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STATISTICAL ANALYSIS OF THE RESULTS OF CHILLING OF SEA BITTERN

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Statistical analysis of the data, collected during earlier studies [1] carried out on various scales of operations with respect to chilling of sea bittern has been undertaken making use of statistical parameters [2,3,4] pertaining to measures of central tendency, measures of dispersion, limits of reliablity, tests of significance and regression analysis. It has been demonstrated by the analysis that i) data in different instances are almost normally distributed, (ii) the systematic error for all practical purposes is absent and (iii) the error allowance is tenable. Previously drawn conclusions [1] concerning the performance of the chiller(s) are confirmed and also substantiated by the tests of significance. The relationships derived earlier from the graphs regarding 25 litre chiller are in complete conformity with those obtained by regression analysis. The calculated values are close to the observed data and the difference is within the permissible limits of standard errors.

Key words: Chilling study, Sea bittern, Statistical analysis.

Introduction

The present paper concerns the application of statistics to our previous work [1]. Studies were undertaken on the recovery of magnesium sulphate by chilling sea bittern. Data were collected on variables such as design and capacity of chiller, cooling temperature, and concentration of magnesium sulphate in solution. Other parameters studied were: density of sea bittern, time of chilling, and effect of heating bittern (prior to chilling) on the recovery of magnesium sulphate. The main objective is to analyse and evaluate the conclusions and relationships derived previously, with the applications of basic statistical methods.

Material and Methods

Chilling of aliquot amount of raw material (initial solution) of known composition of normal or heated sea bittern, was carried out in two sizes of chillers differing in design of cooling systems. The first one was a 25 litre capacity unit in which cooling was effected through jacket using Freon-11 gas and the second one, a 400 litre capacity chiller, wherein cooling was arranged through coils using Freon-22 gas. The chillers were fitted with suitably designed stirring system to enhance the rate of heat transfer and to homogenise the composition of contents. Samples were collected during chilling at definite time intervals and the corresponding temperatures recorded; collected samples were immediately filtered and analysed. At the end of each experiment the chilled slurry was withdrawn, filtered and the filtrate (final solution) was also analysed. Thus data (kinetics) concerning concentrations of magnesium sulphate in solutions and corresponding temperatures were collected and analysed statistically.

The composition of raw material (sea bittern) is sensitive to host of conditions [5] and it is impossible to obtain analytically identical samples on different occasions. Amongst various factors affecting the composition of sea bittern, temperature has dominating effect. During summer season, bittern is marked by high magnesium sulphate content, whereas in peak winter it is characterized by low magnesium sulphate content [7]. Hence in winter seasons, prior to chilling, the raw material was first heated to fixed high temperature (110–114°) and designated as "heated bittern" which in turn was instrumental in investigating the effect of heating on the recovery of magnesium sulphate. For the ease of representation, the type of raw material and capacities have been designated into Blocks *viz* (I) Block A: 25 litre experiments with normal bittern; (II) Block B: 25 litres experiments with heated bittern; and (III) Block C: 400 litre experiments with normal bittern.

As far the methods of estimating the statistical quantities, suitable relationships [6] have been used for the tests of significance, and standard errors with regard to intercept and slope etc. Regression analyses of the data and other statistical parameters have been calculated using Casio Fx 7200-G, calculator.

Results and Discussion

Initial and final concentrations of the data of different sets of experiments concerning magnesium sulphate in solution alongwith its percent recovery and simple statistical parameters are listed in Table 1. The observed data with respect to the concentration of magnesium sulphate and its recovery (theoretical) as a function of temperature have been reported elsewhere [1], whereas the corresponding values of the variables (concentration and recovery) calculated from regression results and the percentage errors are not presented for the sake of brevity. The results of the tests of significance (F and T-tests) are listed in Tables 2-a and 2-b. Summarized results of graphical solutions and regression analysis for respective cases are recorded in Table-3.

and also demonstrate tenability of the error allowance. In the operation of low temperature crystallization of magnesium sulphate from sea bittern, residual concentration of magnesium sulphate in solution, and corresponding temperature

TABLE 1. CONCENTRATIONS AND RECOVERIES OF MAGNESIUM SULPHATE, AND STATISTICAL DATA.

Blocks	A			B			C		
	%$MgSO_4$ in solution		%	%$MgSO_4$ in solution		%	%$MgSO_4$ in solution		%
Expt. No.	Initial	Final	Recovery	Initial	Final	Recovery	Initial	Final	Recovery
1	6.25	3.08	50.72	7.85	3.37	57.07	8.02	4.75	40.77
2	6.14	2.90	52.77	7.82	3.25	58.44	8.03	5.41	32.53
3	6.32	2.88	54.43	8.18	3.16	61.37	8.03	5.31	38.87
4	6.28	3.01	52.07	8.06	3.01	62.66	8.02	5.18	35.41
5	5.29	2.76	47.83	7.69	3.01	60.86	8.02	5.35	33.29
6	5.65	2.73	51.68	7.75	3.20	58.71	7.88	5.16	34.56
7	5.54	2.77	50.00	–	–	–	8.00	5.00	37.50
8	6.01	3.10	48.42	–	–	–	–	–	–
Statistical parameters:									
Number of trials (n)	8	8	8	6	6	6	7	7	7
Degress of freedom(d.f)	7	7	7	5	5	5	6	6	6
Measure of central tendency:									
Average (X)	5.94	2.90	50.99	7.89	3.17	59.85	8.00	5.17	36.13
Median (Md)	6.08	2.89	51.20	7.84	3.18	59.78	8.02	5.18	35.41
Measure of dispersion:									
Range (R)	1.03	0.37	6.47	0.49	0.36	8.18	0.15	0.66	8.24
Standard deviation(S)	0.39	0.1465	2.2133	0.189	0.1403	2.109	0.054	0.23	3.03
Variance $(S)^2$	0.1525	0.0215	4.898	0.0358	0.0197	4.449	0.0029	0.0525	9.154
Coeff. of Variation	6.58	5.04	4.34	2.40	4.43	3.52	0.673	4.44	8.37
Limits of reliability:									
Limits of standard deviation or symmetric confidence interval:									
(X + 2S)	6.72	3.20	55.42	8.27	3.45	64.07	8.11	5.62	42.18
(X - 2S)	5.15	2.61	46.56	7.51	2.89	55.63	7.89	4.71	30.08
Limits of standard error of mean:									
(X + tS/ n)	6.26	3.03	52.84	8.09	3.31	62.07	8.05	5.38	38.93
(X - tS/ n)	5.61	2.78	49.14	7.69	3.02	57.64	7.95	4.95	33.33

TABLE 2A. 't' TEST (WITHIN BLOCKS).

Block		Calculated	Critical	d.f.	Difference
A	t	20.613	2.262	9*	Sigft.
B	t	49.176	2.228	11*	Sigft.
C	t	31.81	2.365	7	Sigft.

Mean value of the set of data alone does not convey much sense but its closeness with the value of the median signifies that the data is normally distributed. The values of measures of dispersion of initial solutions only inform regarding the extent of variations in the compositions of the raw material. On the other hand, the values of the parameters concerning final solutions and recoveries in different blocks indicate the erratic performance or otherwise of equipment. The limits of reliability, apart from enlightening the type of distribution, may also be indicative of the absence or presence of systematic errors

follow a definite relationship. Hence during chilling, magnesium sulphate in solution decreases whereas the values of the other statistical terms (pertaining to initial solution in a set of experiments) may increase or decrease depending on the efficiency and performance of the equipment. Thus decrease in concentration would provide a fair measure of the efficiency of the equipment within block; for other terms relating to measure of dispersion, increase in their values shall be indicative of erratic performance whereas decrease of the smooth one. It was rational to calculate percent changes in the values of the parameters (based on initial solution) to obtain necessary guideline concerning the performance of the equipment. The blockwise ratios of the changes (Table 4a) might be called a hypothetical situation wherein the values of measures of dispersions with regard to block A were unit and assumed to remain unchanged during processing. In addition, the blockwise ratios of the parameters concerning corresponding streams are listed in Table 4b. The data provided some quantitative idea regarding relative performance of the respective equipment.

F-Test was not feasible in case of within blocks, however, it was employed to compare data of two sets of experiments between blocks. The t-test helped to evaluate any significant difference in the mean concentrations of magnesium sulphate (or recoveries) of the corresponding streams. Of the two types of t-test, pooled t-test was generally employed, whereas paired t-test was preferred to evaluate any significant change in the

TABLE 2B. 't' AND F' TESTS (BETWEEN BLOCKS).

Types of stream		A and B				A and C			
		Calculated	*Critical	d.f.	Diffference	Calculated	*Critical	d.f.	Difference
Initial solutions	°F	4.259	4.876	-(7,5)	Insigft.	52.586	4.207	-(7,6)	Sigft.
	t	12.32	2.179	12 *	Sigft.	*14.76	2.998	-(7)	Sigft.
Final solutions	°F	1.091	4.876	-(7,5)	Insigft.	2.442	3.866	-(6,7)	Insigft.
	t	3.494	2.160	-(13)*	Sigft.	17.931	2.447	-(6)	
Recoveries:	°F	1.01	4.876	-(7,5)	Insigft.	1.866	3.866	-(6,7)	Insigft.
	t	7.615	2.160	-(13)*	Sigft.	*12.087	2.447	-(6)	Sigft.

*Paired t-test, °Two tailed F-test, *Degree of freedom calculated by appropriate relationships (6,8)

TABLE 3. SUMMARISED GRAPHICAL AND REGRESSION ANALYSES.

S. Blocks	A		B		C	
No. parameters	From graph	By regression	From graph	By regression	From graph	By regression
I – % Magnesium sulphate in solution vs. temperature (°C)						
		Actual ± (S.E.)		Actual ± (S.E.)		
1. Intercept (C)	1.6	1.573 ± 0.171	1.15	1.1645 ± 0.2224	1.75	2.50
2. Slope (m)	0.318	0.314 ± 0.018	0.413	0.4148 ± 0.0231	0.342	0.2903
3. Coefficient of Correlation (r)		0.985	–	0.992	–	0.89
Temp. (°C) at which The $MgSO_4$ insolution would be zero:	-5	-5	-2.78	-2.8	-5.1	-8.6
II – Recoveries of magnesium sulphate vs temperature						
1. Intercept:						
D	74.5	74.34 ± 4.65			–	–
E	75.0	71.73 ± 2.34			–	–
F			86.5	84.52 ± 0.65	–	–
2. Slope D	-5.46	-5.07 ± 0.51	–	– –	–	–
E	-4.9	-5.64± 0.271	–	– –	–	–
F	–	– –	-5.14	-5.08 ± 0.078	–	–
3. Coefficient of Correlation(r)						
D	0.98	– –	–	– –	–	–
E	0.997	– –	–	– –	–	–
F	0.997	– –	-0.99	– –	–	–
4. Temp.(°C) at which recovery of $MgSO_4$ would be 100%						
D	-4.67	-5.1	–	– –	–	–
E	-5.1	-5.4	–	– –	–	–
F	–	–	-2.8	-3.0	–	–

S.E.: Standard error, D and E refer to different set of lines obtained in block A, F refers to the line in Block B

TABLE 4A. CHANGES IN STATISTICAL PARAMETERS AS A RESULTS OF PROCESSING

	Blocks			Blockwise ratios of the changes		
	A	B	C	A	B	C
Decrease in mean Concentration	3.04	4.72	2.83	1 :	1.553 :	0.931
% Increase or decrease in values of the parameters (expressed as % of initial solution)						
1. Range	35.9	73.47	440	1 :	2.046 :	12.26
2. Standard deviation	37.56	74.31	425.9	1 :	1.976 :	11.34
3. Coefficient	76.6	184.6	662.7	1 :	2.41 :	8.65

caused marked improvement in the recovery.

Regression analysis. The results of graphical solutions provided guidelines for the selection of data for regression analysis. In all the instances the regression analysis was confined to linear portions only. Regression analysis of the percent recovery versus temperature graph (400 litre experiments) was dropped because of it being a curve. In case of 25 litre normal bittern, two separate lines were obtained on the basis of their composition ranges [1]. Accordingly, regression analysis in that instance was carried out for each of the two sets separately.

Examination of Table 3 showed a close agreement between the corresponding values of regression results and

TABLE 4B. BLOCKWISE RATIOS OF THE PARAMETERS FOR CORRESPONDING STREAMS.

Streams	Initial solutions			Final solution			Recoveries		
	A	B	C	A	B	C	A	B	C
1. Range	1 :	0.476 :	0.146	1 :	0.973 :	1.784	1 :	1.264 :	1.274
2. Standard Deviation	1 :	0.438 :	0.138	1 :	0.958 :	1.57	1 :	0.953 :	1.369
3. Coefficient of variation	1 :	0.365 :	0.102	1 :	0.879 :	0.881	1 :	1.021 :	1.929

mean concentration and recovery of magnesium sulphate due to the change in equipment design. Detailed examination of Tables 1 and Table 4 (a and b) revealed the following:

The observed data of respective blocks were found to be almost normally distributed because (i) values of means were close to the corresponding values of medians in all the instances and (ii) data in different instances occurred within the limits of standard deviations ($x \pm 2S$). Systematic errors were considered to be absent because the values of the limits of standard errors of means for 95% confidence level were within the range of observed data, which also signified that the error allowance was tenable in these instances. The data further suggested that 25 litre chiller was more efficient and that heating improved the recovery which, nevertheless, was associated with increased erratic performance. The performance of 400 litre chiller was indicated to be comparatively inefficient and erratic.

The calculated and critical values [6,8] of F-test between blocks (Table 2b), suggested insignificant difference in the variances of 25 and 400 litre chillers which was in contravention with the observation, and previous conclusions. Under the circumstances, however, there was no evident reason to reject previously drawn conclusions on the basis of the results of F-test alone. The calculated and critical values [6,8] of t-tests (Tables 2a and 2b) showed statistically significant difference in the magnesium sulphate content in different streams of both the instances of within and between blocks. In addition, the results of between blocks also indicated that the performance of 25 litre chiller was more smooth and efficient and heating graphical solutions of block A and B (25 litre chiller). Nevertheless, there was a significant difference in the graphical and regressions results of block C (400 litre chiller). This again substantiated the previously drawn conclusion concerning the performance of the chillers. The predicted temperature at which the concentration of magnesium sulphate in solution would reduce to zero or recovery of magnesium sulphate would be 100%, was found to agree closely by both the graphical solutions and the regression results. The calculated values from regression data (excepting few outliers) were within an average of ± 4% of the observed data for concentration vs temperature lines.

Conclusion

It could be established from the foregoing that the data in different instances were normally distributed, the systematic error was absent and error allowance was tenable. The appropriate application of the simple statistical parameters confirmed that the performance of 25 litre chiller (cooling effected through jacket) was efficient and smooth and that of 400 litre chiller (cooling arranged through coils) was inefficient and erratic. This was further substantiated by the tests of significance. It was also confirmed that the recovery of magnesium sulphate was markedly improved by heating the sea bittern to a fixed temperature prior to chilling. Regression results for 25 litre chiller demonstrated close agreement with graphical ones. Calculated values were within an average of ±4% of the observed data for concentration vs temperature lines. The gap of observed and calculated values was higher for recovery vs temperature lines. However, it was not of much concern because the graphical and regression results were agreeing within the limit to standard errors. The validity of the regression results (25 litre chiller) was not only established by the above conclusions but was also substantiated by the high values of correlation coefficients.

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