International Journal of Applied Research 2021; 7(4): 182-186

ISSN Print: 2394-7500
ISSN Online: 2394-5869
Impact Factor: 8.4
IJAR 2021; 7(4): 182-186
www.allresearchjournal.com
Received: 20-02-2021
Accepted: 26-03-2021

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Application of statistical tools in the analysis of adsorption data

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DOI: https://doi.org/10.22271/allresearch.2021.v7.i4c.8485

Abstract
This study was carried out to analyse the experimental data by hypothesis testing using various statistical tests. It enabled us to make significant statements about the adsorption parameters. Dried mango leaf powder was used as an adsorbent to remove Cu (II), Zn (II) and Pb (II) ions from contaminated water samples. Student's t-tests, F-test and Chi-square test and ANOVA were used for the analysis of data. The calculated values of t, F and chi-square were compared with their tabulated values listed in literature within 5% level of significance. Results showed the experimental data in an accepted region on the probability charts, signifying the validity of data % zinc ions removed, equilibrium time, the effectiveness of adsorption in the removal of zinc ions, equality of variance of two samples of different concentrations and difference of means of multiple samples.

Keywords: Statistical analysis, hypothesis testing, probability charts, waste water treatment, adsorption, heavy metals

Introduction
Adsorption is a known phenomenon in water treatment since ancient times. It is a common phenomenon in the gaseous phase, but is used effectively in the treatment of waste water. Charcoal prepared from wood char, sand and charcoal filters in water purification by Egyptians and Sumerians since 3750 BC are reported in the literature [1, 2]. During several decades, the concentration of trace heavy metals, synthetic organic chemicals (SOCs) and natural organic materials (NOMs) has increased in water bodies and drinking water supplies to harmful levels. Unlike organic pollutants, heavy metals are known for their toxicity, persistency and non-biodegradability. They find their way into water bodies through industrial, domestic and municipal discharges. Their presence in water is a serious threat to all forms of life because of their mutagenic and carcinogenic nature. Their presence in the body above the prescribed limits can cause severe damages to vital organs of the body, such as kidney, liver, brain, the reproductive system and the nervous system [3].

Of all the methods of waste water treatment, adsorption with agricultural waste is one of the trusted methods in heavy metal removal for its cost effectiveness, availability of wide range of adsorbents and significant efficiency in removing metals from contaminated water. Reseachers have studied adsorbents prepared from agricultural wastes to remove heavy metal ions from polluted water, such as sawdust, tea waste, palm shell, coconut shell, bamboo activated charcoal, olive cake, coir, rice husk etc. [4, 5, 6]. They obtained %age of heavy metal ions removed w.r.t. adsorbent dose, time, temperature, pH and metal ion concentration in the sample. This experimental data was analysed by fitting them into non-linear forms such as Langmuir and Freundlich isotherm models.

Various hypothesis tests for the analysis of experimental data are classified as 1) parametric tests, the standard tests, include z-test, t-test, F-test and χ^2-test 2) Non-parametric tests, the distribution-free tests of hypotheses, do not dependent on assumptions based on the characteristics of the parent population [7]. In this paper, the adsorption process used to remove the metal ions from the contaminated solutions was described qualitatively and quantitatively statistically.

Materials and Method
Adsorption study of Zn (II), Cu (II) and Pb (II) on mango leaf powder was done batch wise. A stock solution of zinc metal ions was prepared in the lab.

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Analytical grade Zn metal chips (1 g) dissolved in a few drops of conc. HCl. This concentrated solution was further diluted with distilled water to 1 litre. Stock solutions of copper and lead were also prepared with analytical grade nitrate of the respective metal diluted to 1 litre with distilled water. Stock solutions were further diluted to various concentrations in the range 10-100 mg/L with the help of distilled water. Mango tree leaves used as adsorbent were collected from the local area were washed, dried and crushed to a size of 200 mesh. The crushed powder was washed thoroughly to remove the colour, dried in a hot air oven for six hours till bone dried and then stored in air tight container. The dried powder was used to determine the % removal of Zn (II), Cu (II) and Pb (II) ions from the above solutions. 12 Erlenmeyer flasks containing 1-10 g/L mango leaf powder each were used in the 'Orbital' constant temperature variable speed shaker at a time at 20^{o}C and 150 rpm for 100 minutes in the pH range 2-8 to carry out the batch experiment. The solutions were filtered through Whatman filter paper no. 40 after each batch experiment. The concentrations of metal ions in the filtrates were determined by Atomic Absorption Spectrophotometer (CHEMICA 001) using air-acetylene flame. Percentage removal of metal ions from the solutions after the batch experiment was calculated as:

$$\% \text{ Removal} = [(C_i - C_o)/C_i]*100 \qquad \text{(Eq. 6)}$$

Where C_o denotes the final zinc ion concentration (mg/L) and C_i denotes the initial zinc ion concentration in the solution (mg/L).

Equilibrium adsorption capacity (mg adsorbate/g adsorbent) is calculated as

$$q_e = [(C_i - C_e)V]/m \qquad \text{(Eq.7)}$$

Where V denotes the volume of the solution in litres and m denotes the mass (g) of the adsorbent used (Kaushal and Singh, 2016 b,c).

Results and Discussion

Data collected from the experiment was analysed with the help of hypotheses testing within 5% level of significance.

1. Hypotheses are tested to judge the maximum % removal of the zinc, copper and lead metal ions from the samples: The samples contained 100 mg/L of the respective metal ions, an adsorbent dose of 10 g/L and different pH values at 20^{0}C was done with two-tailed t-test

Null hypothesis H_o: μ_{Ho} = Maximum % removal of metal ions from the contaminated sample = 75 % for zinc, 86 % for copper and 79 % for lead.

Alternate hypothesis H_a: $\mu_{Ho} \neq$ 75 % for zinc, 86 % for copper and 79 % for lead.

$t = (\bar{X} - \mu_{Ho})/(\sigma_s/\sqrt{n}) = t_{observed,}$ for (n-1) degree of freedoms

Where σ_s = Standard deviation, $\bar{X}$ = Average value of X and n = sample size.

Xi = % removal of metal ions from the contaminated samples.

Average value of X = $\bar{X} = \Sigma X_i/n$ and Standard deviation = $\sigma_s = \sqrt{[\{\Sigma(X_i - \bar{X})^2\}/(n-1)]}$ [7, 8, 9, 10, 11].

Table 1: 2-tailed t-distribution

		Zinc			Copper			Lead		
N	**pH**	**Xi**	**Xi- X̄**	**μHₒ**	**Xi**	**Xi- X̄**	**μHₒ**	**Xi**	**Xi- X̄**	**μHₒ**
1	2	15	-39.14	75	32	-31.43	86	23	-35.00	79
2	3	30	-24.14	75	45	18.43	86	45	-13.00	79
3	4	63	8.86	75	65	1.57	86	68	10.00	79
4	5	75	20.86	75	86	22.57	86	79	21.00	79
5	6	72	17.86	75	80	16.57	86	72	14.00	79
6	7	67	12.86	75	72	8.57	86	63	5.00	79
7	8	57	2.86	75	64	0.57	86	56	-2.00	79
$\bar{X}$		54.14			63.43			58.00		
σ_s		22.81			19.10			18.97		
d.f.		6			6			6		
t_{obs}		-2.420			-1.603			-2.371		
t_{tab}		-2.447			-2.447			-2.447		

Calculations showed for a sample size of 7, the standard deviation σ_s was 22.81, 19.10 and 18.97 for zinc, copper and lead respectively. $t_{observed}$ was -2.420, -1.603 and -2.371 for Zn II, Cu II and Pb II respectively. Whereas $t_{tabulated}$ was -2.447 for 2-tailed t-distribution at 5% level of significance [12]. $t_{observed} < t_{tabulated}$ indicated that the observed values of t lie within the accepted region of the probability chart. Hence, the null hypothesis is accepted.

2. Hypothesis testing to judge the time required to attain equilibrium: One-tailed t-test within 5% level of significance was used for the testing the equilibrium time.

H_o: μH_o = Contact time to reach equilibrium (60 mins for Zn II, 120 mins for Cu II and 80 mins for Pb II) Alternate hypothesis $H_a > \mu H_o$.

Table 2: 1-tailed t-distribution

		Zinc			Copper			Lead		
n	**Time (min)**	**Xi**	**Xi- X̄**	**μHₒ**	**Xi**	**Xi- X̄**	**μHₒ**	**Xi**	**Xi- X̄**	**μHₒ**
1	10	24	-43.08	60	32	-35.42	120	36	-31.25	80
2	20	50	-17.08	60	40	-27.42	120	45	-22.25	80
3	30	63	-4.08	60	48	-19.42	120	52	-15.25	80
4	40	70	2.912	60	58	-9.42	120	60	-7.25	80
5	50	73	5.92	60	66	-1.42	120	68	0.75	80

6	60	75	7.92	60	72	4.58	120	74	6.75	80
7	70	75	7.92	60	76	8.58	120	77	9.75	80
8	80	75	7.92	60	80	12.58	120	79	11.75	80
9	90	75	7.92	60	82	14.58	120	79	11.75	80
10	100	75	7.92	60	84	16.58	120	79	11.75	80
11	110	75	7.92	60	85	17.58	120	79	11.75	80
12	120	75	7.92	60	86	18.58	120	79	11.75	80
$\overline{X}$		67.08			67.41			67.25	11.75	80
σ_s		15.51			18.75			15.34		
d.f..		11			11			11		
t_{obs}		1.58			-9.71			-2.88		
t_{tab}		1.796			1.796			1.796		

Xi = Quantity of metal ions removed from samples of initial metal ions concentration 100 mg/l for 2 hours. Degrees of freedom = d.f. = n-1 = 11

Average value of X = $\overline{X} = \Sigma X_i/n$ and Standard deviation = $\sigma_s = \sqrt{[\{\Sigma(X_i - \overline{X})^2\}/(n-1)]}$ [7, 8, 9, 10, 11].

Calculations (Table 2) showed the standard deviation σ_s was 15.51, 18.75 and 15.34 for Zn II, Cu II and Pb II respectively., $t_{observed}$ was 1.58, -9.71 and -2.88 for respectively, whereas the t_{tab} = 1.796 for 1-tailed t-test for 11 degrees of freedom [12]. $t_{observed} < t_{tabulated}$ indicated that the observed values of t lie within the accepted region of the probability chart. Hence, the null hypothesis was accepted.

3. Hypothesis testing to test the equality of variance of two n-populations was done with F-test.

H_o: μ_{Ho} = Variances of two populations of different concentrations (100 mg/L and 50 mg/L) of Zn II, Cu II and Pb II are same i.e. $\sigma_{p1}^2 = \sigma_{p2}^2$

H_a: $\sigma_{p1}^2 \neq \sigma_{p2}^2$

For F-test, F = $(\sigma_{s1}^2 / \sigma_{s2}^2)$ or $(\sigma_{s2}^2 / \sigma_{s1}^2)$ = $F_{observed}$, F is always taken > 1.

Table 3: F- distribution

Sample 1: 100 mg/L

		Zinc			Copper			Lead		
n	**pH**	**X_{i1}**	**$X_{i1} - \overline{X}_1$**	**μH_o**	**X_{i1}**	**$X_{i1} - \overline{X}_1$**	**μH_o**	**X_{i1}**	**$X_{i1} - \overline{X}_1$**	**μH_o**
1	2	15	-39.14	75	32	-31.43	86	23	-35.00	79
2	3	30	-24.14	75	45	18.43	86	45	-13.00	79
3	4	63	8.86	75	65	1.57	86	68	10.00	79
4	5	75	20.86	75	86	22.57	86	79	21.00	79
5	6	72	17.86	75	80	16.57	86	72	14.00	79
6	7	67	12.86	75	72	8.57	86	63	5.00	79
7	8	57	2.86	75	64	0.57	86	56	-2.00	79
$\overline{X}$		54.14			63.43			58.00		
σ_{s1}^2		520.14			364.62			360.00		

Sample 2: 50 mg/L

		Zinc			Copper			Lead		
n	**pH**	**X_{i2}**	**$X_{i2} - \overline{X}_2$**	**μH_o**	**X_{i2}**	**$X_{i2} - \overline{X}_2$**	**μH_o**	**X_{i2}**	**$X_{i2} - \overline{X}_2$**	**μH_o**
1	2	24	-36.71	75	38	-30.00	86	29	-34.86	79
2	3	42	-18.71	75	49	-19.00	86	51	12.86	79
3	4	69	8.28	75	72	4.00	86	74	10.14	79
4	5	82	21.28	75	89	21.00	86	84	20.14	79
5	6	76	15.28	75	83	15.00	86	78	14.14	79
6	7	70	9.28	75	75	7.00	86	66	2.14	79
7	8	62	1.28	75	70	2.00	86	65	1.14	79
$\overline{X}$		60.71			68.00			63.86		
σ_{s2}^2		423.57			332.67			349.14		
F_{obs}		1.23			1.20			1.06		
F_{tab}		4.28			4.28			4.28		

Xi = % removal of metal ions from the contaminated samples and Degrees of freedom = d.f. = n-1

Average value of X = $\overline{X} = \Sigma X_i/n$ and Standard deviation = $\sigma_s = \sqrt{[\{\Sigma(X_i - \overline{X})^2\}/(n-1)]}$. [7, 8, 9, 10, 11].

Calculations (Table 3) showed that the variances σ_{s1}^2 and σ_{s2}^2 are 520.14 & 423.57 for Zn II, 364.62 & 332.67 for Cu II and 360 & 349.14 for Pb II. $F_{observed}$ was 1.23, 1.20 and 1.06 for Zn II, Cu II and Pb II respectively. Whereas $F_{tabulated}$ = 4.28 [12]. $F_{observed} < F_{tabulated}$ indicated that the observed values of F lie within the accepted region of the probability chart. Hence for all the three ions, the null hypothesis, was accepted.

4. Hypothesis testing to test the effectiveness of the experiment in removing heavy metal ions was done with χ^2-test.

Experiments were conducted for values of pH varying from 2 to 8, metal ion concentration in the range 10 to 100 mg/L and adsorbent dose 1 to 10 g/L. Metal ion removal frequencies were observed for % removal between groups 0-20% (1), 20-40% (2), 40-60% (3), 60-80% (4) and 80-100% (5) for zinc, copper and lead ions. Since the observed frequencies in groups 1 and 5 i.e. % removal in the range 0-

20% and 80-100% were less than 10, they were combined with groups 2 and 4 respectively to make the frequencies greater than 10. The values of expected frequencies for each group were equal and 12 each.

H_o: μ_{Ho} = Adsorption is an effective technique for removal of Zn II, Cu II and Pb II

H_a: Adsorption is not an effective technique for removal of Zn II, Cu II and Pb II For chi-square test

$\chi^2 = \Sigma\{(O_i - E_i)^2/E_i\}$, [7, 8, 9, 10, 11].

O_i = Observed frequencies of metal ion removal in the i^{th} row.

E_i = Expected frequencies of metal ion removal in the i^{th} row.

Table 4: Chi Square distribution to test the effectiveness of the experiment

S. No.	Groups		Zinc	Copper	Lead	Rearranging groups to make frequencies > 10		Zinc	Copper	Lead
n	**% removal**	**E_i**	**O_i**	**O_i**	**O_i**	**n**	**E_i**	**O_i**	**O_i**	**O_i**
1	0-20%	12	4	7	3	1&2	24	19	19	16
2	20-40%	12	15	12	13	3	12	18	22	17
3	40-60%	12	18	22	17	4&5	24	23	19	27
4	60-80%	12	17	16	18					
5	80-100%	12	6	3	9					
	d.f.							4	4	4
	χ^2_{obs}							3.583	2.417	8.625
	χ^2_{tab}							9.488	9.488	9.488

Calculations (Table 4) showed that $\chi 2_{observed}$ = 3.58, 2.42 and 8.625 for Zn II, Cu II and Pb II respectively. Whereas $\chi^2_{tabulated}$ is 9.488 [12]. $\chi^2_{observed} < \chi^2_{tabulated}$ indicated that the observed values of χ^2 lie within the accepted region of the probability chart. Hence null hypothesis was accepted.

5. **Analysis of variance (ANOVA)** we compared adsorption capacities of mango tree leaves for three different heavy metal ions for varying values of adsorbent dose (Table 5).

Table 5: Anova
Here samples are % removal from 100 ppm solutions of Zn II, Cu II and Pb II

n	Adsorbent dose, g/L	% removal from 100 ppm concentration		
		Cu	**Zn**	**Pb**
1	2	20	25	22
2	4	40	40	42
3	6	58	64	56
4	8	72	75	71
5	10	90	87	85
Sum		280	291	276
Mean ā		56	58.2	55.2

n	% removal For Cu (a_1)	$(a_1 - \bar{a}_1)^2$	% removal For Zn (a_2)	$(a_2 - \bar{a}_2)^2$	% removal For Pb (a_3)	$(a_3 - \bar{a}_3)^2$
1	20	1296	25	1102.24	22	1102.24
2	40	256	40	331.24	42	174.25
3	58	4	64	33.64	56	0.64
4	72	256	75	282.24	71	249.64
5	90	1156	87	829.44	85	888.04
Sum	280	2968	291	2578.8	276	2414.8
Mean ā	56		58.2		55.2	

Sum of squares within (SSW) = $(a_1 - \bar{a}_1)^2 + (a_2 - \bar{a}_2)^2 + (a_3 - \bar{a}_3)^2$ = 7961.6

n	Total observations a_i	$(a_i - \bar{a}_i)^2$
1	20	1329.82
2	40	271.15
3	58	2.35
4	72	241.28
5	90	1124.48
6	25	999.15
7	40	271.15
8	64	56.75
9	75	343.48
10	87	932.28
11	22	1187.95
12	42	209.28
13	56	0.22
14	71	211.22
15	85	814.15
Sum	847	7985.73
Mean $\bar{a}_i$	56.47	

Mean of sample means $\bar{\bar{a}} = (\bar{a}_1 + \bar{a}_2 + \bar{a}_3)/3 = 56.47$ and Sum of squares within (SSW) = 7961.6

Sum of squares total (SST) = 7985.73 and Sum of squares between (SSB) = 24.13

Degrees of freedom: d.f for SSB = 2, d.f. for SSW = 12

MS between = SSB / d.f for SSB = 12.07 and MS within = SSW / d.f for SSW = 663.47

F_{cal} = MS between/ MS within = 0.018 and $F_{tab} = 19.41$

$F_{tab} < F_{cal}$, Null hypothesis i.e. the mean of samples from 3 different populations are same is accepted.

H_o= Samples are drawn from three populations having the same mean

H_a= Samples are drawn from three populations which do not have same mean

F-ratio (Eq. 5) calculated $F_{observed} = 0.018$ and tabulated $F_{tabulated} = 19.41$ for (2, 12) degrees of freedom [13, 14]. Since $F_{observed} < F_{tabulated}$, null hypothesis was accepted.

Conclusions and Recommendations

In the above study, the experimental data was obtained for the removal of Zn II, Cu II and Pb II ions from the contaminated water samples. The null hypotheses were defined and experimental data was tested at 5% level of significance each. Calculated values of z, t-test, χ^2–test, F-test and ANOVA were compared with tabulated values available in literature and were found to be within accepted regions of the probability charts. Hence the null hypotheses were accepted, validating the experimental data statistically. Paired t-test to compare two related samples, statistical tests for correlation coefficients and adsorption isotherm are recommended for future studies.

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