Modeling of Multi Solute Effluent Adsorption Studies for Treatment of K Acid

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Abstract: Wastewater 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. Till date, no single method has been identified which can alter either in better water treatment or save energy or money. This paper presents a comparison of single solute and multi solute streams and the kinetic modelling studies and adsorption isotherms modelling. The Langmuir equation and Freundlich equation were used to model adsorption and the reaction kinetics were identified. 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.

I. INTRODUCTION

Dyes have played a vital role in modernization of textile industry, depending on the material of cloth used as well as texture and colour to be imparted on it; several types of dyes have been formulated and are produced commercially. Dyes and dye intermediate effluents are aesthetic pollutants as they are coloured and they also create issues with light entering the water bodies, thereby affecting the organisms in it. Also, these effluents may be toxic/ carcinogenic in nature, which badly affect the life forms.[1]–[3]

Simultaneously, research has always led by the invention of a wide range of treatment technologies (precipitation, coagulation–flocculation, sedimentation, flotation, filtration, membrane processes, electrochemical techniques, biological process, chemical reactions, adsorption and ion exchange) with changing success rates has led a path to increase progress in the scientific community. [4]–[10]

Adsorption via activated carbon (and other clay materials) is found to be a promising technique because of ease of operation, low cost and better decolouration. A notable trend in the development of activated carbon (AC), an adsorbent with its large porous surface area, controllable pore structure, thermo-stability and low acid/base reactivity has been found [11], in terms of its versatility for removal of a broad type of organic and inorganic pollutants dissolved in aqueous media, even from gaseous environment [12]. Despite its prolific use in adsorption processes, the biggest barrier of its application by the industries is its high cost and difficulties associated with regeneration [12]. With awareness rising about industrial activities has intensified several deteriorations affecting

several ecosystems and posing a serious threat to human health and environment, it has become utmost importance to enforce stringent rules and regulations concerning the emission of contaminants from industrial waste streams by various regulatory agencies.[4], [13]

In the urge to explore novel adsorbents in the aim of an ideal adsorption system, it is essential to establish the most suitable adsorption equilibrium correlation [14], which is definitely needed for reliable prediction of adsorption parameters and quantitative comparison of adsorbent behavior for different adsorbent systems (or for varied experimental conditions)[15], [16]. In the perspective, equilibrium relationships, generally known as adsorption isotherms, describe how pollutants interact with the adsorbent materials, and thus are critical for optimization of the adsorption mechanism pathways, expression of the surface properties and capacities of adsorbents, and effective design of the adsorption systems [17], [18] .

II. ADSORPTION ISOTHERMS

An adsorption isotherm is an important curve that describes the phenomenon governing the retention (or release) or mobility of a substance from the aqueous porous media or aquatic environments to a solid-phase at a constant process parameters namely, temperature and pH. [10], [19], [20] Adsorption isotherms (AI) are used for (i) characterization of porous solids (ii) overall improvement of adsorption mechanism pathways (iii) degree of affinity with adsorbents and (iv) design of industrial adsorption processes. [10], [21]–[23]

In past century, a number of equilibrium isotherm models have been established from three fundamental approaches.

These three approaches are:

(i). Kinetic Mechanism: Here the adsorption equilibrium is defined at state of dynamic equilibrium, i.e., both adsorption and desorption rates are equal.

(ii). Thermodynamic Approach: Here, parameters from Ideal Gas Law, Entropy and Deviation from ideality play a vital role in determining the isotherms.

(iii).Potential Theory: It is used for generation of characteristic curves.

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. [10], [12], [24]–[28]

This study is restricted to two, two parameter isotherms namely: Langmuir Isotherm Model and Freundlich Isotherm Model.

A.   Langmuir Isotherm Model

It is one of the simplest and oldest isotherm model which is still the best fit for many cases. This model considers only the monolayer adsorption and considers the adsorption of ideal gas onto an idealized surface. The gas is presumed to bind at a series of distinct sites on the surface of solid.

In its derivation, Langmuir isotherm refers to homogeneous adsorption, which each molecule possess constant enthalpies and sorption activation energy (all sites possess equal affinity for the adsorbate)[29], with no transmigration of the adsorbate in the plane of the surface [30].

Graphically, it is characterized by a plateau, an equilibrium saturation point where once a molecule occupies a site, no further adsorption can take place. Moreover, Langmuir theory has related rapid decrease of the intermolecular attractive forces to the rise of distance. Hereby, a dimensionless constant, commonly known as separation factor (R_L) defined by Weber and Chakravorti [31] can be represented as:

$$\frac{C_e}{q_e} = \frac{1}{BQ_0} + \frac{C_e}{Q_0} \tag{1}$$

$$R_L = \frac{1}{(1 + B\,Q_0)} \tag{2}$$

Here, R_L value indicates the adsorption nature to be either unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$).

B.   Freundlich Isotherm Model

Freundlich isotherm is applicable to adsorption processes that occur on heterogeneous surfaces. This isotherm gives an expression which defines the surface heterogeneity and the exponential distribution of active sites and their energies. The linear form of the Freundlich isotherm is as follows: [10], [23], [32]

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{3}$$

1/n indicates the relative distribution of the energy and the heterogeneity of the adsorbate sites.

Freundlich isotherm has an inherent disadvantage of lacking a fundamental thermodynamic basis, not approaching the Henry's law at infinite dilution.[33]

C.   Kinetic Models

The kinetic values of adsorption can be analyzed using pseudo-first-order and pseudo-second-order kinetic models. These models correlate solute uptake to predict the required reactor volume.

The pseudo-first-order equation of Lagergren [34]is generally expressed as in Equation (3):

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{3}$$

After integration and applying boundary conditions, $q_t = 0$ to $q_t = q_t$ at t = 0 to t = t, the integrated form of Equation (3) becomes:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{4}$$

The pseudo-first-order rate constant, k_1, can be obtained from the slope of the graph of ln (qe-q) versus time t. as shown by Equation (4)

The pseudo-second-order chemisorption kinetic rate equation is expressed in Equation (5) [35], [36]:

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \tag{5}$$

After integration and applying boundary conditions, $q_t = 0$ to $q_t = q_t$ at t = 0 to t = t, the integrated form of Equation (5) becomes:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e t} \tag{6}$$

III.   KALE ACID AND SAMPLE COLLECTION

Kale acid is a dye intermediate used for the manufacture of various dyes. A typical batch process has a completion of about 196 hours with various unit processes like Sulfonation, Nitration, Reduction, Fusion, and Isolation. The solid mass is usually filtered and washing is done at each stage to recover the product and improve the quality. Samples of wastewater at four different stages were collected in sealed carboys and they were considered as single solute stream (S1 to S4) and multi solute streams were also prepared by mixing the streams as MS1 (S1+S2), MS2 (MS1+S3) and MS3 (MS2+S4). While carrying out

experimental studies on the wastewater from each carboy sample was analyzed for pH and COD.

During experiment 100 ml of sample was taken from the respective carboy in Erlenmeyer flask in which 0.5%, 1.0%, 1.5%, 2.0% activated carbon was added in 100 ml of sample and the mixture was stirred using magnetic stirrer at 150 rpm for the different time interval of 30, 60, 90 and 120 min to the end. After the adsorption it was then filtered using filter paper and the filtrate were analyzed for COD using open reflux method. At the end of 120 minutes, the stirring was stopped and the experiment was terminated. All the experiments were carried out at room temperature of around 30°C.

IV.   RESULTS AND DISCUSSION

The results obtained for COD measurements are shown in Table-1 It is lucid from the results that activated carbon definitely be used as adsorbent which indicates 60% to 80% reduction in the COD values for single stream and 73 % to 85% for multi solute streams.

Sr. No.	Type of Sample (Sample Name)	COD Initial	COD Final After 2 Hours				Percentage Reduction
			Activated carbon added per 100 ml of sol.				
			0.5g	1g	1.5g	2g	
1	Stream 1 (S1)	30092	7823	6620	6319	6018	80.00
2	Stream 2 (S2)	32032	8968	8264	8008	7047	78.00
3	Stream 3 (S3)	35096	15372	14670	14389	13968	60.20
4	Stream 4 (S4)	38200	17572	17151	15662	14134	63.00
5	Mixed Stream 1 (S1+S2) (MS1)	30121	8019	5456	4815	4495	85.08
6	Mixed Stream 2 (MS1+S3) (MS2)	30767	10768	10922	9261	8276	73.10
7	Mixed Stream 3 (MS2 + S4) (MS3)	34409	12215	10632	8602	7914	77.00

Table 1: Summary sheet for COD Measurements

The various results obtained from kinetic data were fitted in the Langmuir isotherm equation and Freundlich isotherm equation and the constants are as shown in table-2 for single stream and table-3 for multi solute streams.

Sr. No.	Type of Sample	Langmuir equation		Freundlich equation	
		Q_o ,l/mg	B	n	K_f ,l/mg
1	Stream 1 (S1)	0.066313	8870.588	0.203583	$1.95*10^{-7}$
2	Stream 2 (S2)	0.052513	10022.63	0.189394	$3.10*10^{-8}$
3	Stream 3 (S3)	0.009285	15838.24	0.070721	$6.92*10^{-25}$
4	Stream 4 (S4)	0.026337	21094.44	0.208899	$4.91*10^{-8}$

Table 2: Constants for Isotherms modeling for single solute streams

Sr. No.	Type of Sample	Langmuir equation		Freundlich equation	
		Q_o, l/mg	B	n	K_f, l/mg
1	Mixed Stream 1 (MS1)	0.12014	7566.36	0.27631	4.07E-05
2	Mixed Stream 2 (MS2)	0.05589	17890	0.29146	3.04E-05
3	Mixed Stream 3 (MS3)	0.09113	15675.7	0.38925	0.001009

Table 3: Constants for Isotherms modeling for multi solute streams

A.   Kinetic Data Modeling

Single solute data

The results of the COD values were fitted to the pseudo first order kinetics and the pseudo second order kinetics for

all the single solute streams as shown in the fig-1 and fig-2 and the results obtained are shown in the table-4.
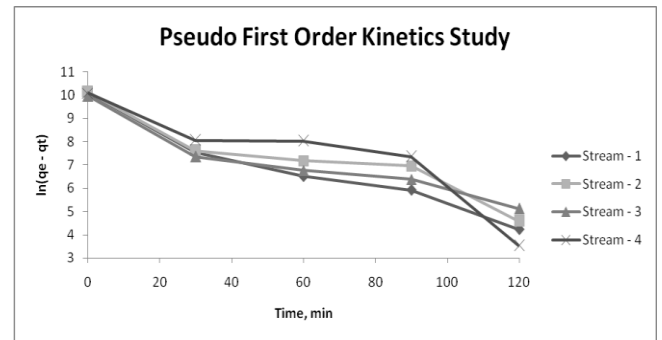

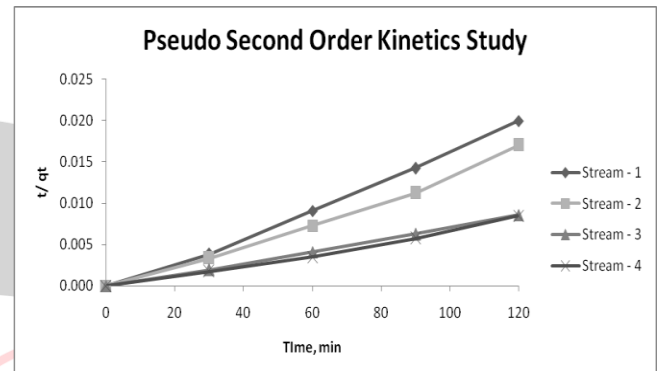Figure 1: Pseudo first order kinetic study fitting to single solute streams

Figure 2: Pseudo second order kinetic study fitting to single solute streams

First Order Kinetics				Second Order Kinetics			
Stream	Slope	Intercept	R^2	Stream	Slope	Intercept	R^2
S1	-0.0446	9.5267	0.9457	S1	0.0002	-0.0006	0.9957
S2	-0.0311	8.9129	0.7773	S2	0.0001	-0.0006	0.9889
S3	-0.0356	9.2527	0.8877	S3	0.00007	-0.0001	0.999
S4	-0.0461	10.176	0.8293	S4	0.00008	-0.0003	0.9894

Table 4: Kinetic Data Fitting For Single Solute Streams

Multi solute data

The results of the COD values were fitted to the pseudo first order kinetics and the pseudo second order kinetics for all the multi solute streams are as shown in the fig-3 and fig-4 and the results obtained are shown in the table-5.
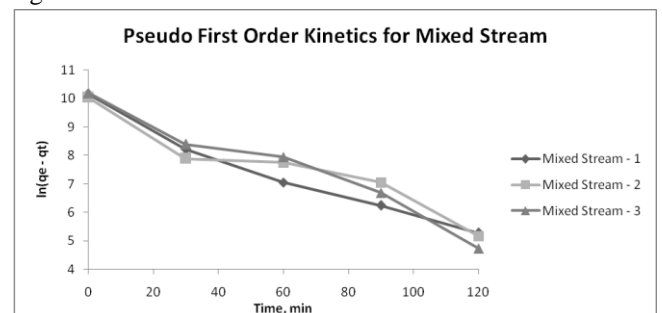

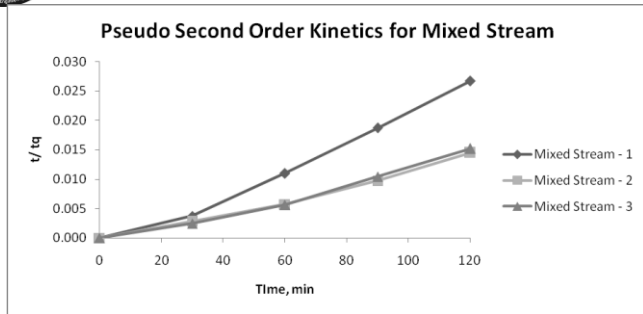Figure 3: Pseudo first order kinetic study fitting to multi solute streams

Figure 4: Pseudo second order kinetic study fitting to multi solute streams

First Order Kinetics				Second Order Kinetics			
Stream	Slope	Intercept	R^2	Stream	Slope	Intercept	R^2
MS1	-0.0392	9.7398	0.9676	MS1	0.0002	-0.0016	0.9855
MS2	-0.0352	9.6888	0.9121	MS2	0.0001	-0.0006	0.9861
MS3	-0.0420	10.113	0.9646	MS3	0.00001	-0.0009	0.9810

Table 5: Kinetic Data Fitting For Multi Solute Streams

The kinetic data for reduction in COD for single stream using Langmuir equation showed constants Q_0 ranging from 0.009 l/mg to 0.066 l/mg and B ranging from 8870 to 21094 Freundlich equation n ranging from 0.07 to 0.2088 and K_F, ranging from $1.95*10^{-7}$ l/mg to $6.92*10^{-25}$ l/mg and for multi stream using Langmuir equation showed constants, Q_0 ranging from 0.055 l/mg to 0.120 l/mg and B ranging from 7565 to 1789 Freundlich equation n ranging from 0.276 to 0.389 and K_F, ranging from $3.05*10^{-5}$ l/mg to 0.01 l/mg.

Figure 2 and 4 shows the linear relationship of the graph plot of t/q_t versus t $t/q_t \ versus \ t$, from which q_e and k can be determined from the slope and intercept, respectively for both the single solute streams and the multi solute streams. The linear regression correlation coefficient R^2 value (0.99) for pseudo second order was higher than R^2 value (0.97) for pseudo first order reaction kinetics (Table 4,5) for both the type of streams. These results confirm that the adsorption data were well represented by the pseudo-second-order kinetic model.

V.   CONCLUSION

The optimum amount of Activated Carbon to be added is 2g/100ml of effluent for both single and mixed feed, this leads to reduction in almost 60 – 80% of COD for single stream while 73 - 85% for mixed stream solute which clearly reveals synergism. The result dictates that the use of activated carbon for adsorption in the pre-treatment of waste rather than using it in tertiary treatment gives better COD reductions. The study also reveals that the pseudo-second order kinetic model can be used to design the system for adsorption.

APPENDIX

B	Langmuir constant, (per mg)
Q_0	Adsorbate initial concentration, (mg/L)
R_L	Adsorption nature

K_F	Adsorption capacity, (L/mg)
$\dfrac{1}{n}$	Adsorption intensity
q_e	Sorption capacities at equilibrium, (mg/g)
q_t	Sorption capacities at time t
k_1	Rate constant of pseudo-first-order sorption, (min⁻¹)
k_2	Rate constant of pseudo-second-order sorption, (g/(mg•min))
t	Contact Time, min

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