Removal of Zinc (Zn^{2+}) from metal solutions by using Mountain Laurel and Willow Oak leaves

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Abstract: Natural wastes like Mountain Laurel and Willow Oak leaves have been used as an adsorbent for the removal of zinc from metal solutions. These adsorbent showed an effective removal of zinc from metal solutions. Mount Laurel and Willow Oak leaves have shown more than 80 % of removal efficiency. Physicochemical properties of these adsorbents have been keyed out by batch studies to realize about the adsorption capabilities of selected adsorbents. The main aim of this research is to examine the utilization possibilities of less expensive adsorbents for the excretion of zinc from metal solutions. Results showed that Mountain Laurel leaves are more effective in the removal of zinc metal.

Keywords: Adsorption, Zinc, Batch studies, Mountain Laurel and Willow Oak.

1.INTRODUCTION:

Zinc is found naturally at low concentrations in many rocks and soils, principally as sulphide ores and to a lesser level as carbonates. . It has toxic effects on human and ecological environment which are present in several types of effluent. Zinc can be introduced into water naturally by corroding of minerals from rocks and soil, however, since the zinc ore is only slightly soluble in water. High natural levels of zinc in water are usually associated with higher concentrations of other metals such as lead and cadmium. Mostly zinc is introduced into water by artificial pathways such as byproducts of steel production or coal-fired power stations, or from the burning of waste textiles.Zinc is also used in some plant foods that may leach into groundwater. Older galvanized metal pipes and well cribs were

coated with zinc that may be dissolved by soft, acidic waters. Zn is an essential nutrient for body growth and maturation; however drinking water holding in high levels of zinc can lead to stomach cramps, nausea and vomiting. Water with a zinc concentration of more than 5mg/l may start to be become chalky in appearance with a noticeable deterioration in taste. Certain population groups may be exposed to higher concentrations of zinc than the world-wide population. People who work in coal mines, people who play with the refining and smelting of nonferrous metals and people who live near waste sites and metal smelting operations may be exposed to high levels of Zn.

Price is an important parameter for comparing the adsorbent materials [1]. Activated carbon has been experienced as a highly effective adsorbent for the manipulation of heavy metals in metal solutions, but is readily soluble under extreme pH conditions [2]. Activated carbon is most widely used adsorbent, as it has good capacity for adsorption of carcinogenic metals. Yet, the high cost of activated carbon and 10-15% loss during the regeneration has disincentive in the use of activated carbon in the developing countries [3]. Therefore, in that location is increasing research interest in using alternative low-cost adsorbents. Many such materials have been investigated, including microbial biomass, peat, leaf mould, compost, palm press fibre, sugar cane bagasse, coal, wheat, wool fibre and by products of rice mill, soybean and cottonseed hulls [4-7]. Ion exchange resins are all effective but expensive. Coal and straw, are low cost but ineffective. Peat moss has been distinguished as very effective in adsorbing heavy metals. Muhammad et al, [8] used slow sand filters to get rid of heavy metals (Cu, Cd, Cr, Pb). Quek et al, [9] used the sago waste, to adsorb lead and copper ions from solution. Mahavi et al, [10] studied about tea waste as an adsorbent for the removal of hard metals (Cd, Pb, Ni) from industrial waste. Above 95% removal of lead, 86% for Nickel and 77% for Cadmium were identified using tea waste.

The banana and lemon peel have the removal efficiencies of 87.5% and 90.5% for Zinc at the pH of 4 as reported by Sunil Rajoriya, et al. [11]. Arshad et al, [12] 2008 studied about the removal of zinc from water by using leaves and root bark of the Neem tree. Batch adsorption studies were carried out and demonstrated the maximum adsorption capacity of zinc for neem leaves and root bark is 147.08mgZn/g at pH 4 and 137.67mgZn/g at pH 5 respectively. HorsfallJr and Abia[13] investigate the removal effect of Cassava waste on the adsorption of Zn^{2+} and Cd^{2+} ions. It was identified that treated cassava waste sustains a much higher adsorption capacity for Zn^{2+} and Cd^{2+} ions compared to untreated sample. The adsorption capacities of treated cassava waste were reported to be 647.48 mg Cd/g and 559.74 mg Zn/g, as compared to just 86.68 mg Cd/g and 55.82 mg Zn/g when using untreated cassava waste. More investigation about non-living plant biomass materials are efficient in the removal of heavy metals from the environment (Lujan et al., 1994; Mofa, 1995; Gardea-Torresdey et al, 1996).
A routine of studies have been carried on and evaluated the application of adsorption for the removal of Zn^{2+}. These admit the utilization of natural materials such as bagasse [17], moss [18], bentonite[19], and mixed mineral [20], microbial and algal biomass, including seaweed, yeast, fungi, and bacteria [21]; industrial and agricultural wastes such as corn cobs, peanut hulls, hazelnut shells, cornstarch, waste tea leaves, sea nodule residue, blast furnace slag, sugar beet pulp, lignite, lignin, and powdered waste sludge [24,25,19–22]. Despite the relative simplicity and potential cost-effectiveness of adsorption, metal removal using low-cost adsorbents is relatively unproven and needs more development before it may be practiced routinely in practice.

2. MATERIALS AND METHODS

2.1.Adsorbent:

The adsorbent used for this study are Mountain Laurel and Willow Oak leaves were gathered and utilized for the removal of Zn in the effluent. The collected adsorbent was washed with double distilled water. The adsorbent were oven dried at 100˚C to remove the moisture content. The dried adsorbents were grounded with domestic grinder. After grounded, adsorbent were sieved (40-50 mesh size) and stored in a clean plastic container.

2.2. Adsorbate:

All reagents used were of analytical reagent grade. Zinc solution (1000mg/l) was prepared using metal nitrate salts in double distilled water and required concentrations (25,50,75&100 mg/l) were made by reducing the zinc solution (1000mg/l) with distilled water. The pH was adjusted to 5 to prevent hydrolysis.

2.3. Adsorptionexperiment :(Batch studies and isotherms)

The natural adsorbent like Mountain Laurel and Willow Oak leaves were investigated in this study. These two adsorbents were used for the removal of zinc from metal solutions.
The experiment was conducted by adding 0.2g of dried adsorbent in 100 ml metal solutions. The initial concentration of the metal solution varying from the range of 10-100mg/l. The pH of the metal ion solutions was maintained at 5±0.5. pH meter with a combination of electrodes were employed for

the measurements of pH in the metal solutions. The samples were shaken for 1 hour at (25±1˚C) in a wrist action shaker. The treated metal solutions were filtered and analyzed for metal ion concentration using an Atomic Adsorption spectrophotometer.

The isotherm experiment was conducted by adding 0.4g/100ml of dry adsorbents to the initial metal solutions of varying the concentrations (20,40,60,80&100mg/l). The samples were shaken for 40 minutes for equilibrium studies. Therefore, further studies were conducted at 40 minutes of contact time.The percentage removal of zinc from the metal solutions were calculated according to the following equation:

$$\% \text{ removal} = \frac{C_i - C_f}{C_i} \times 100$$

where C_i and C_f are the initial and final zinc concentration in mg/l respectively.

3.RESULT AND DISCUSSION:

3.1 Effect of pH:

To investigate about the effect of pH, the pH of metal solutions varied from 2 to 9. The pH of the solutions was adjusted by using 0.1N hydrochloric acid solution or 0.02N sodium hydroxide solution. The initial metal solution concentration was maintained to be 50mg/l of zinc solution. About 2g of dry adsorbent were added separately to the metal solutions with varying pH.

Table.1. Effect of pH - Mountain Laurel Leaves

S.No	pH	Initial conc [mg/l]	Final conc [mg/l]	% removal of Zn
1.	2	50	34.69	30.62
2.	3	50	32.91	34.18
3.	4	50	30.39	39.23
4.	5	50	27.43	45.14
5.	6	50	29.94	40.12
6.	7	50	33.38	33.25
7.	8	50	35.23	29.54
8.	9	50	36.87	26.27

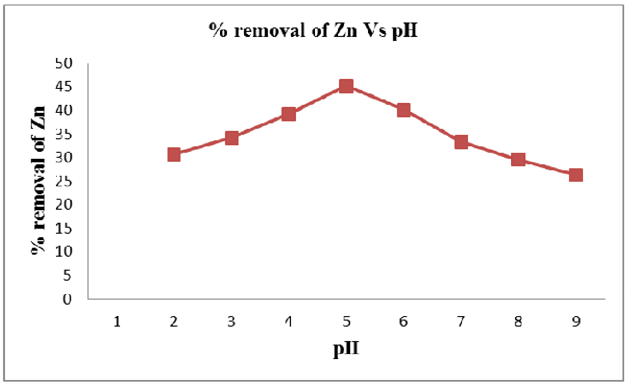

Fig.1. Effect of pH - Mountain Laurel leaves

(Initial concentration=50mg/l,
Adsorbent dosage=0.2g/100ml,
pH=2 to 9,Temp=25±2˚C,Contact time=60 min, Maximum % removal of Zn at pH=5)

Table.2. Effect of pH - Willow Oak leaves

S. No	pH	Initial conc [mg/l]	Final conc [mg/l]	% removal of Zn
1.	2	50	36.29	27.42
2.	3	50	34.13	31.74
3.	4	50	32.23	35.54
4.	5	50	29.63	40.74
5.	6	50	31.94	36.12
6.	7	50	33.58	32.84
7.	8	50	36.79	26.42
8.	9	50	39.24	21.52

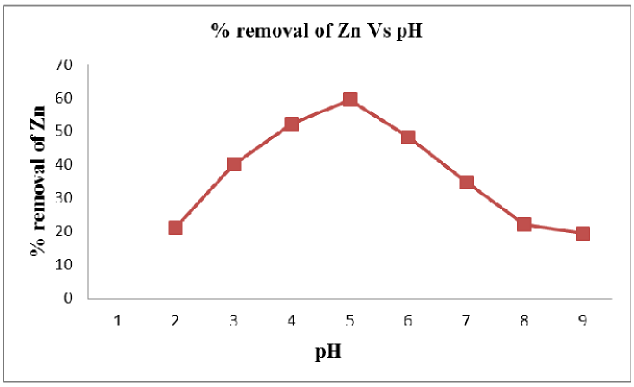

Fig.2. Effect of pH - Willow Oak leaves.

(Initial concentration=50mg/l,
Adsorbent dosage=0.2g/100ml,
pH=2 to 9,Temp=25±2˚C,Contact time=60 min,Maximum % removal of Zn at pH=5)

3.2. Effect of adsorbent dose:

The study was conducted to identify the optimal dosage of adsorbent for the removal of Zn from the metal solution. The dosage of the adsorbent varied from 0.1 to 0.5g in 100ml of metal solutions. The metal solutions of initial concentration of 50mg/l were shaken for 60 minutes at a pH of 5.

Table.3. Effect of adsorbent dosage – Mountain Laurel leaves

S.No	Dose [g/100ml]	Initial conc [mg/l]	Final conc[mg/l]	% removal of Zn
1.	0.1	50	37.73	24.54
2.	0.2	50	34.21	31.58
3.	0.3	50	30.13	39.74
4.	0.4	50	27.14	45.72
5.	0.5	50	27.11	45.78

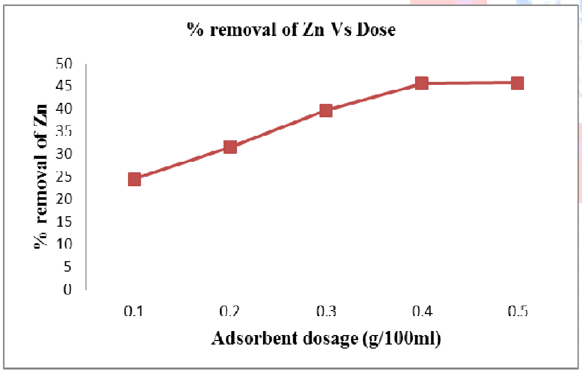

Fig.3. Effect of adsorbent dosage - Mountain Laurel leaves

(Initial concentration=50mg/l, Adsorbent dosage=0.1 to 0.5g/100ml, pH=5,Temp=25±2˚C,Contact time=60 min, Maximum % removal of Zn at adsorbent dosage=0.4g/100ml)

Table.4. Effect of adsorbent dosage- Willow Oak leaves

S. No	Dose [g/100ml]	Initial conc [mg/l]	Final conc [mg/l]	% removal of Zn
1.	0.1	50	39.41	21.18
2.	0.2	50	36.01	27.98
3.	0.3	50	33.23	33.55
4.	0.4	50	29.74	40.53
5.	0.5	50	29.56	40.88

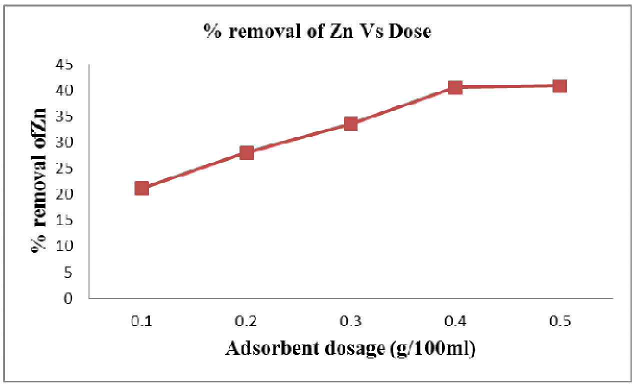

Fig.4. Effect of adsorbent dosage – Willow Oak leaves

(Initial concentration=50mg/l, Adsorbent dosage=0.1 to 0.5g/100ml, pH=5,Temp=25±2˚C,Contact time=60 min, Maximum % removal of Zn at adsorbent dosage=0.4g/100ml)

3.3. Effect of contact time:

The experiments were conducted to find the contact time for the maximum removal of Zn from the metal solution. Dosage of the adsorbent are kept as 0.4g in 100ml of metal solutions for Mountain Laurel and Willow Oak leaves. The metal solutions of initial concentration of 50mg/lwere shaken for varying contact time from 0 to 60 minutes.

Table 5: Effect of contact time – Mountain Laurel leaves

S.No	Time (min)	Initial conc [mg/l]	Final conc[mg/l]	% removal of Zn
1.	10	50	30.40	39.20
2.	20	50	24.89	50.22
3.	30	50	15.88	68.24
4.	40	50	13.48	73.04
5.	50	50	13.39	73.22
6.	60	50	13.11	73.78

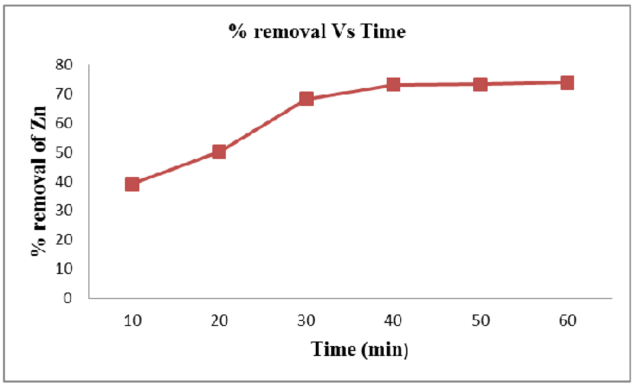

Fig.5. Effect of adsorbent dosage – Mountain Laurel leaves

(Initial concentration=50mg/l, Adsorbent dosage=0.4g/100ml, pH=5,Temp=25±2˚C,Contact time=0 to 60 min ,Maximum % removal of Zn obtained at contact time = 40 minutes)

Table 6: Effect of contact time –Willow Oak leaves.

S. No	Time (min)	Initial conc [mg/l]	Final conc [mg/l]	% removal of Zn
1.	10	50	30.34	39.32
2.	20	50	24.58	50.30
3.	30	50	18.85	62.30
4.	40	50	14.51	70.98
5.	50	50	14.39	71.22
6.	60	50	14.26	71.48

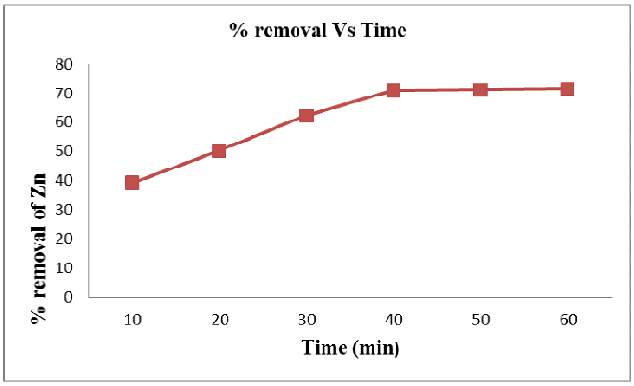

Fig.6. Effect of adsorbent dosage – Willow Oak leaves

(Initial concentration=50mg/l, Adsorbentdosage=0.4g/100ml, pH=5,Temp=25±2˚C, Contact time=0 to 60 min ,Maximum % removal of Zn obtained at contact time = 40 minutes)

3.4. Effect of initial concentration:

The study was conducted to identify the initial concentration for the maximum removal of Zn from the metal solution. Dosage of the adsorbent are kept as 0.4g in 100ml of metal solutions for Mountain Laurel and Willow Oak leaves. The metal solutions of initial concentration was varied (25,50,75,100,125mg/l) were shaken for contact time of 40 minutes.

Table 7: Effect of initial concentration– Mountain Laurel leaves

S.No	Initial conc [mg/l]	Final conc [mg/l]	% removal of Zn
1.	10	1.16	88.40
2.	15	2.25	85.00
3.	20	3.87	80.65
4.	25	5.39	78.44
5.	30	6.82	77.27
6.	35	8.32	76.23
7.	40	10.16	74.60
8.	45	11.71	73.98
9.	50	13.49	73.02

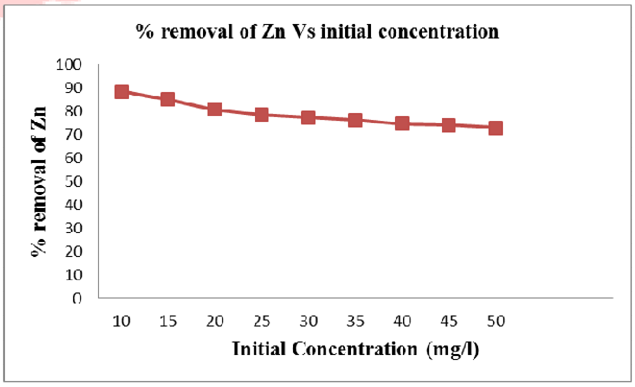

Fig 7: Effect of initial concentration - Mountain Laurel leaves

(Initial concentration=10 to50mg/l, Adsorbent dosage=0.4/100ml, pH=5,Temp=25±2˚C, Contact time=40 min)

Table 8: Effect of initial concentration – Willow Oak leaves

S.No	Initial conc [mg/l]	Final conc [mg/l]	% removal of Zn
1.	10	1.52	84.80
2.	15	2.45	83.67
3.	20	3.54	82.30
4.	25	4.64	81.44
5.	30	5.83	80.57
6.	35	7.17	79.51
7.	40	9.09	77.28
8.	45	11.25	75.00
9.	50	14.51	70.98

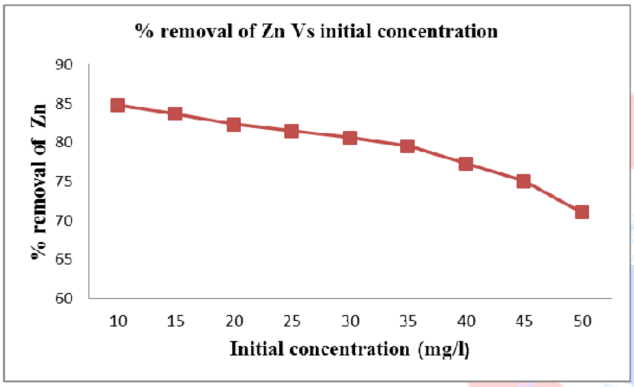

Fig 8: Effect of initial concentration – Willow Oak leaves

(Initial concentration=10 to50mg/l, Adsorbent dosage=0.4/100ml, pH=5,Temp=25±2˚C, Contact time=40 min)

4. ADSORPTION ISOTHERMS:

Adsorption isotherm is a functional expression for the variation of adsorption with the concentration of the adsorbate in bulk solution at a constant temperature. The amount of adsorbed material per unit weight of adsorbent increases with increasing concentration of the solute to be adsorbed but not in direct proportion. The batch adsorption experiments were directed to determine the adsorption capacity of Mountain Laurel and Willow Oak leaves to a fair degree by determining the adsorption isotherm. Freundlich adsorption isotherm is the relationship between the amounts of zinc adsorbed per unit mass of adsorbent (X/M) and the absorption of the zinc at equilibrium (Ce). Here Kf and n is the constants. A Freundlich adsorption isotherm equation was obtained for the adsorption of zinc on Mountain Laurel and Willow Oak leaves at room temperature (25±1˚C) at optimum conditions of contact time and dose of adsorbent.

$$\frac{X}{M}=K_fC_e^{1/n}$$

The logarithmic form of the equation becomes,

$$\log\frac{X}{M}=\log K_f+\frac{1}{n}\log C_e$$

The Langmuir model represents one of the first theoretical treatments of non-linear sorption, and has been successfully applied to a wide range of organizations that exhibit limiting or maximum sorption capacities. The model assumes a fixed number of accessible sites are used on the adsorbent surface, all of which have the same energy, and adsorption is reversible. The Langmuir isotherm is given by

$$\frac{X}{M}=\frac{abCe}{1+bCe}$$

The constants in the Langmuir isotherm can be defined by plotting 1/(X/M) versus ($1/C_e$) and making use of the above equation rewritten as:

$$\frac{1}{X/M}=\frac{1}{a}+\frac{1}{ab}\frac{1}{Ce}$$

The table 9 shows the results of the batch adsorption experiment for the zinc removal by Mountain Laurel leaves.

Table 9: Data forFreundlich adsorption isotherms for Zn- Mountain Laurel leaves

S. No	Initial Conc. (mg/l)	Final Conc. (Ce) (mg/l)	Dose M (g)	X (mg/l)	Log X/M	Log Ce
1.	10	1.16	4	8.84	0.34	0.06
2.	15	2.25	4	12.75	0.50	0.35
3.	20	3.87	4	16.13	0.61	0.59
4.	25	5.39	4	19.61	0.69	0.73
5.	30	6.82	4	23.18	0.76	0.83
6.	35	8.32	4	26.68	0.82	0.92
7.	40	10.16	4	29.84	0.87	1.01

8.	45	11.71	4	33.29	0.92	1.07
9.	50	13.49	4	36.51	0.96	1.13

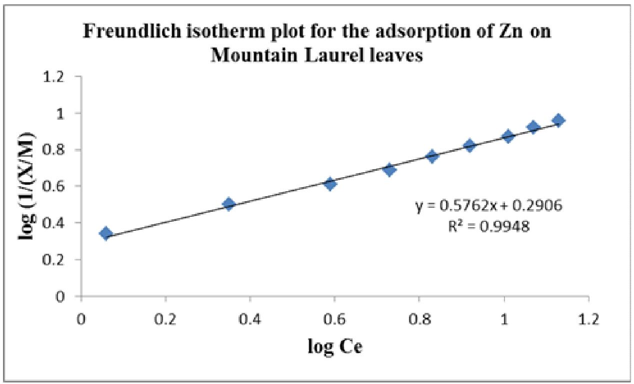

Fig9: Freundlich isotherm plot for the adsorption of Zn on Mountain Laurel leaves

Fig 9 shows the Freundlich isotherm plot for the zinc removal by Mountain Laurel leaves. The adsorption capacity and intensity was found to be 1.74 and 1.735 respectively.

Table 10: Data for Langmuiradsorption isotherms for Zn- Mountain Laurel leaves

S. No	Initial Conc. (mg/l)	Final Conc. (Ce) (mg/l)	Dose M (g)	X (mg/l)	1/(X/M)	1/Ce
1.	10	1.16	4	8.84	0.45	0.86
2.	15	2.25	4	12.75	0.31	0.44
3.	20	3.87	4	16.13	0.25	0.26
4.	25	5.39	4	19.61	0.20	0.19
5.	30	6.82	4	23.18	0.17	0.15
6.	35	8.32	4	26.68	0.15	0.12
7.	40	10.16	4	29.84	0.13	0.09
8.	45	11.71	4	33.29	0.12	0.08
9.	50	13.49	4	36.51	0.11	0.07

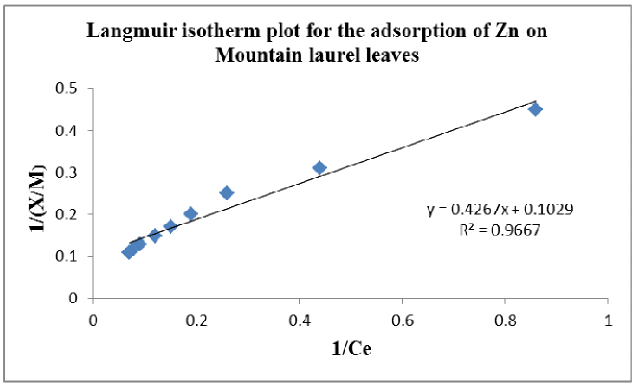

Fig10: Langmuir isotherm plot for the adsorption of Zn on Mountain Laurel Leaves

Fig10 shows the Langmuir isotherm plot for the adsorption of zinc removal by Mountain Laurel leaves. The empirical constants (a and b) were found to be 0.241 and 9.718 respectively.

The data obtained from these studies were best fit with the Freundlich adsorption isotherm.The table 10 shows the results of the batch adsorption experiment for the zinc removal by Willow Oak leaves.

Table 11: Data for Freundlich adsorption isotherms for Zn- Willow Oak leaves

S. No	Initial Conc. (mg/l)	Final Conc. (Ce) (mg/l)	Dose M (g)	X (mg/l)	Log X/M	Log Ce
1.	10	1.52	4	8.48	0.33	0.18
2.	15	2.45	4	12.55	0.49	0.39
3.	20	3.54	4	16.46	0.61	0.55
4.	25	4.64	4	20.36	0.71	0.67
5.	30	5.83	4	24.17	0.78	0.77
6.	35	7.17	4	27.83	0.84	0.86
7.	40	9.09	4	30.91	0.89	0.96
8.	45	11.25	4	33.75	0.93	1.05
9.	50	14.51	4	35.49	0.95	1.16

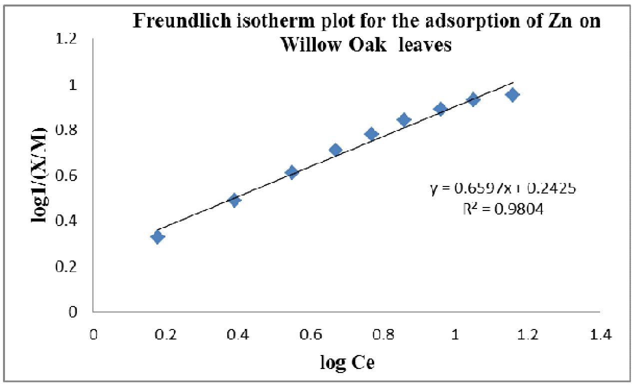

Fig11: Freundlich isotherm plot for the adsorption of Zn on Willow Oak leaves

Fig 11 shows the Freundlich isotherm plot for the zinc removal by Willow Oak leaves. The adsorption capacity and intensity was found to be 1.66 and 1.516 respectively.

Table 12: Data for Langmuir adsorption isotherms for Zn- Willow Oak leaves

S. No	Initial Conc. (mg/l)	Final Conc. (Ce) (mg/l)	Dose M (g)	X (mg/l)	1/(X/M)	1/Ce
1.	10	1.16	4	8.84	0.47	0.66
2.	15	2.25	4	12.75	0.32	0.41
3.	20	3.87	4	16.13	0.24	0.28
4.	25	5.39	4	19.61	0.19	0.22
5.	30	6.82	4	23.18	0.17	0.17
6.	35	8.32	4	26.68	0.14	0.14
7.	40	10.16	4	29.84	0.13	0.11
8.	45	11.71	4	33.29	0.12	0.09
9.	50	13.49	4	36.51	0.11	0.07

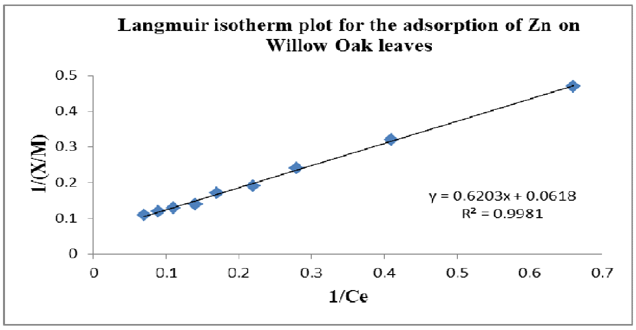

Fig12: Langmuir isotherm plot for the adsorption of Zn on Willow Oak Leaves

Fig12 shows the Langmuir isotherm plot for the adsorption of zinc removal by Willow Oak leaves. The empirical constants (a and b) were found to be 0.099 and 16.18 respectively.
The data obtained from these studies were best fit with the Langmuir adsorption isotherm.

5.CONCLUSION:

This study indicates the following results in the removal of zinc from metal solutions by using Mountain Laurel and Willow Oak leaves as an adsorbent.

1. Mountain Laurel leaves showed the highest removal of Zn was 73.02% for 50mg/l.
2. Willow Oak leaves showed the highest removal efficiency of Zn was 70.98% for 50mg/l.
3. The data obtained in this study by using Mountain Laurel leaves as an adsorbent agree with Freundlich adsorption isotherm.
4. The data obtained in this study by using Willow Oak leaves as an adsorbent agree with Langmuir adsorption isotherm.
5. The adsorption capacities (K_f) for zinc calculated from theFreundlich adsorption isotherm was 1.74 and 1.66 for the Mountain Laurel leaves and Willow Oak leaves respectively.
6. The adsorption intensity (n) for zinc calculated from the Freundlich Adsorption isotherm was 1.735 and 1.516 for the Mountain Laurel leaves and Willow Oak leaves respectively.
7. From Langmuir adsorption isotherm, the empirical constants (a,b) were found to be (0.241, 9.718) and (0.099,16.18) for the Mountain Laurel leaves and Willow Oak leavesrespectively.

From the above results it has been identified that the batch adsorption study concluded that the Mountain Laurel and Willow Oak leaves are real efficient in the removal of zinc from metal solutions.

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