Error Analysis for Modeling of Multi Solute Effluent Adsorption Studies for Treatment of Kale Acid

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Abstract: Waste Water Treatment is the most concerned issue as the chemical industries are progressing over the years, as it has three adverse effects, namely, loss of material, degradation of the fresh source of water and environmental issues. Despite being researched over so many years, wastewater treatment is still a hot research topic as it incurs a lot of money and energy. This paper presents a comparison of single solute and multi solute streams and the kinetic modeling studies and adsorption isotherms modeling. The Langmuir equation and Freundlich equation were used to model adsorption and the reaction kinetics were identified. The experimental data was fitted to models and respective error analysis was performed using five standard equations. The study is made on Kale Acid Effluent but can be applied to other systems also. The results show better COD reduction and easier wastewater treatment method.

Keywords —Adsorption Isotherm, Error analysis, Freundlich, Kinetic Model, Langmuir, Rathi Puranik, Wastewater Treatment

I. INTRODUCTION

As a rule, an adsorption isotherm is a priceless curve depicting the phenomenon representing the retention (or release) or mobility of a substance from the fluid permeable media or aquatic environments to a solid-phase at a constant temperature and pH [1],[2]. Adsorption equilibrium (the ratio between the adsorbed amount with the remaining in the solution) is established when an adsorbate containing phase has been contacted with the adsorbent for sufficient time, with its adsorbate concentration in the bulk solution is in a dynamic balance with the interface concentration [3]. Ordinarily, the scientific relationship, which constitutes a vital part towards the demonstrating investigation, operational outline and material routine with regards to the adsorption frameworks, is normally portrayed by graphically communicating the solid-phase against its residual concentration [4].

Over the years, a wide variety of equilibrium isotherm models (Langmuir, Freundlich, Brunauer–Emmett–Teller, Redlich– Peterson, Dubinin–Radushkevich, Temkin, Toth, Koble–Corrigan, Sips, Khan, Hill, Flory–Huggins and Radke–Prausnitz isotherm), have been formulated in terms of three fundamental approaches [5]. Kinetic consideration is the first approach to be referred. Hereby, adsorption equilibrium is defined being a state of dynamic equilibrium, with both adsorption and desorption rates are equal [6]. Whereas, thermodynamics, being a base of the second approach, can provide a framework of deriving numerous forms of adsorption isotherm models, and potential theory, as the third approach, usually conveys the main idea in the generation of characteristic curve. However, an interesting trend in the isotherm modeling is the derivation in more than one approach, thus directing to the difference in the physical interpretation of the model parameters.[5], [7]

II. ADSORPTION KINETICS MODELING

In order to analyze the adsorption kinetics of Kale Acid Effluent the pseudo-first order (equation 1.) predicted by Lagergren model [8], time dependent method for COD reduction for kinetic study [9] (equation 2.) predicted by Rathi Puranik model and intra-particle diffusion [10] (equation 3.) predicted by Weber Morris model ae frequently used by various researchers to predict the adsorption kinetics.

$$ln(C_t - C_e) = ln\,C_e - (m * t) \qquad (1)$$

$$ln(CODRT) = ln\left(\frac{C_t - C_e}{t}\right) \qquad (2)$$

$$\left(\frac{C_t - C}{C_t}\right) = (m * t^{0.5}) + ln\,C_e \qquad (3)$$

Here C_t is the amount of adsorbate adsorbed at time t (mg g^{-1}), C_e is the adsorption capacity in the equilibrium (mg g^{-1}), m is the pseudo-first-order rate constant (min^{-1}), and t is the contact time (min). The wastewater samples from Kale Acid manufacturing plant were collected and analysed for COD reduction using activated carbon as adsorbent for batch adsorption studies for single solute streams as well as mixed solute streams for time of 2 hours at ambient room temperature of around 30°C.

III. RESULTS AND DISCUSSION

In today's era linear regression analysis is one of the most popular and inevitable tool which is commonly applied for analysis of experimental data obtained from adsorption process. It is used to justify the best fitted relationship that quantify the distribution of adsorbate and

also helps in the verification of the consistency of adsorption models and the theoretical derivations of the adsorption models. [5]

Various methods chosen for error analysis are mentioned below:

A.   Error functions

Sum square error (ERRSQ)

$$ERRSQ = \sum_{i=1}^{n}\left(q_{e,cal} - q_{e,exp}\right)^2_i \qquad (4)$$

It is the sum of the squared differences between each observation and its group's mean. It can be used as a measure of variation within a data set. If all cases within the data are identical the ERRSQ would then be equal to 0. The effect of concentration ranges on error analysis using ERRSQ has been discussed elsewhere. [3], [5], [11]

Average relative error (ARE)

$$ARE = \frac{100}{n}\sum_{i=1}^{n}\left|\frac{\left(q_{e,cal} - q_{e,exp}\right)}{q_{e,exp}}\right|_i \qquad (5)$$

This error function attempts to minimize the fractional error distribution across the entire concentration range. [5], [12]

Hybrid fractional error function (HYBRID)

$$HYBRID = \frac{100}{n-p}\sum_{i=1}^{n}\left[\frac{\left(q_{e,cal} - q_{e,exp}\right)}{q_{e,exp}}\right]_i \qquad (6)$$

This error function improves the fit of the ARE method at low concentration values. Instead of n as used in ARE ARE the sum of the fractional errors is divided by (n-p) where p is the number of parameters in the isotherm equation. [5], [13]

Sum of absolute errors (EABS)

$$EABS = \sum_{i=1}^{n}\left|q_{e,cal} - q_{e,exp}\right|_i \qquad (7)$$

The isotherm parameters determined by this method provide a better fit as the magnitude of the errors increase, biasing the fit towards the high concentration data. [5], [14]

Coefficient of determination (R^2)

$$R^2 = \left\{\left(\frac{1}{n}\right) \times \sum_{i=1}^{n}\frac{\left[(q_{e,meas} - q_{e,mean}) \times (q_{e,cal} - q_{e,mean})\right]}{(\sigma_{meas} \times \sigma_{cal})}\right\}^2 \qquad (8)$$

The coefficient of determination is a key output of regression analysis. It is interpreted as the proportion of the variance in the dependent variable that is predictable from the independent variable.[5], [15]

Standard deviation of relative errors ($S_{RE} S_{RE}$)

$$S_{RE} = \frac{100 \times \sigma}{\left|q_{e,mean}\right|} \qquad (9)$$

It tells whether the "regular" standard deviation is a small or large quantity when compared to the mean for the data set. [5], [16]

Nonlinear chi-square test ($\chi^2 \chi^2$)

$$\chi^2 = \sum_{i=1}^{n}\left(\frac{q_{e,meas} - q_{e,cal}}{\sigma_i}\right)^2 \qquad (10)$$

Chi-square calculations are used to compare observed and expected values. Usually, these calculations are used in the context of categorical outcomes, to compare observed and expected distribution of subjects among the categories.[5]

The methodology for calculation has been mentioned in previous literature. [5]

For the Weber – Morris Method, Hybrid Fractional Error, Average Relative Error and Non Linear Chi Square Tests are not applicable as certain measured values of $q_{e,exp}$ tends to be zero, resulting in an undefined value.

The table 1 shows the change in concentration in the Streams and Mixed Streams with completion time as well as half time, along with their fitted data in the models as discussed above. Table 2 shows the deviation in the results obtained from experimental values as well as fitted data. These errors have been discussed above and justify the result. Table 3 and 4 and Fig 2 and 3, shows the fitted result for Rathi-Puranik Model and Weber Morris Model respectively. Similarly, Fig 1 shows the fitted result for Lagergren model.

Sr. No.	C_i	t	$t_{\frac{1}{2}}$	C	$\log(C-C_{eq})$ (1)	$\log CODrt = \log\frac{C-C_i}{t}$ (2)	$\frac{c-c_i}{c_i}$ (3)
Stream – 1 $C_i = 12240, C_{eq} = 4500$							
1	12240	0	0.00	12240.00	3.888741	-----	0.00
2	12240	30	5.48	5263.20	2.882638	2.366535	0.57
3	12240	60	7.75	5018.40	2.714665	2.080482	0.59
4	12240	90	9.49	4773.60	2.437116	1.918869	0.61
5	12240	120	10.95	4528.80	1.459392	1.807941	0.63
Stream – 2 $C_i = 5672, C_{eq} = 2150$							
1	5672	0	0.00	5672.00	3.546789	--------	0.00
2	5672	30	5.48	2779.28	2.798844	1.984185	0.51
3	5672	60	7.75	2665.84	2.712515	1.699861	0.53
4	5672	90	9.49	2438.96	2.460838	1.555369	0.57
5	5672	120	10.95	2212.08	1.792952	1.459885	0.61
Stream – 3 $C_i = 2496, C_{eq} = 1120$							
1	2496	0	0.00	2496.00	3.138618	--------	0.00
2	2496	30	5.48	1422.72	2.481041	1.553592	0.43
3	2496	60	7.75	1272.96	2.184578	1.309289	0.49
4	2496	90	9.49	1223.04	2.013006	1.150572	0.51
5	2496	120	10.95	1148.16	1.449633	1.050457	0.54
Mixed Stream – 1 $C_i = 6263.12, C_{eq} = 2150$							
1	6263.12	0	0.00	6263.12	3.614171	'----------	0.00
2	6263.12	30	5.48	2576.32	2.629736	2.089528	0.59
3	6263.12	60	7.75	2406.16	2.408511	1.808094	0.62
4	6263.12	90	9.49	2349.44	2.299812	1.638343	0.62
5	6263.12	120	10.95	2179.28	1.466571	1.531887	0.65
Mixed Stream – 2 $C_i = 4454.902, C_{eq} = 1750$							
1	4454.902	0	0.00	4454.90	3.432152	--------	0.00
2	4454.902	30	5.48	2361.10	2.786111	1.843815	0.47
3	4454.902	60	7.75	2138.35	2.589227	1.586690	0.52
4	4454.902	90	9.49	2004.71	2.406039	1.434958	0.55
5	4454.902	120	10.95	1781.96	1.504620	1.347808	0.60

Table 1: Experimental Data Modeling

Stream	Value	EERSQ Sum Square Errors	HYBRID Hybrid Fractional Error	ARE Average Relative Error	EABS Sum Of Absolute Error	R² Coefficient Of Determination	σ_{RE} Standard Deviation Of Relative Errors	χ^2 Non Linear Chi Square Test
Stream -1 Fitting	33.8267	1.1950	-6.0412	3.0206	1.8130	4.5282	0.3698	0.3973
Stream -2 Fitting	36.7409	0.8064	-5.3998	2.6999	1.5648	4.9183	0.3297	0.2795
Stream -3 Fitting	31.0678	2.3149	-11.0252	5.5126	2.8958	4.1589	0.4786	0.8889
Mixed Stream -1 Fitting	36.7409	1.1039	-6.7885	3.3943	1.9248	4.9183	0.3680	0.3910
Mixed Stream -2 Fitting	36.7409	1.1039	-6.7885	3.3943	1.9248	4.9183	0.3680	0.3910

Table 2: Data Analysis for Lagergren Model Fitting

Stream	Value	EERSQ Sum Square Errors	HYBRID Hybrid Fractional Error	ARE Average Relative Error	EABS Sum Of Absolute Error	R² Coefficient Of Determination	σ_{RE} Standard Deviation Of Relative Errors	χ^2 Non Linear Chi Square Test
Stream -1 Fitting	11.3770	0.0114	0.6289	0.7115	0.1888	4.7027	0.0255	0.0069
Stream -2 Fitting	16.8796	1.1927	-13.4970	6.7485	2.1762	6.9772	0.2954	0.5936
Stream -3 Fitting	16.8796	1.2260	-13.6905	6.8453	2.2062	6.9772	0.2993	0.6108
Mixed Stream -1 Fitting	16.8796	1.0649	-12.7230	6.3615	2.0562	6.9772	0.2799	0.5277
Mixed Stream -2 Fitting	16.8796	1.0960	-12.9165	6.4583	2.0862	6.9772	0.2837	0.5438

Table 3: Data Analysis for Rathi - Puranik Model Fitting

Stream	Value	EERSQ Sum Square Errors	EABS Sum Of Absolute Error	R² Coefficient Of Determination	σ_{RE} Standard Deviation Of Relative Errors
Stream -1 Fitting	0.8659	0.097696	0.52856	2.837546	0.079491
Stream -2 Fitting	1.0451	0.060979	0.45296	3.424783	0.071125
Stream -3 Fitting	1.0451	0.039158	0.3443	3.424783	0.045738
Mixed Stream -1 Fitting	1.0451	0.106479	0.54704	3.424783	0.09257
Mixed Stream -2 Fitting	1.0451	0.044251	0.39416	3.424783	0.060377

Table 4: Data Analysis for Weber Morris Model Fitting
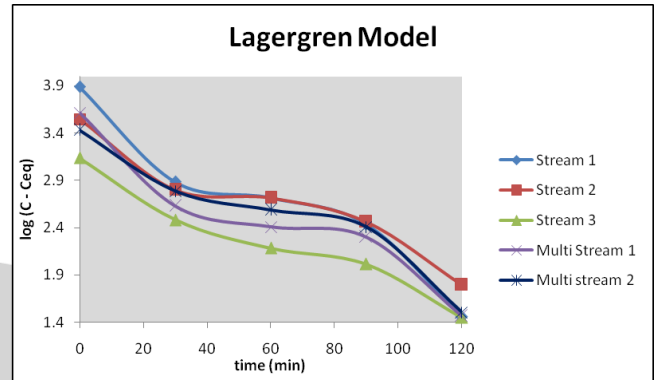

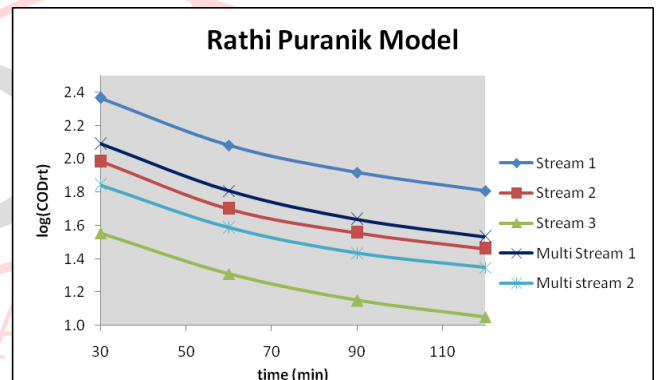Figure 1: Values obtained from fitting data into Lagergren Model

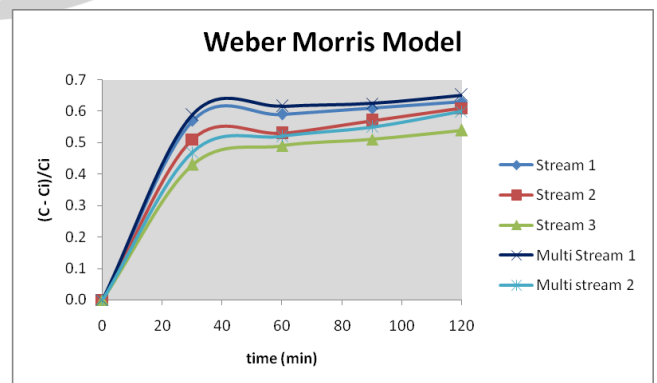Figure 2: Values obtained from fitting data into Rathi Puranik Model

Figure 3: Values obtained from fitting data into Weber Morris Model

IV. CONCLUSION

This paper presents a comparison of single solute and multi solute streams and the kinetic modeling studies and adsorption isotherms modeling. The Langmuir equation and

Freundlich equation were used to model adsorption and the reaction kinetics were identified using Weber Morris, Lagergren and Rathi Puranik model. The experimental data was fitted to models and respective error analysis was performed using five standard equations. The higher value of coefficient of Determination predicted by Rathi Puranik model clearly indicates the better form of kinetic study predicted than by Weber Morris and Lagergren model. The non linear chi squared test also shows a better prediction for Rathi Puranik model over Lagergren model fitting. The study is made on Kale Acid Effluent but can be applied to other systems also.

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