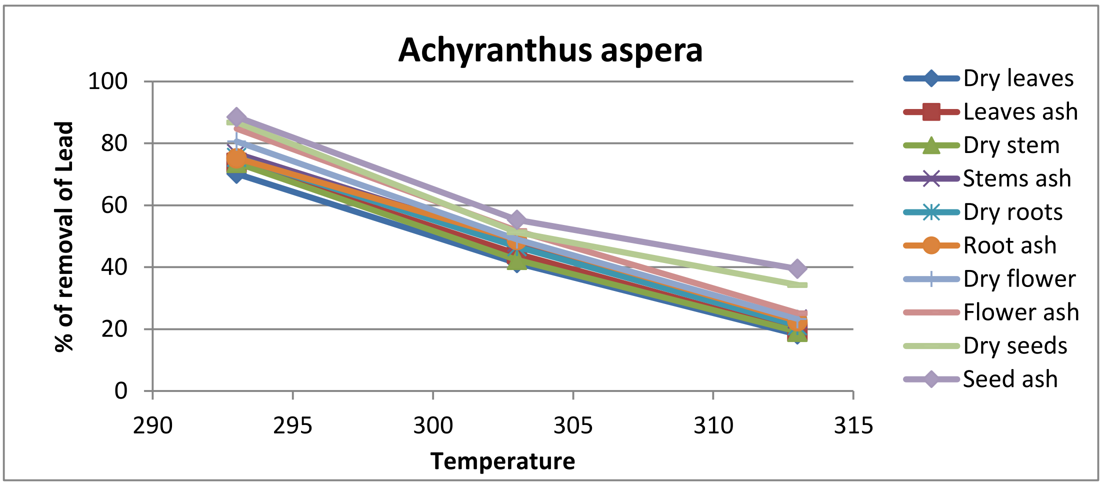
Graph-6 Effect of Doses on % of removal of Lead by Phyllanthus amarus

4.4. Effect of temperature on the adsorption of Lead

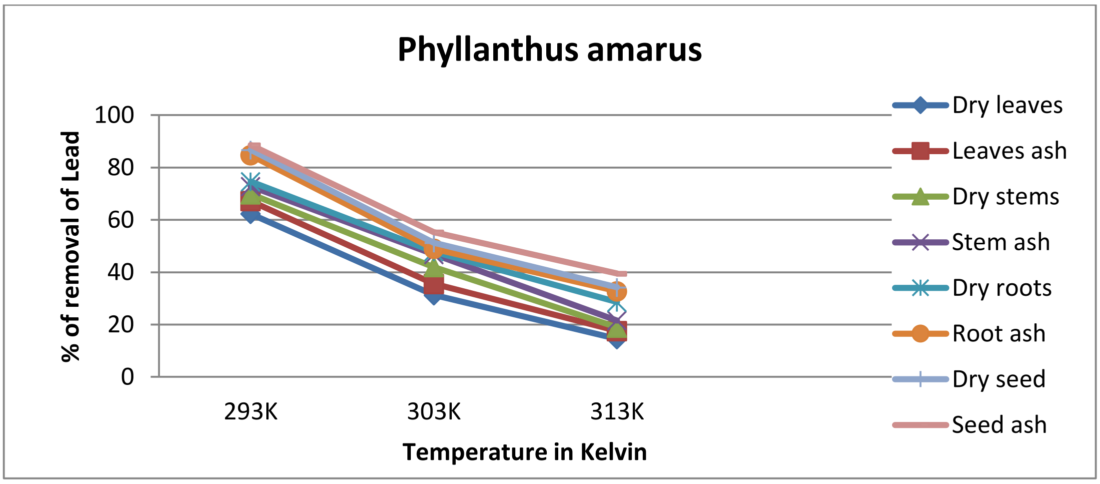
At 293K, adsorption of Lead was high by all adsorbents of two plants. P.amarus fruits ash has shown maximum adsorption of 88.54% followed by dry fruits 86.75% and root ash 84.69% of adsorption. A.aspera flower ash has shown highest adsorption among its adsorbent powders. Temperature of bio-sorbents solution increased by heating the solutions, it is observed that adsorption rate is decreased with increase in the temperature upto313K. Least adsorption was shown by P.amarus dry leaves 14.51% among the two plants at 313K temperature. The % of removal of Lead by biosorbent powders were presented in theTable-4.The absorption isotherms are shown in the Graph-7 and 8.

Table 4 Effect of temperature on % of removal of Lead by Achyranthus aspera and Phyllanthus amarus

Temp.	dry leaves	leaves ash	dry stems	stems ash	dry roots	Root ash	dry flower	flower ash	Dry seed	Seed ash
293K	70.17 62.31	73.68 67.24	73.68 69.82	76.66 72.81	75.43 74.61	75.18 84.70	80.61	84.69	70.11 86.75	69.38 88.54
303K	41.32 31.32	44.35 35.56	42.35 41.99	48.09 46.85	46.62 47.87	48.81 49.0	49.0	51.73	45.72 51.27	42.76 55.26
313K	18.29 14.51	19.25 17.58	19.14 18.93	23.25 21.58	21.13 28.59	22.56 32.79	23.31	25.17	21.14 34.25	19 39.47



Graph-7 Effect of Temperature on % of removal of Lead by Achyranthus aspera



Graph-8 Effect of Temperature on % of removal of Lead by Phyllanthus amarus

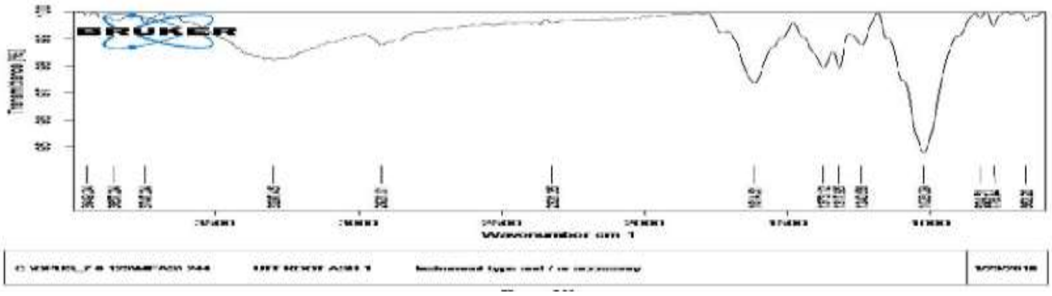


Figure 2. FT-IR spectra of Achyranthes aspera root ash before adsorption

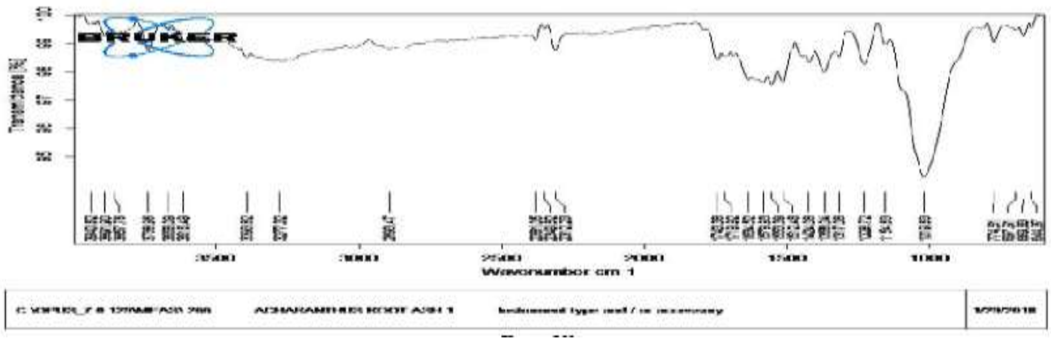


Figure 3. FT-IR spectra of Achyranthes aspera root ash after adsorption

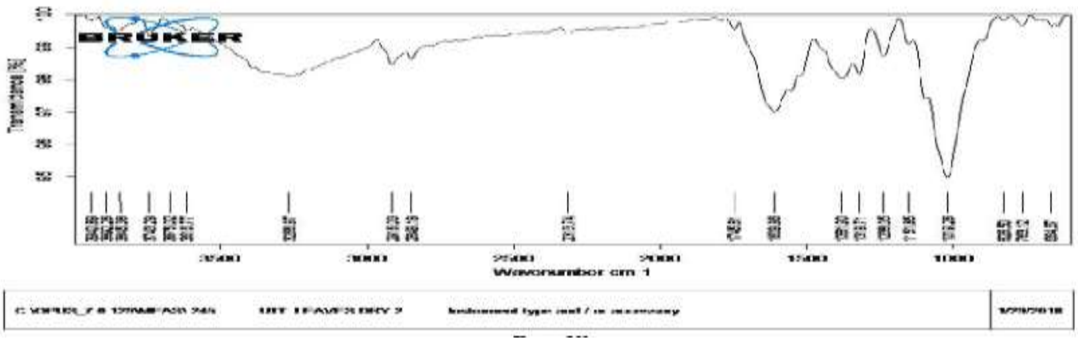


Figure 4. FT-IR spectra of Achyranthes aspera leaves dry before adsorption

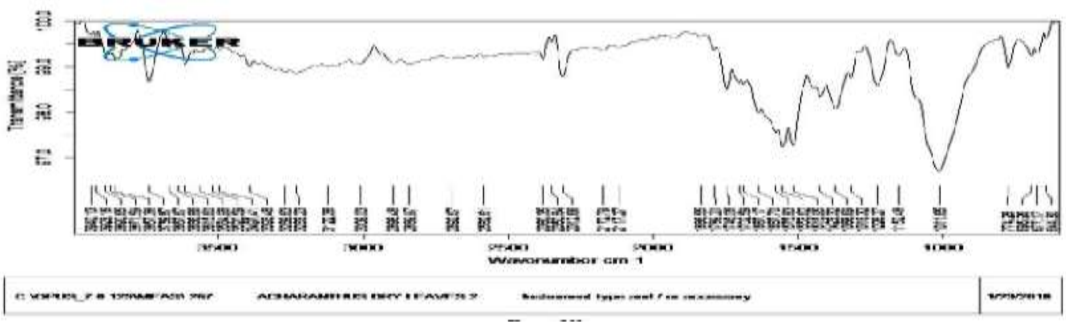


Figure 5. FT-IR spectra of Achyranthes aspera leaves dry after adsorption

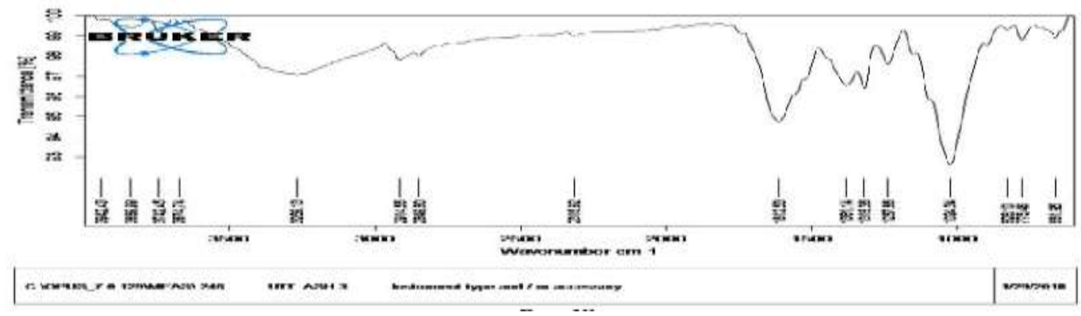


Figure 6. FT-IR spectra of Achyranthes aspera leaves ash before adsorption

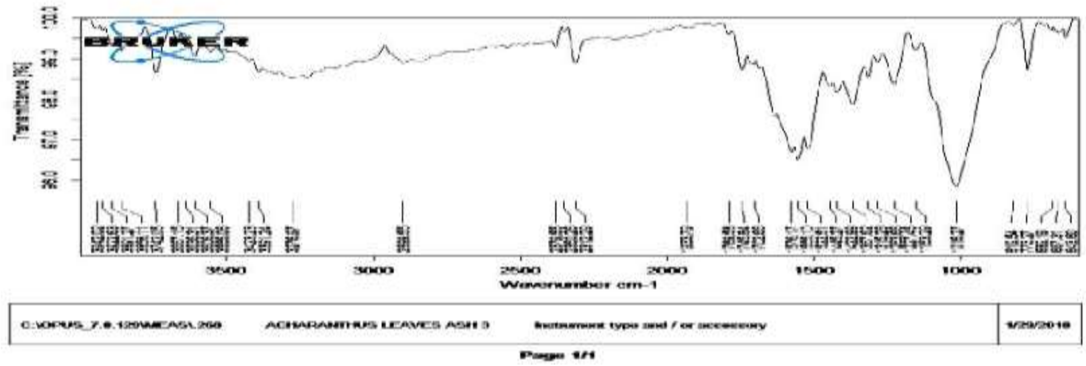


Figure 7. FT-IR spectra of Achyranthes aspera leaves ash after adsorption

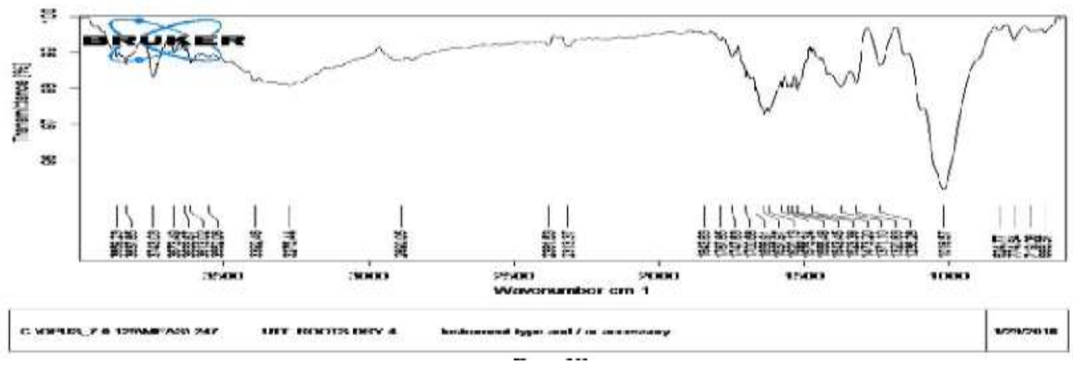


Figure 8. FT-IR spectra of Achyranthes aspera roots dry before adsorption

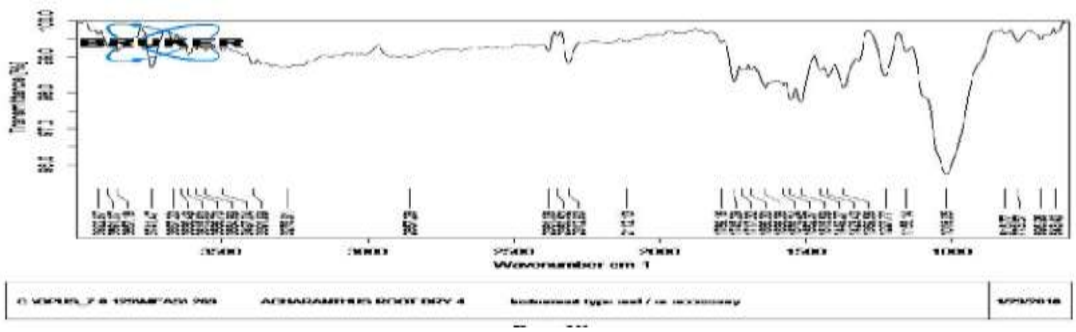


Figure 9. FT-IR spectra of Achyranthes aspera roots dry after adsorption

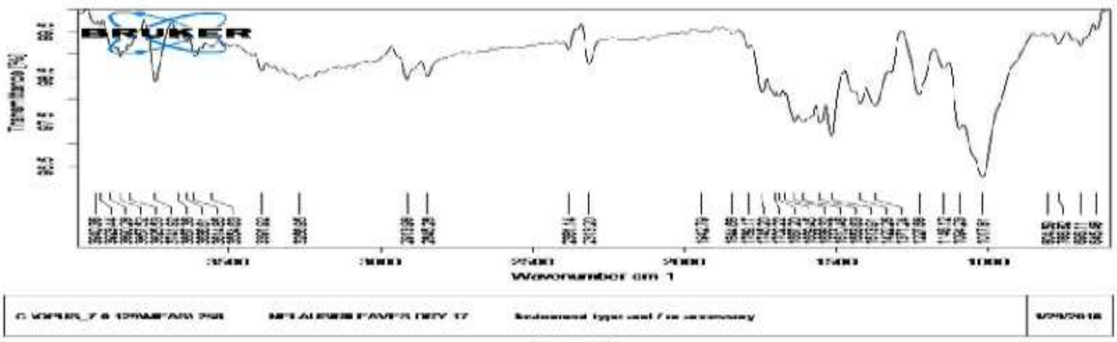


Figure 10. FT-IR spectra of Phyllanthus amarus leaves dry before adsorption

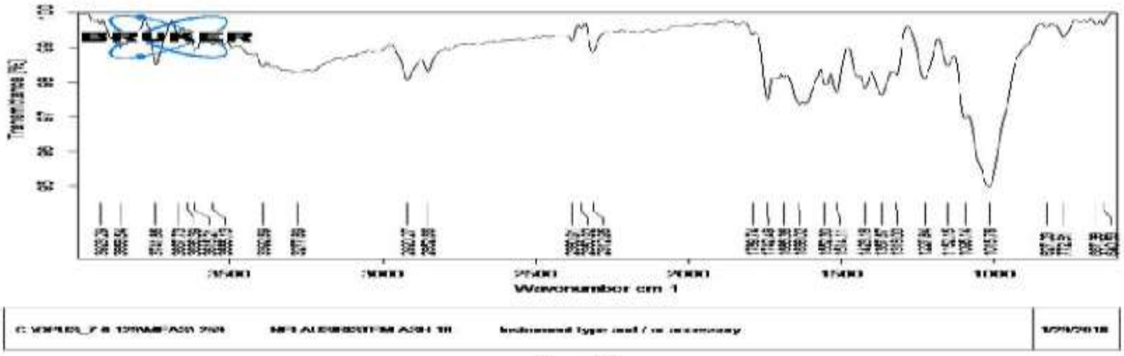


Figure 12. FT-IR spectra of Phyllanthus amarus stem ash before adsorption

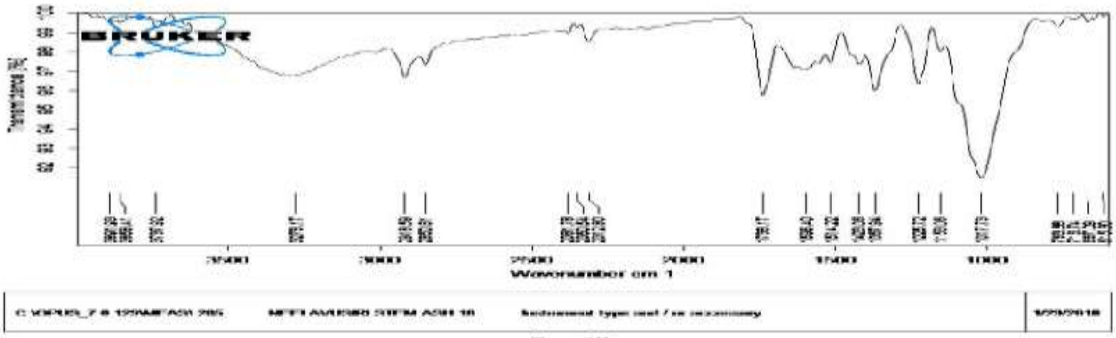


Figure 13. FT-IR spectra of Phyllanthus amarus stem ash after adsorption

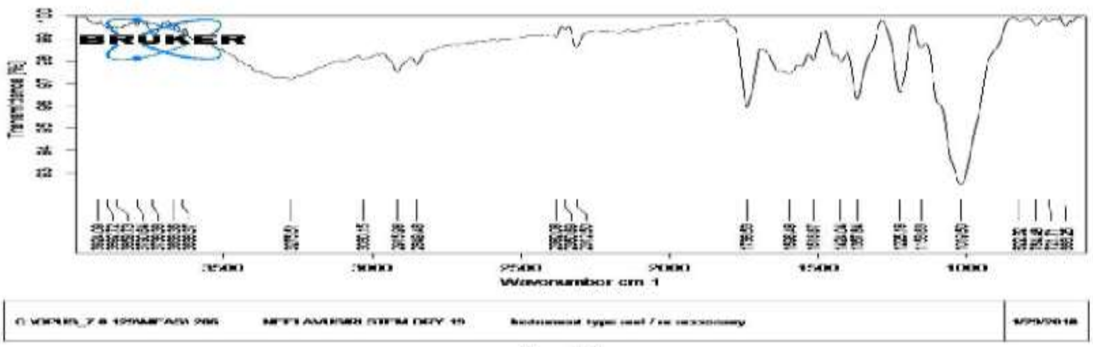


Figure 14. FT-IR spectra of Phyllanthus amarus stem dry before adsorption

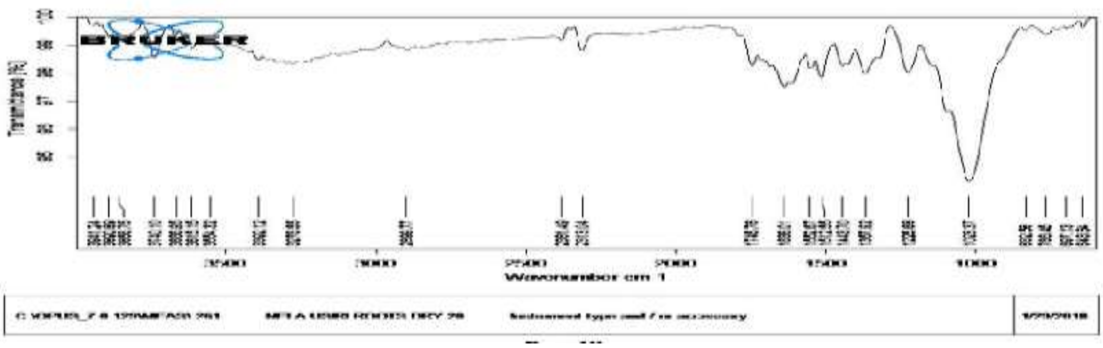


Figure 15. FT-IR spectra of Phyllanthus amarus roots dry before adsorption

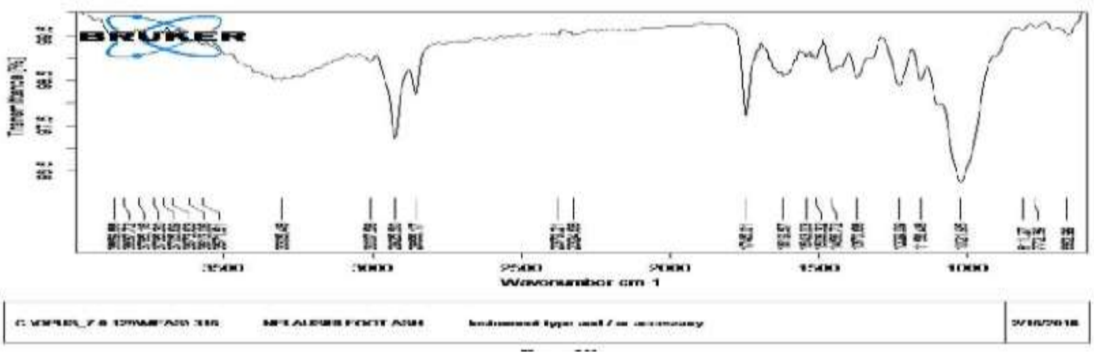


Figure 16. FT-IR spectra of Phyllanthus amarus roots ash before adsorption

5. CONCLUSIONS

The bio-sorbents extracted from Achyranthus aspera and Phyllanthus amarus plants were used for the removal of Lead from polluted water by developing a new and simple volumetric method. The developed method is experimented with different pH range, adsorbent doses, different times and Temperatures. In this we find out P.amarus plant has shown high adsorption than A. aspera plant. The percentage of removal of Lead is 88.54% with seeds ash powder of P.amarus and 84.69% with flower ash of A.aspera at pH 6. The least adsorption of Lead 14.01 was observed by P.amarus in this experiment. The removal of Lead is high by most of the bio-sorbents powder of the two plants. The developed method is inexpensive and sustainable for the removal of Lead from polluted water which makes soil and water free Lead pollution.

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