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Batch Adsorption From Solution

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A batch adsorption equation was derived by integrating an irreversible rate equation obtained by neglecting the desorption term of the Langmuir adsorption-rate equation. The integrated equation was in reasonably good agreement with experiment and provided a means for determining from the data the parameters q_0 and k_1. These constants, namely, the adsorptive capacity and the adsorption rate constant, completely characterized the adsorption system at that temperature. Agreement was found between these *batch* adsorption parameters and their counterparts previously derived from *column* adsorption experiments when both types of adsorption were performed simultaneously.

1. Introduction

The study of adsorption from solution of one or more solutes by solid adsorbents has lagged in comparison with the advances made in gas adsorption. The problem is more complicated for a number of reasons: (1) The systems of interest are invariably multi-component and, hence, the possibility of competition exists for the available adsorption sites if, indeed, the same sites are involved. (2) Equations of state are less well understood for liquid systems than for gases. (3) The isotherms applicable to gas adsorption have been studied in great detail. The differences between physical and chemical adsorption are usually well defined and the parameters of the isotherm equation are meaningful. In contrast, the isotherms applicable to adsorption from solution are complicated by the fact that no clean-cut distinction can generally be made between physical adsorption and chemisorption. Complete reversibility is seldom if, indeed, ever attained. A Freundlich adsorption equation which often fits the data well is limited in its usefulness because its parameters lack physical significance. (4) The additional complications resulting from the greater viscosity in liquids than in gases as well as the contribution to the overall complexity attributable to diffusion can well be appreciated.

Adsorption from solution is customarily conducted either as a column or as a batch operation. In the former instance the solution is allowed to percolate through a column usually held in a vertical position such as is the common practice with ion exchange columns. In a batch operation, a quantity of adsorbent is mixed all at once with a quantity of solution and the system kept in agitation for a convenient period of time. Separation of the resultant solution is accomplished by filtering, centrifuging, or decanting.

It should be possible to characterize a solution-adsorbent system by either column or batch technique and arrive at the same result since the physical and/or chemical forces applicable in each case must be identical. Furthermore, the results obtained from a batch experiment should be somewhat more reliable because of several reasons. Among the most serious objections to column experiments are: (1) The overall complexity and expense of experimental equipment; (2) the inherent difficulties associated with maintaining a constant flow rate; (3) the difficulty of assuring a constant temperature throughout the column; (4) the appreciable probability of channeling within the packed column; (5) the variability in the results associated with classification by particle size during settling of the column; (6) the errors inherent in any of the various methods of settling of the column; and (7) the relatively large expenditure both in time and manpower required for a column experiment.

Previous attempts to solve the kinetics of batch adsorption from solution have been, for the most part, disappointing. A certain measure of success was reported by Dryden and Kay [1] [1] despite the fact that their equation (based on a solution of the finite bath theory) assuming a *linear* adsorption isotherm was applied to systems which obeyed the *Freundlich* isotherm. Their use of the "fractional approach to equilibrium" was a refinement of the work of Eagle and Scott [2] which, in turn, was an outgrowth of the earlier application by Geddes [3].

The aforementioned approach while providing a measure of the adsorption rate constant can give no estimate of the maximum extent of adsorption which might conceivably correlate with surface area. Other investigators assuming either a Langmuir representation [4, 5, 6, 7] or (less frequently) a B.E.T. behavior [8, 9, 10, 11] applied to solutions were able to estimate adsorptive capacities. However, since their applications were made using the equations derived for $t=\infty$, no kinetic information can be expected.

2. Theoretical Development

The present investigation treats the problem of batch adsorption in a manner analogous to that recently found extremely useful in column adsorption [12]. The kinetic form of an adsorption equation which may reasonably be expected to fit the data is integrated subject to a "conservation" equation, i.e.,

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[1] Figures in brackets indicate the literature references at the end of this paper

a conservation of mass equation applied to the adsorbable solute.

2.1. Adsorption Rate

The kinetic form of a Langmuir adsorption equation before attainment of equilibrium may be represented as follows:

$$\frac{dq}{dt}=k_1c(q_0-q)-k_2q \tag{1}$$

where

q=the amount of solute adsorbed per gram of the adsorbent at any time, t;
q_0=the maximum value q would have if all the adsorption sites were filled;
c=the solute concentration at any time, t; and
k_1, k_2=the specific adsorption and desorption rate constants.

While eq (1) can be handled in its complete form [2] as shown, the result is unwieldy and some doubt exists that the additional precision that may result in some instances can justify the resultant increase in complexity. Furthermore, the presence of the last term of eq (1) implies *complete* reversibility, a condition which is rarely encountered in any practical case concerned with adsorption from solution. Accordingly, the kinetic equation adopted in this work is, simply:

$$\frac{dq}{dt}=k_1c(q_0-q). \tag{2}$$

Further justification for this simplification is the fact that in the column work already mentioned [12] quite satisfactory agreement was found in comparing columns of different dimensions, although the desorption rate constant k_2 had been eliminated from the integrated equation in that case also. Equation (2) simply states that the rate of adsorption is proportional at any instant to the concentration of the solute and to the number of unfilled adsorption sites.

The "conservation equation" for batch adsorption may be expressed in the form:

$$c_0V=cV+qW \tag{3}$$

where c_0 is the initial concentration of the solute, V the volume of solution, and W the mass of the adsorbent.

Equation (2) is easily integrated subject to eq (3) and the boundary conditions that $q=0$ and $c=c_0$ when $t=0$. This resultant integrated equation may be expressed as:

$$\ln\frac{\frac{c}{c_0}}{1-\frac{q}{q_0}}=-\left(\frac{Wq_0}{Vc_0}-1\right)c_0k_1t. \tag{4}$$

Perhaps the best representation of the adsorption equation is obtained by eliminating c, entirely, between eqs (3) and (4) to obtain:

$$\frac{q}{q_0}=\frac{1-e^{-\left(\frac{Wq_0}{Vc_0}-1\right)c_0k_1t}}{\frac{Wq_0}{Vc_0}-e^{-\left(\frac{Wq_0}{Vc_0}-1\right)c_0k_1t}}. \tag{5}$$

At $t=0$, the numerator of the fraction vanishes, so $q=0$.

When $Wq_0/Vc_0>1$, the exponent of e is negative, so that the exponential terms are always less than unity. Thus the denominator is always greater than the numerator and $0<q/q_0<1$. Furthermore, under these conditions there is not enough adsorbate in the system to satisfy the capacity of the adsorbent, so as $t\rightarrow\infty$ the value of q tends toward Vc_0/W. Conversely, when $Wq_0/Vc_0<1$, the exponent of e is positive and the exponential terms become greater than unity and increase in magnitude with time. Again the quotient is always positive with a value between zero and one. Now, however, as $t\rightarrow\infty$ the limiting value of q is q_0 as expected.

Also from eq (5) it can be seen that: [3]

$$\lim_{\frac{W}{V}\rightarrow 0}\frac{q}{q_0}=1-e^{-c_0k_1t}. \tag{6}$$

The slope of the curve $q=f(t)$ is even more revealing. By differentiating eq (5) with respect to t, one obtains:

$$\frac{\partial q}{\partial t}=q_0c_0k_1\left[\frac{\frac{Wq_0}{Vc_0}-1}{\frac{Wq_0}{Vc_0}-e^{-\left(\frac{Wq_0}{Vc_0}-1\right)c_0k_1t}}\right]^2 e^{-\left(\frac{Wq_0}{Vc_0}-1\right)c_0k_1t}. \tag{7}$$

Now if the exponent in eq (7) is greater than zero, then at relatively large values of t

$$\frac{\partial q}{\partial t}\approx\frac{q_0c_0k_1\left(\frac{Wq_0}{Vc_0}-1\right)^2}{e^{-\left(\frac{Wq_0}{Vc_0}-1\right)c_0k_1t}} \tag{8}$$

which, in turn, goes to zero as $t\rightarrow\infty$.

If the exponent in eq (7) is less than zero, then as t grows large

$$\frac{\partial q}{\partial t}\approx q_0c_0k_1\left[\frac{\frac{Wq_0}{Vc_0}-1}{\frac{Wq_0}{Vc_0}}\right]^2 e^{-\left(\frac{Wq_0}{Vc_0}-1\right)c_0k_1t} \tag{9}$$

which, in the limit as $t\rightarrow\infty$, again goes to zero.

The integrated equation corresponding to eq (5) which was found to apply to *column* [12] adsorption is repeated here for convenience:

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[2] See eq 19.

[3] This is essentially the equation derived by Harned [13] in 1920.

$$\ln\left(\frac{c_0}{c}-1\right)=\frac{k_1q_0x}{\dot{V}}-\frac{k_1c_0y}{\dot{V}} \tag{10}$$

where $\dot{V}$ is the volume velocity; x is the mass of adsorbent upstream from the point at which effluent is collected; and y is the throughput or volume of effluent which has passed up to that time. Since the effluent in column adsorption is usually collected only at the end of the column, the value of x is constant. Thus, eq (10) is readily adapted for evaluating the parameters q_0 and k_1 from the linear plot of $\ln\left(\frac{c_0}{c}-1\right)$ against y. For the present work where batch adsorption is involved, no simple linear representation of eq (4) or (5) is possible for testing goodness of fit and for evaluating the parameters q_0 and k_1. Consequently it was necessary to resort to methods of successive approximations. Two such methods which were found to be helpful are given in the appendix.

3. Experimental Techniques

The batch adsorption experiments were conducted in stoppered erlenmeyer flasks agitated mechanically by means of a water bath shaking apparatus thermostated at 80 °C. The older experiments involved the use of a service bone char (Char 32) as the adsorbent in various U.S. sieve fractions both separately and in recombined mixtures. The adsorbate was the colorant in a Louisiana raw sugar liquor (of 60 Brix sucrose concentration). The concentration of the colorant was considered to be proportional to the optical density (or attenuation index assuming no scattering) as measured by a Beckman DU spectrophotometer at 560 mμ wavelength. The resonableness of this assumption was discussed in some detail in the previous work [12]. The proportionality constant, k_0, is not known, so that only comparative results are possible from all the colorant adsorption experiments. The length of time of each adsorption measurement was limited, in the earlier work, to 3 hr and the volume of solution was fixed as was the initial concentration. Six different weights of adsorbent were used in each experiment. A comparison was also made at that time with an activated carbon, namely Darco S–51, in an otherwise identical system.

The more recent series of experiments was designed to compare the results of batch adsorption with column adsorption for the same systems. Again a service bone char (Char 117–B) was used in all comparisons. A particular Hawaiian raw sugar liquor (Sugar 17) was tested both by batch and by column experiments all at 80 °C. Time, as well as weight of adsorbent, was allowed to vary among batches. The adsorption of colorant (optical density at 420 mμ wavelength), sulfate ion, and total cations, were determined independently for the two methods. The $[SO_4]^=$ determination was made by a turbidimetric method applied to suspensions of precipitated $BaSO_4$ as described by Gee et al. [14]. Total cations were determined by an ion exchange technique using Amberlite IR–120 in the hydrogen-form followed by titration with a standard base [15].

4. Comparison of Parameters Derived From Related Batch Experiments

4.1. Comparison Among Sieve Sizes of the Same Adsorbent

Table 1a gives the data obtained from one of the colorant adsorption batch experiments in the older series. The first method described in the appendix for determining the values of q_0 and k_1 from the experimental data was applied here. After four or five trials, the improved choice of $q_0 \approx 9.80\ k_0$ resulted in the quantities computed as shown in table 1b. In comparison with previous trials the quantity computed for Δq_0 was sufficiently close to zero, that no further refinement was deemed to be justified.

The data of table 1a were used to plot q against c/c_0 as shown by the open circles and curve of figure 1.

The corresponding values of q computed according to eq (5) using the two parameters q_0 and k_1 from table 1b are shown in crosses. The agreement is seen to be quite good except at the tail end of the curve where the amount of adsorbent used was small.

Table 2 summarizes the results for the same bone char but for various sieve sizes (both separately and in combination) tested with the same sugar solution for adsorption of colorant. The values listed for q_0 and k_1 were derived in each case by a method described in the appendix.

For the case of sieve fraction (30 on 35), the value of 8.58 k_0 for q_0 seems somewhat low in line with the other members of the series. Likewise its k_1 value of 0.182 $1/k_0$ appears to be high. Interestingly enough, the values derived by application of the theory to the reconstituted 50 percent mixtures agree rather well with the arithmetic means of the independently determined separate fractions. It should be noted in the last line of table 2 that the mixture included the (30 on 35) fraction which exhibited the anomalous behavior already mentioned. Its contribution in the case of the mixed sample must have been consistent with its separate behavior to have resulted in such close agreement between derived value and averaged value for q_0.

It is seen that the value of q_0 varied about 2½-fold between the coarser and finer fractions as shown in Figure 3. If the entire surface within a porous adsorbent particle were accessible to the adsorbate, the particle size should have little (if any) influence on the capacity for adsorption per unit mass of adsorbent providing the surface area were large. The sample of bone char used in this work had a B.E.T. total area (determined with N_2 gas at 77 °K) of about 80 $m^2 \cdot g^{-1}$. It can easily be shown that the external or boundary area of (48 on 80) mesh char particles is about 0.01 $m^2 \cdot g^{-1}$. A 3½-fold increase in particle size to (20 on 30) mesh would decrease this particle

TABLE 1a. *Typical data obtained by varying the amount of adsorbent from batch to batch*

Expt. (22-29), char 32 through 20 on 30 with Louisiana raw sugar liquor. $c_0=k_0(-\log t_{560})=0.349k_0$ mM·ml^{-1}; $V=78$ ml; $q=(c_0-c)\div(W/V)$.

Batch No.	W	c	c_0-c	W/V	q	t	c/c_0	ln c_0/c
	g	*mM·ml*$^{-1}$		*g·ml*$^{-1}$	*mM·g*$^{-1}$	*hr*		
1	2.00	0.302 k_0	0.047 k_0	0.026	1.808 k_0	3.00	0.865	0.145
2	5.00	.257 k_0	.092 k_0	.064	1.438 k_0	3.00	.736	.307
3	10.02	.195 k_0	.154 k_0	.128	1.203 k_0	3.00	.559	.582
4	14.99	.143 k_0	.206 k_0	.192	1.073 k_0	3.00	.410	.892
5	19.99	.105 k_0	.244 k_0	.256	0.953 k_0	3.00	.301	1.200
6	24.98	.0802 k_0	.269 k_0	.320	.841 k_0	3.00	.230	1.470

TABLE 1b. *Improved estimate of parameters (method 1) applied to data of table 1a for* $q_0=9.80\ k_0$ mM·g^{-1}

Batch No.	Order of computations														
	1	2	3	4	6	9	10	11	12	13	5	7	8	14	15
	q/q_0	q/q_0^2	$1-q/q_0$	$-\ln(1-q/q_0)$	$\partial F/\partial k_1$	F	ΔF	$(W/V)k_1t$	$\dfrac{q/q_0^2}{1-q/q_0}$	$\partial F/\partial q_0$	$\ln c_0/c+\ln(1-q/q_0)$	Eq. (7a)		Eq. (9a)	
1	0.184	0.0188	0.816	0.203	−0.283	0.156	−0.011	0.0130	0.0230	−0.0100	−0.058	$141.179k_1=23.5897$	$k_1=0.16709\ 1/k_0$ ml·mM^{-1}·hr^{-1}	$4.630\times10^{-2}\Delta q_0=25.8\times10^{-6}$	$\Delta q_0=5.57\times10^{-4}k_0$ mM·g^{-1}
2	.147	.0150	.853	.159	.835	.299	.008	.0321	.0176	.0145	.148				
3	.123	.0126	.877	.131	2.716	.585	−.003	.0642	.0144	.0498	.451				
4	.109	.0111	.891	.115	4.598	.883	.009	.0962	.0125	.0837	.777				
5	.0972	.00992	.903	.102	6.479	1.185	.015	.1283	.0110	.1173	1.098				
6	.0858	.00876	.914	.0900	8.361	1.487	−.017	.1604	.0096	.1508	1.380				

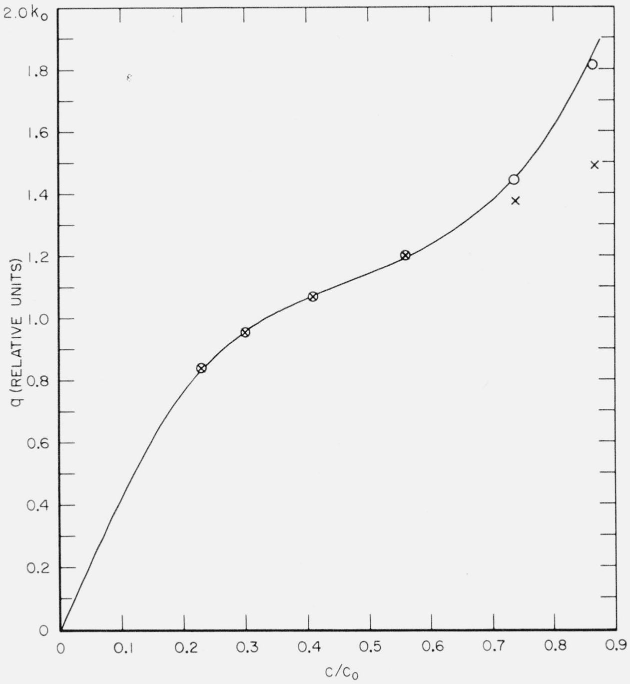

FIGURE 1. *Batch adsorption curve for colorant (contained in a Louisiana raw sugar liquor) using a (20 on 30) mesh service bone char.*

Three hour experimental points are shown by circles, calculated points by crosses.

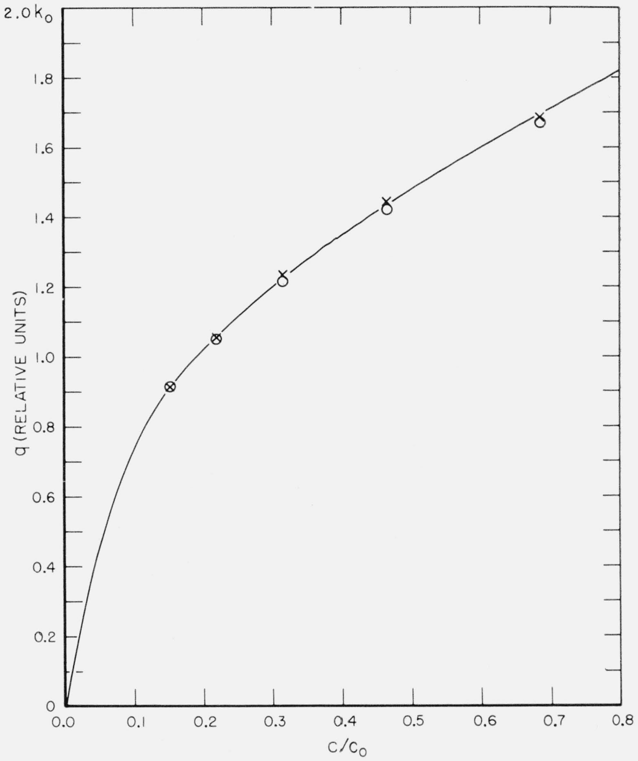

FIGURE 2. *Batch adsorption curve for colorant (contained in a Louisiana raw sugar liquor) using a 50 percent mixture of (20 on 30) mesh and (48 on 80) mesh service bone char.*

Three hour experimental points are shown by circles, calculated points by crosses.

area to 0.003 $m^2 \cdot g^{-1}$ and result in a decrease in B.E.T. area of less than 0.01 percent. It is interesting to speculate whether the observed variation of capacity for adsorption with sieve fraction was caused by the possibility that the service char may have restricted access to its interior brought on by the building up of mineral deposits, etc., resulting from repeated cycles of raw sugar filtration and high temperature kilning.

TABLE 2. *Relative values of adsorptive capacity* q_0 *and rate constant* k_1 *for the adsorption of colorant from a Louisiana raw sugar liquor on service bone char 32 of various sieve fractions*

Sieve sizes (US standard mesh) single closely sieved fractions	q_0 determined values	k_1 determined values
	$mM \cdot g^{-1}$	$ml \cdot mM^{-1} \cdot hr^{-1}$
(20 on 30)	9.90 k_0	0.165 $1/k_0$
(30 on 35)	8.58 k_0	.182 $1/k_0$
(35 on 48)	10.25 k_0	.144 $1/k_0$
(48 on 80)	23.00 k_0	.0895 $1/k_0$
Fines (smaller than 80 mesh)	24.79 k_0	.227 $1/k_0$

50% mixtures of sieve fractions	q_0		k_1	
	Determined values	Average of individual values	Determined values	Average of individual values
(20 on 30) and (48 on 80)	17.30 k_0	16.5 k_0	0.118 $1/k_0$	0.127 $1/k_0$
(30 on 35) and (48 on 80)	16.00 k_0	15.8 k_0	.105 $1/k_0$	0.136 $1/k_0$

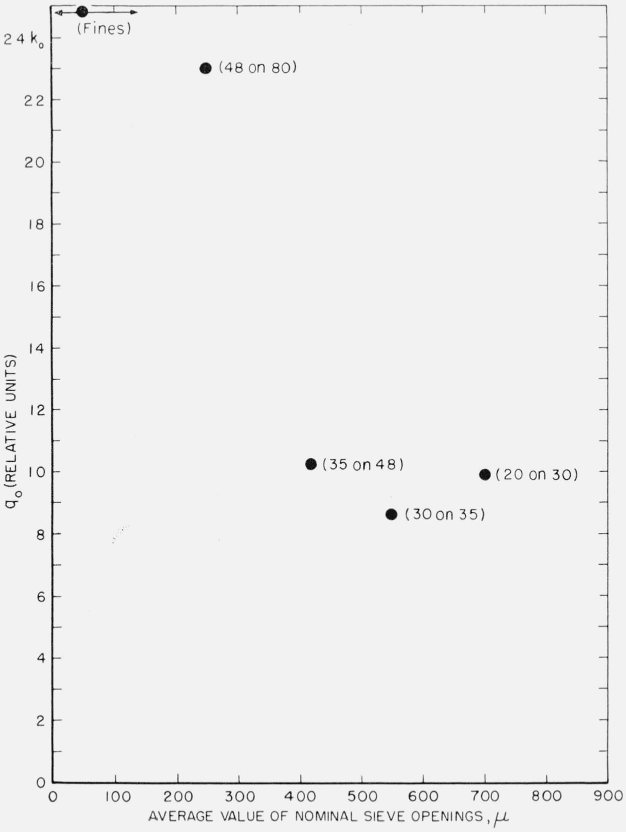

FIGURE 3. *Adsorption capacity of various sieve fractions of a service bone char for colorant plotted against mean particle diameter within each fraction.*

5. Comparison Between Two Different Adsorbents

It is interesting to compare the behavior of a decolorizing carbon (Darco S–51) with a service bone char in connection with the same sugar solution and under identical conditions in all other respects. The observed curve and calculated points for q of the decolorizing carbon are shown in figure 4. The magnitude of q_0 and k_1 are in qualitative agreement with known behavior when activated carbon is compared with bone char.

If the relative number of adsorption sites (as estimated by the magnitude of q_0) were a constant fraction of the surface area for different carbon adsorbents, one might hope to use this as a tool to compare surface areas. The ratio of their relative colorant adsorptive capacities of 53.5 k_0 for Darco S–51 to, say, 10 k_0 for (20 on 30) mesh service bone char would predict a surface area for the activated carbon of $80 \times 53.5/10 = 428$ $m^2 \cdot g^{-1}$. Published values of about 500 $m^2 \cdot g^{-1}$ [16] based on B.E.T. nitrogen adsorption isotherms have been given for the surface area of Darco S–51. Of course, considerably more work would have to be done in this connection before such an inference could be verified.

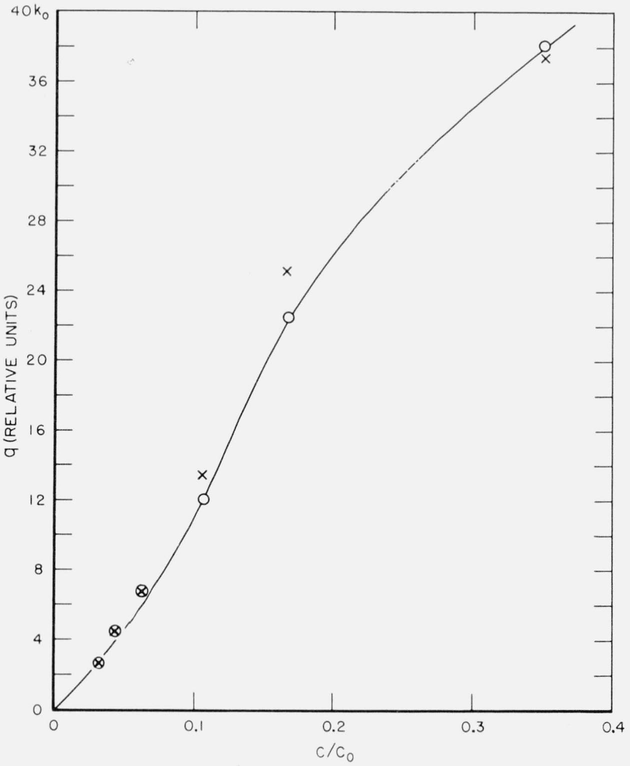

FIGURE 4.—*Batch adsorption curve for colorant (contained in a Louisiana raw sugar liquor) using a decolorizing (vegetable) carbon.*

Three hour experimental points are shown by circles, calculated points by crosses.

6. Batch Versus Column Adsorption—Comparison of q_0 and of k_1

A Hawaiian raw sugar solution was studied by means of a column experiment and a batch experiment using a service bone char as the adsorbent in each case. The adsorption of colorant as well as certain inorganic components, notably sulfate ion and alkaline-earth cations, were determined at the same time. The alkaline-earth cations consisted almost entirely of calcium ions and (to a much lesser extent) magnesium.

6.1. Colorant Adsorption Parameters

For the column experiment a cylindrical column of 500 ml capacity was used with 562 g of char leaving a total void volume of about 300 ml. The flow rate of sugar solution was held at 300 ml·hr^{-1}. When plotted according to eq (10), the results are shown in figure 5. The last seven points form a reasonably good straight line. From the slope of this line and its intercept on the zero-throughput axis, a value of 4.66 k_0 for q_0 and 0.0685 $1/k_0$ for k_1 were estimated. The first three points corresponding to no more than one column displacement are probably too high. Remnants of the settling liquor not completely displaced would make c abnormally low and, consequently, $\left(\frac{c_0}{c}-1\right)$ would be too high.

The data of the batch experiment (26–B$_2$) performed with aliquots of the same raw sugar solution and of the same bone char carried out at the same temperature and on the same day are available for comparison. It should be noted that in batch experiments of the recent work, time was not held constant in all of the samples, but was deliberately varied from ½ hr to 4 hr. The data collected are shown to the left of the double rule in table 3.

By applying the methods of successive approximation described in the appendix the values of 8.52 k_0 and 0.0490 $1/k_0$ were obtained for q_0 and k_1, respectively. These parameters applied to eq (5) were used to calculate the quantity q for each batch. These calculations and results are shown to the right of the double rule in table 3. The differences between $q_{(obs)}$ and $q_{(calc)}$ are given in the last column. The sum of the squares of these differences is 1.83 k_0^2, hence the mean square deviation between calculated and observed values of q amounts to 0.305 k_0^2. This yields a value of 0.55 k_0 as "standard error of estimate" for the quantity q based on the above calculations, although it should not be interpreted as experimental error. Attention should be called to the apparent anomaly between samples 4 and 5. The concentration may have been erroneously recorded as the same, but it is equally likely that the experimental error was great enough to have given identical readings for the 1½-hr and 2-hr samples. The data were treated as though the latter was the case. It is significant that even if the 1½-hr point had been omitted and the computations had been based on the seven remaining batches, the value thus obtained for q_0 would have differed by no more than about 3½ percent.

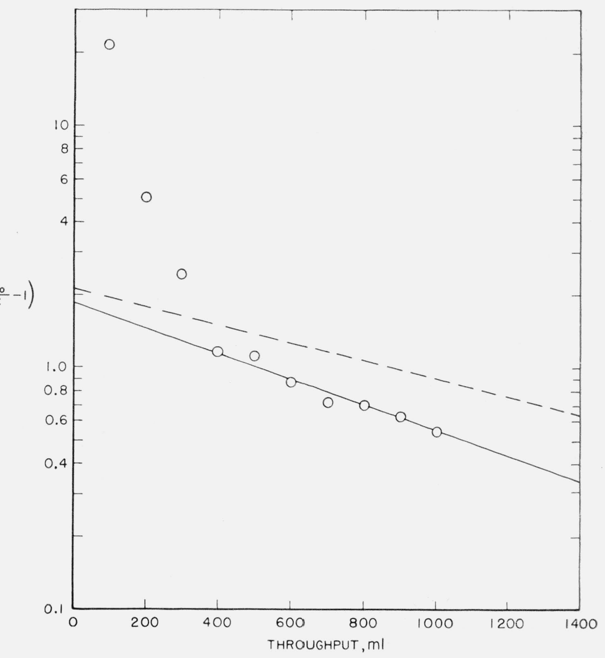

FIGURE 5. *Column adsorption of colorant (contained in a Hawaiian raw sugar liquor) by a service bone char shown by experimental points.*

Solid line was selected as best fit for these data. (Perfect agreement with batch adsorption would have required the experimental column points to have fallen on broken line.)

All in all, considering the assumptions inherent in the derivation of the adsorption rate equation as well as the experimental errors present in the batch and column adsorption methods, the values of

TABLE 3. *Batch adsorption of colorant and test of improved estimate of parameters*

Batch expt 26 B_2; V=49.5 ml; c_0=5.21 k_0 mM·ml^{-1}.

Sample No.	W	t	c	W/V	$q_{(obs)}$	$\frac{Wq_0}{Vc_0}$	$\left(\frac{Wq_0}{Vc_0}-1\right)c_0k_1t$	Exponential term of eq (5)	Numerator of eq (5)	Denominator of eq (5)	q/q_0 (calculated)	$q_{(calc)}$	Δq
	g	hr	$mM\cdot ml^{-1}$	$g\cdot ml^{-1}$	$mM\cdot g^{-1}$							$mM\cdot g^{-1}$	$mM\cdot g^{-1}$
2	50.0	0.5	3.68 k_0	1.010	1.515 k_0	1.652	0.0832	0.920	0.0798	0.732	0.109	0.929 k_0	0.561 k_0
3	50.0	1.0	3.32 k_0	1.010	1.871 k_0	1.652	.1664	0.847	.153	.805	.190	1.619 k_0	.252 k_0
4	50.0	1.5	2.66 k_0	1.010	2.525 k_0	1.652	.2497	0.779	.221	.873	.253	2.156 k_0	.369 k_0
5	50.0	2.0	2.66 k_0	1.010	2.525 k_0	1.652	.3329	0.717	.283	.935	.303	2.582 k_0	−.057 k_0
7	50.0	4.0	1.99 k_0	1.010	3.188 k_0	1.652	.6658	0.514	.486	1.138	.427	3.638 k_0	−.450 k_0
6	60.0	4.0	1.62 k_0	1.212	2.962 k_0	1.982	1.0028	0.367	.633	1.615	.392	3.340 k_0	−.378 k_0
8	40.0	4.0	2.59 k_0	0.808	3.243 k_0	1.321	0.3278	0.721	.279	0.600	.465	3.962 k_0	−.719 k_0
9	30.0	4.0	2.21 k_0	0.606	4.950 k_0	0.9910	−.00919	1.0092	−.0092	−.0182	.505	4.303 k_0	.647 k_0

$8.52k_0$ versus $4.66k_0$ for q_0 and $0.0490\ 1/k_0$ versus $0.0685\ 1/k_0$ for k_1 derived from batch and column, respectively, are rather encouraging. If the column experiment had yielded results for q_0 and k_1 in identical agreement with those obtained from the batch experiment, the dashed line shown in figure 5 would have resulted.

6.2. Sulfate Adsorption Parameters

The results obtained in the adsorption of sulfate ion by bone char from raw sugar solution are especially significant. Since the concentration of sulfate can be measured in *absolute* units (only relative units for colorant concentration), a means was available for the first time for estimating that fraction of the surface of the adsorbent on which sulfate-adsorption sites existed.

Data collected from the column experiment are given in table 4. A semi-logarithmic plot of the dimensionless quantity $\left(\frac{c_0}{c}-1\right)$ against throughput gave a reasonably good straight line (in accordance with eq (10)) with intercept on the zero-throughput ordinate of ln 10 (or 2.303) and with a slope of -2.373×10^{-3} ml^{-1}. From these results the values of q_0 and k_1 were easily determined:

$$q_0=34.1\ \mu\text{eq}\cdot\text{g}^{-1}$$

$$k_1=0.036\ \text{ml}\cdot\mu\text{eq}^{-1}\ \text{hr}^{-1}.$$

TABLE 4. *Column adsorption of sulfate*

Weight of adsorbent, 562 g; flow rate 300 ml·hr^{-1}; concentration of $[SO_4]^=$ in on-liquor, $c_0=9.88$ mM·l$^{-1}\approx$ 19.76 μeq·ml^{-1}; temperature = 80 °C.

Throughput	$\left(\frac{c_0}{c}-1\right)$
ml	
100	8.69
200	5.81
300	4.68
400	3.22
500	2.97
600	2.17
900	1.66
1,200	0.871
1,500	.680
1,800	.607
1,900	.116

The corresponding batch adsorption experiment for sulfate ion was performed, the data of which are given in table 5 (to the left of the double rule). By use of the methods described in the appendix, the final values obtained were

$$q_0=35.4\ \mu\text{eq}\cdot\text{g}^{-1}$$

$$k_1=0.0287\ \text{ml}\cdot\mu\text{eq}^{-1}\cdot\text{hr}^{-1}.$$

With these numerical values for the batch adsorption capacity and rate constant, the remainder of table 5 (to the right of the double rule) was calculated. A comparison between the calculated values of q and the corresponding observed values discloses a mean square deviation of 1.75 μM$^2\cdot$g^{-2} (with six degrees of freedom). Considering the number of variables involved and the experimental difficulties associated especially with column adsorption, the agreement attained for $[SO_4]^=$ between column and batch adsorption is very good. In kinetic studies of this type, agreement within the same order of magnitude is often acceptable.

6.3. Alkaline Earth Cation Adsorption Parameters

The adsorption of calcium and magnesium ions should in all fairness be treated separately, since each ion must follow its own unique adsorption isotherm. The only justification that could be given for treating the mixture as a composite would be the assumption that the individual ion adsorption characteristics might not be too different one from the other. Furthermore, since the data were already available, they were tested according to the present theory. The data for the column experiment when plotted according to eq (10) were reasonably well fitted by a straight line as shown in figure 6. From this it may be estimated:

$$q_0\approx8.6\ \mu\text{eq}\cdot\text{g}^{-1}$$

and

$$k_1\approx0.0059\ \text{ml}\cdot\mu\text{eq}^{-1}\cdot\text{hr}^{-1}$$

for the adsorptive capacity and rate constant, repectively.

The corresponding batch experiment was applied to the adsorption of [calcium plus magnesium] with the data shown in the left half of table 6 subjected

TABLE 5. *Batch adsorption of sulfate and test of improved estimate of parameters*

Batch experiment 26 B_2; V=49.5 ml; c_0=9.90 μM·ml^{-1} [a, b]

Sample No.	W	t	c	W/V	[a]$q_{(obs)}$	$\frac{Wq_0}{Vc_0}$	$\left(\frac{Wq_0}{Vc_0}-1\right)c_0k_1t$	Exponential term of eq (5)	Numerator of eq (5)	Denominator of eq (5)	q/q_0 (calculated)	[a]$q_{(calc)}$	[a]Δq
	g	*hr*	*μM·ml⁻¹*	*g·ml⁻¹*	*μM·g⁻¹*							*μM·g⁻¹*	*μM·g⁻¹*
2	50.0	0.5	5.07	1.010	4.78	1.809	0.229	0.796	0.204	1.013	0.201	3.56	1.22
3	50.0	1.0	3.36	1.010	6 47	1.809	.459	.632	.368	1.177	.313	5.55	0.92
4	50.0	1.5	2.88	1.010	6.95	1.809	.688	.503	.497	1.306	.381	6.76	.19
5	50.0	2.0	2.73	1.010	7.10	1.809	.918	.400	.600	1.409	.426	7.55	−.45
7	50.0	4.0	1.86	1.010	7.96	1.809	1.836	.160	.840	1.649	.509	9.03	−1.07
6	60.0	4.0	1.35	1.212	7.05	2.171	2.657	.070	.930	2.101	.442	7.84	−0.79
8	40.0	4.0	3.27	0.808	8.21	1.447	1.014	.363	.637	1.084	.588	10.43	−2.22
9	30.0	4.0	2.07	.606	12.92	1.085	0.1929	.826	.174	0.259	.672	11.92	1.01

[a] Computations have been carried in units of micromoles, but these dimensions were converted to micro equivalents in reporting q_0 and k_1.

[b] Slight difference in values of c_0 between column and batch experiments is a result of heated blank sample No. 1 in batch experiment redetermined.

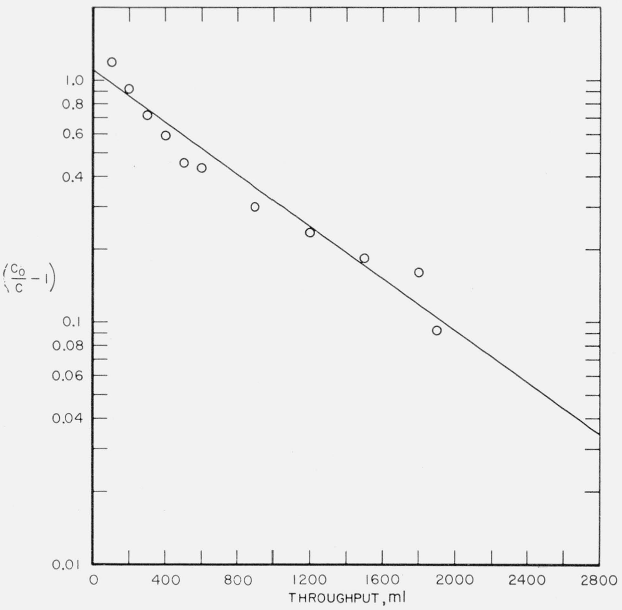

FIGURE 6. *Column adsorption of total cations (principally calcium and magnesium) from a Hawaiian raw sugar liquor by a service bone char.*

to the method of calculation already described. The right half of table 6 (to the right of the double rule) was computed corresponding to

$$q_0 \approx 70.3\ \mu\text{eq}\cdot\text{g}^{-1}$$

and

$$k_1 \approx 0.0030\ \text{ml}\cdot\mu\text{eq}^{-1}\cdot\text{hr}^{-1}$$

after several successive approximations. No appreciable improvement in the degree of fit was indicated although, in this case, a mean square deviation as large as 58.1 $\mu\text{eq}^2\cdot\text{g}^{-2}$ (with six degrees of freedom) was estimated between the observed and calculated values of q.

A comparison of batch with column-derived parameters in this instance discloses a twofold discrepancy in the rate constant, while the adsorptive capacities disagreed by almost an order of magnitude.

7. Fraction of Surface Area Available for Adsorption

It was stated at the beginning of the section on sulfate adsorption that the capacity for adsorption in absolute units could be used to estimate the fraction of the surface to which the adsorption of each species was confined. In the case of $[SO_4]^=$, for example, it was found that the maximum capacity, q_0, amounted to about 35 $\mu\text{eq}\cdot\text{g}^{-1}$ for a service bone char (Char 117–B) whose B.E.T. area is about 80 $\text{m}^2\cdot\text{g}^{-1}$ (measured by nitrogen adsorption at 77 °K). If the effective area of an adsorption site for the nitrogen molecule is taken as 16.2 A^2, there would be required 812 μM of nitrogen per gram of char to cover a monolayer for the particular bone char used. The sulfate ion is a tetrahedron with a sulfur-oxygen interatomic separation of 1.51 A [17] and an oxygen radius of 1.32 A. If the effective area of an adsorption site for the sulfate ion is roughly 28 A^2, then the fraction of the total surface that could accommodate sulfate adsorption at the maximum adsorptive capacity of the char (measured by q_0) would amount to only about 3¾ percent.

8. Temperature Dependence

Very little has been said here concerning k_1, the adsorptive rate constant. Data at several temperatures would certainly be of prime importance in order to ascertain whether eq (5) might be made even more general. It would be anticipated that k_1 might be replaced by an exponential Arrhenius type formulation to describe the temperature dependence of adsorption providing temperature has no more than a trivial effect upon q_0, as was found by Hirst and Lancaster [18].

9. Shapes of Adsorption Curves

The practical (finite time) adsorption curves, some examples of which are given here in figures 1, 2, and 4, should not be confused with equilibrium adsorption isotherms. The experimentally observed curves may have so many different shapes that they are difficult to catalog. Figure 7, for example, is a plot of the results already given for the batch adsorption of sulfate ion by bone char from a raw

TABLE 6. $[Ca]^{++}$ *plus* $[Mg]^{++}$ *composite adsorption and test of improved estimate of parameters*

Batch experiment 26 B_2; V=49.5 ml; c_0=64.50 μeq·ml^{-1}

Sample No.	W	t	c	W/V	$q_{(obs)}$	$\frac{Wq_0}{Vc_0}$	$\left(\frac{Wq_0}{Vc_0}-1\right)c_0k_1t$	Exponential term of eq (5)	Numerator of eq (5)	Denominator of eq (5)	q/q_0 (calculated)	$q_{(calc)}$	Δq
	g	*hr*	*μeq·ml⁻¹*	*g·ml⁻¹*	*μeq·g⁻¹*							*μeq·g⁻¹*	*μeq·g⁻¹*
2	50.0	0.5	48.9	1.010	15.4	1.101	0.0099	0.9902	0.00985	0.111	0.0887	6.2	9.2
3	50.0	1.0	45.1	1.010	19.2	1.101	.0198	.9804	.0196	.121	.162	11.4	7.8
4	50.0	1.5	41.9	1.010	22.4	1.101	.0297	.9708	.0292	.130	.225	15.8	6.6
5	50.0	2.0	41.7	1.010	22.6	1.101	.0396	.9612	.0388	.140	.277	19.5	3.1
7	50.0	4.0	39.6	1.010	24.7	1.101	.0792	.9239	.0761	.177	.430	30.2	−5.5
6	60.0	4.0	37.5	1.212	22.3	1.321	.2517	.778	.222	.543	.409	28.8	−6.5
8	40.0	4.0	45.0	0.808	24.1	0.881	−.0933	1.0977	−.0977	−.217	.450	31.6	−7.5
9	30.0	4.0	41.7	.606	37.6	.6605	−.2662	1.3000	−.3000	−.6395	.469	33.0	4.6

sugar solution. The 4-hr experimental points (circles) show a maximum appearing at about 0.3 on the c/c_0 axis. Similar maxima have shown up in numerous other investigations reported in the literature [19–26] for which various explanations have been proposed. The present theory, i.e. eq (5), does not predict these phenomena despite the fact that it appears to do so, as in figure 7. This is a result of the fact that the value of c in the abscissa is the *observed* concentration. The maximum in the calculated values would disappear if plotted against recomputed values of c determined from these least-square q-values according to eq (3). A horizontal shift would then result in the position of each of the calculated points (squares in fig. 7). The resultant adsorption curve connecting these new positions would resemble, in general appearance, the shape of the familiar Freundlich Isotherm.

From a physical point of view, the observed concentration c is not an independent variable, since its values cannot be preselected as can values of W/V and of c_0. It is significant that no maximum in the observed adsorption curve appears when q is plotted as a function of W/V instead of c for the 4-hr points of figure 7.

Regardless of whether the batch experiment is performed by holding c_0 constant (as was done here) or by holding W/V constant if in each case the time is held constant, the slope of the adsorption curve is always greater than zero according to eq (5). This may be proved by the following considerations:

At constant t, eq (5) expresses q as a function of two variables. Therefore, a differential change in q is given by eq (11)

$$dq = \left.\frac{\partial q}{\partial (W/V)}\right|_{c_0} d(W/V) + \left.\frac{\partial q}{\partial c_0}\right|_{W/V} dc_0. \tag{11}$$

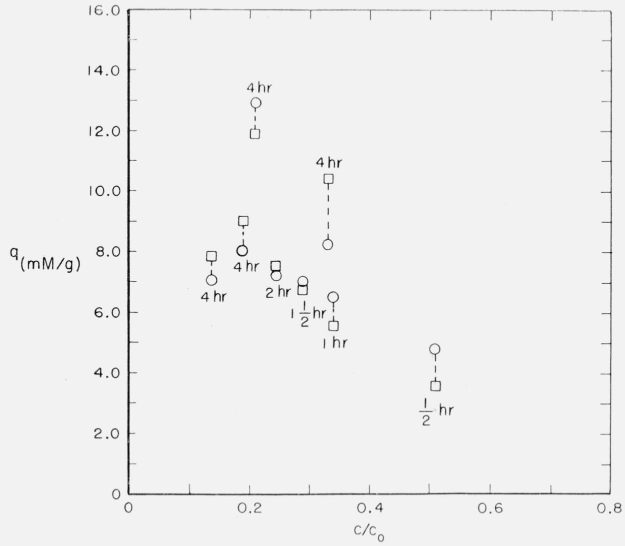

FIGURE 7. *Batch adsorption results for sulfate ion (contained in a Hawaiian raw sugar liquor) by a service bone char at designated durations of contact time.*

Experimental points are shown by circles, calculated points by squares.

When each variable, in turn, is held constant the slope of the adsorption curve may be expressed as

$$\left.\frac{\partial q}{\partial c}\right|_{c_0} = \left.\frac{\partial q}{\partial (W/V)}\right|_{c_0} \left.\frac{\partial (W/V)}{\partial c}\right|_{c_0} \tag{12}$$

and

$$\left.\frac{\partial q}{\partial c}\right|_{W/V} = \left.\frac{\partial q}{\partial c_0}\right|_{W/V} \left.\frac{\partial c_0}{\partial c}\right|_{W/V} \tag{13}$$

It is clear from inspection that $\left.\frac{\partial (W/V)}{\partial c}\right|_{c_0}$ is negative and that $\left.\frac{\partial c_0}{\partial c}\right|_{W/V}$ is positive. Now if it can be shown that $\left.\frac{\partial q}{\partial (W/V)}\right|_{c_0}$ is always negative and that $\left.\frac{\partial q}{\partial c_0}\right|_{W/V}$ is always positive, then it must follow that $\frac{dq}{dc}$ is greater than zero throughout its entire range.

Equation (5) may be differentiated with respect to w/v to obtain:

$$\left.\frac{\partial q}{\partial (W/V)}\right|_{c_0} = \frac{\left[\frac{q_0^2}{c_0}(c_0k_1t)\left(\frac{Wq_0}{Vc_0}-1\right)+\frac{q_0^2}{c_0}\right]e^{-\left(\frac{Wq_0}{Vc_0}-1\right)c_0k_1t}-\frac{q_0^2}{c_0}}{\left[\frac{Wq_0}{Vc_0}-e^{-\left(\frac{Wq_0}{Vc_0}-1\right)c_0k_1t}\right]^2} \tag{14}$$

from which it can be shown that eq (14) is indeed negative providing its numerator is negative. This reduces to the requirement that:

$$e^{+\left(\frac{Wq_0}{Vc_0}-1\right)c_0k_1t} > 1+\left(\frac{Wq_0}{Vc_0}-1\right)c_0k_1t.$$

When $\frac{Wq_0}{Vc_0}>1$ and the exponential term is expressed as a series expansion, the proof is self-evident. When $\frac{Wq_0}{Vc_0}<1$, the above inequality is rearranged to an equivalent form, namely:

$$\frac{1}{e^{+\left(1-\frac{Wq_0}{Vc_0}\right)c_0k_1t}} > \frac{1}{1+\left(1-\frac{Wq_0}{Vc_0}\right)c_0k_1t+\left(1-\frac{Wq_0}{Vc_0}\right)^2(c_0k_1t)^2+\ldots}$$

where the power series results from the reciprocal of $1-\left(1-\frac{Wq_0}{Vc_0}\right)c_0k_1t$. Again the inequality is proved by a term-for-term comparison with the series expansion of the exponential.

For the case where W/V is held constant, it can be shown again from eq (5) that:

$$\left.\frac{\partial q}{\partial c_0}\right|_{W/V}=\frac{\frac{q_0}{c_0}\left(\frac{Wq_0}{Vc_0}\right)-\left[\frac{q_0}{c_0}\left(\frac{Wq_0}{Vc_0}\right)+\frac{q_0}{c_0}(c_0k_1\,t)\left(\frac{Wq_0}{Vc_0}-1\right)\right]e^{-\left(\frac{Wq_0}{Vc_0}-1\right)c_0k_1t}}{\left[\frac{Wq_0}{Vc_0}-e^{-\left(\frac{Wq_0}{Vc_0}-1\right)c_0k_1t}\right]^2} \tag{15}$$

and by the same type of reasoning as in the previous case, it follows that $\left.\frac{\partial q}{\partial c_0}\right|_{W/V}>0$.

10. Simplified Method for Evaluating Parameters

Most of the present treatment included in eqs (11) through (15) has been concerned with the special requirements of eq (5) that q be considered a function of the ratio W/V or of c_0, but that t be held constant. The least-squares method (method 2 illustrated in the appendix) of determining the optimum values for q_0 and k_1 is exact and applicable in all cases—even when the values of the three independent variables are simultaneously changed from batch to batch. At best, however, the method is laborious, since it is based on a process of successive approximations. The experimental arrangement also is somewhat inefficient in that it limits each batch to one experimental point. The experimental setup would be much simpler if, say, only one flask were used and the course of adsorption as a function of time were measured *in situ*. This would be equivalent to the consideration of q as a function only of t. This gives rise to the simplest and quickest determination of q_0 and k_1 from only two measurements by judicious choice of the intervals. Let q_1 correspond to the time t_1, and q_2 to time t_2 such that $t_2=2t_1$. If eq (5) is solved for its exponential term and the data of these two experimental points are substituted back, the following pair of equations results:

$$\left.\begin{aligned} e^{-\left(\frac{Wq_0}{Vc_0}-1\right)c_0k_1t_1}&=\frac{q_0-q_1\left(\frac{Wa_0}{Vc_0}\right)}{q_0-q_1} \\ e^{-2\left(\frac{Wq_0}{Vc_0}-1\right)c_0k_1t_1}&=\frac{q_0-q_2\left(\frac{Wq_0}{Vc_0}\right)}{q_0-q_2} \end{aligned}\right\}. \tag{16}$$

They may be solved simultaneously by squaring both sides of the first equation and eliminating the exponent. The equation which remains may be solved directly for q_0 to yield eq (17).

$$q_0=\frac{q_1^2\left[q_2\left(\frac{W}{Vc_0}\right)-1\right]}{q_1^2\left(\frac{W}{Vc_0}\right)-2q_1+q_2}. \tag{17}$$

Then, by back substitution it can be shown that:

$$k_1=\frac{\ln\left[\frac{q_0-q_1\left(\frac{Wq_0}{Vc_0}\right)}{q_0-q_1}\right]}{c_0t_1\left(1-\frac{Wq_0}{Vc_0}\right)}. \tag{18}$$

An excellent opportunity for testing the self-consistency of eqs (17) and (18) is afforded by the previously cited reference of Dryden and Kay [1]. They used a conductivity cell head attached to the adsorption flask to measure changes in concentration of aqueous acetic acid as a function of time. The adsorbent was steam-activated coconut carbon. The total duration of their adsorption experiment was 60 min (at 30±0.5 °C) at the end of which time, adsorption was virtually complete. The weight, W, of the carbon was 3.00 g; the volume V of solution was 100 ml; and the initial concentration c_0 of acetic acid was 0.0306 N. After the first 5 min, Dryden and Kay measured the following concentrations at the times indicated:

t min	c meq·ml^{-1}
10. 0	0. 0200
15. 0	. 0185
20. 0	. 0166
30. 0	. 0155
45. 0	. 0147
60. 0	. 0140

The 10.0 and 20.0 min data give rise to q_1 and q_2 values of 0.3533 and 0.4667 meq·g^{-1}, respectively, by application of eq (3). These, in turn, may be substituted in eqs (17) and (18) to yield q_0 and k_1 directly. A second independent determination results from the 15.0 and 30.0 min data and a third determination from the 30.0 and 60.0 min data. These determinations are, respectively:

q_0 meq·g^{-1}	k_1 ml·meq^{-1}·min^{-1}
0·576	3·94
·573	3·55
·565	3·74

In dimensions comparable to the work of the present paper this would correspond to about 570 μeq·g^{-1} for q_0 and about 0.22 ml·μeq^{-1}·hr^{-1} for k_1. It is seen, for example, that Dryden and Kay's charcoal exhibited about ten times the capacity for acetic acid adsorption from aqueous solution as did our service bone char for sulfate from a raw sugar liquor. Also, their rate constant was greater by about the same factor despite their lower temperature, as might have been anticipated qualitatively because of the differences in viscosities.

The methods given in the appendix for determining the parameters from batch adsorption were devised for desk calculator computation. Where many batch experiments are to be made on a routine basis, or where it may be preferred to use eq (19) in place of eq (5) it is more practical to enlist the services of a digital computer.

11. General Equation When Desorption Is Appreciable

In the event that the desorption rate constant k_2 is retained in the integration of eq (1), the resultant adsorption equation becomes:

$$\frac{(M-N)-q}{(M+N)-q}=\frac{M-N}{M+N}\,e^{-2N\left(\frac{W}{V}\right)k_1t} \tag{19}$$

where

$$M=\frac{V}{2W}\left[\frac{k_2}{k_1}+c_0\left(1+\frac{Wq_0}{Vc_0}\right)\right]$$

and

$$N=\left(M^2-\frac{V}{W}\,q_0c_0\right)^{\frac{1}{2}}.$$

Equation (19) reduces to eq (5), as expected, when k_2 is set equal to zero. By the same token W/V is eliminated by means of eq (3), and it is interesting to show that as time, t, goes to infinity, equation (19) reduces to the familiar Langmuir adsorption isotherm:

$$\frac{q}{q_0}=\frac{Kc}{1+Kc} \tag{20}$$

where the equilibrium constant K is defined in the usual way as the ratio of the individual rate constants, k_1/k_2.

12. Summary

A batch adsorption equation was derived which expresses the amount of solute adsorbed per unit weight of adsorbent at constant temperature as a function of solution volume, concentration, amount of adsorbent, and time of contact. The equation is given in terms of only two constants, both of which have physical significance and are extremely useful in adsorption work. One of these parameters, q_0, is a measure of the maximum adsorptive capacity of the adsorbent for the solute or species adsorbed, while the other parameter, k_1, is the specific adsorption rate constant applicable at that temperature.

For known mixtures of different mesh (or grain size) of the same adsorbent the adsorptive capacity appeared to be an additive property.

The relative abundance of adsorption sites exhibited by a family of carbonaceous adsorbents for adsorption of organic colorant molecules was approximately proportional to the known surface areas of the adsorbents.

Adsorptive capacities and rate constants obtained from the batch adsorption equation were in substantial agreement with the numerical values for the same parameters obtained from column adsorption experiments performed simultaneously under identical conditions.

13. Appendix. General Methods for Calculating q_0 and k_1

13.1. Method 1

The first method illustrated is applicable to eq (4). Let $F_{(\mathrm{exp})}$ and $F_{(\mathrm{cal})}$ be defined such that

$$F_{(\mathrm{exp})}=\ln c_0/c \tag{1a}$$

and

$$F_{(\mathrm{cal})}=-\ln\,(1-q/q_0)+k_1\frac{\partial F_{(\mathrm{cal})}}{\partial k_1} \tag{2a}$$

$$\frac{\partial F_{(\mathrm{cal})}}{\partial k_1}=\left(\frac{W}{V}\,q_0-c_0\right)t \tag{3a}$$

$$\frac{\partial F_{(\mathrm{cal})}}{\partial q_0}=\frac{W}{V}\,k_1t-\frac{q/q_0^2}{1-q/q_0} \tag{4a}$$

and

$$\Delta F=F_{(\mathrm{exp})}-F_{(\mathrm{cal})} \tag{5a}$$

A value for q_0 is assumed. Now in the equation:

$$\Delta F=\ln c_0/c+\ln\,(1-q/q_0)-k_1\frac{\partial F_{(\mathrm{cal})}}{\partial k_1} \tag{6a}$$

which may be separately determined for each point, numerical values are assignable to all quantities except k_1 and ΔF. A "best" value of k_1 consistent with the initial choice of q_0 is obtained by least-squaring ΔF over all points. This results in the equation:

$$k_1\sum\left(\frac{\partial F_{(\mathrm{cal})}}{\partial k_1}\right)^2=\sum\left\{\frac{\partial F_{(\mathrm{cal})}}{\partial k_1}\,[\ln\,c_0/c+\ln\,(1-q/q_0)]\right\} \tag{7a}$$

from which the first k_1 is evaluated.

If both q_0 and k_1 were now to be "corrected" by adding to each the quantities Δq_0 and Δk_1, respectively, according to the first terms of a Taylor's expansion in two variables [27], one of the resultant normal equations obtained from all the points would be:

$$\Delta q_0\sum\left(\frac{\partial F_{(\mathrm{cal})}}{\partial q_0}\right)^2+\Delta k_1\sum\left(\frac{\partial F_{(\mathrm{cal})}}{\partial q_0}\,\frac{\partial F_{(\mathrm{cal})}}{\partial k_1}\right)=\sum\left(\frac{\partial F_{(\mathrm{cal})}}{\partial q_0}\cdot\Delta F\right). \tag{8a}$$

However, in the present application k_1 is held constant temporarily while q_0 is allowed to vary, hence the second term of eq (8a) vanishes and there results:

$$\Delta q_0 \sum \left(\frac{\partial F_{(\mathrm{cal})}}{\partial q_0}\right)^2 = \sum \left(\frac{\partial F_{(\mathrm{cal})}}{\partial q_0} \cdot \Delta F\right) \qquad (9\mathrm{a})$$

from which a Δq_0 is computed.

The sign of Δq_0 indicates the direction of the next choice for q_0 although its magnitude usually will grossly underestimate the extent of the correction. However, a plot of Δq_0 against q_0 quickly discloses, after a few trials, the choice of q_0 which causes Δq_0 to vanish. Concurrently, it can be verified that as successive q_0 choices are made closing the gap between the plus and minus values of Δq_0, the magnitude of the corresponding new sums computed for $\Sigma(\Delta F)^2$ tend toward a minimum.

Method 1 is subject to some bias, partly because it compares solution concentrations instead of amounts absorbed per gram and partly because the comparison is logarithmic. Despite these disadvantages, it requires successive choices of q_0 only, and it is applicable over wide ranges. An example of the application of method 1 was indicated in table 1b.

13.2. Method 2

The second method is applicable to eq (5). It is free from the serious limitations of method 1 and follows a more conventional procedure, as given by Scarborough [27]. The value of q obtained by substituting the experimentally observed value of c into eq (3) is termed $q_{(\mathrm{obs})}$. For a given choice of k_1 and q_0, eq (5) may be used to calculate a q for each combination of W, V, t, and c_0, and this value is designated $q_{(\mathrm{calc})}$. Thus, $\Delta q = q_{(\mathrm{obs})} - q_{(\mathrm{calc})}$. By obtaining partial derivatives of q in eq (5) it can be verified that:

$$\frac{\partial q}{\partial k_1} = \frac{\left(\frac{Wq_0}{Vc_0} - 1\right)^2 c_0 q_0 t \, e^{-\left(\frac{Wq_0}{Vc_0}-1\right) c_0 k_1 t}}{\left[\frac{Wq_0}{Vc_0} - e^{-\left(\frac{Wq_0}{Vc_0}-1\right) c_0 k_1 t}\right]^2} \qquad (10\mathrm{a})$$

and

$$\frac{\partial q}{\partial q_0} = \frac{q_{(\mathrm{calc})}}{q_0} + \frac{\frac{Wq_0}{Vc_0}\left\{\left[\left(\frac{Wq_0}{Vc_0}-1\right) c_0 k_1 t + 1\right] e^{-\left(\frac{Wq_0}{Vc_0}-1\right) c_0 k_1 t} - 1\right\}}{\left[\frac{Wq_0}{Vc_0} - e^{-\left(\frac{Wq_0}{Vc_0}-1\right) c_0 k_1 t}\right]^2}. \qquad (11\mathrm{a})$$

For a particular choice of k_1 and q_0, the quantity $\Sigma(\Delta q)^2$ (summed over all n measurements) is a measure of goodness to fit . . . the smaller the summation value, the better the choice of k_1 and q_0. The initial choice of these parameters has been successively improved by adding to k_1 the quantity:

$$\Delta k_1 = \frac{\sum \left(\frac{\partial q}{\partial k_1} \cdot \Delta q\right)}{\sum \left(\frac{\partial q}{\partial k_1}\right)^2} \qquad (12\mathrm{a})$$

and by adding to q_0 the quantity:

$$\Delta q_0 = \frac{\sum \left(\frac{\partial q}{\partial q_0} \cdot \Delta q\right)}{\sum \left(\frac{\partial q}{\partial q_0}\right)^2}. \qquad (13\mathrm{a})$$

It should be pointed out that this procedure assigns *all* of the variability of q first to one parameter and then to the other. Thus, it tends to *over-correct*, but by a lesser amount each trial. After a few such trials have been made, in a given experiment, if is usually possible to converge more quickly by a weighted averaging of the results so far. This separate adjustment has been found to work consistently better than by assigning the variability in q to a *simultaneous* adjustment in k_1 and q_0.

Example: In a batch experiment for adsorption of sulfate ion on service bone char 117–B the following data were obtained: $c_0 = 9.90$ μM.ml^{-1}.

Sample No.	W/V	t	c/c_0	$q_{(\mathrm{obs})}$
	$g \cdot ml^{-1}$	hr		$\mu M . g^{-1}$
2	1. 010	0. 5	0. 512	4. 78
3	1. 010	1. 0	. 339	6. 47
4	1. 010	1. 5	. 291	6. 95
5	1. 010	2. 0	. 244	7. 10
7	1. 010	4. 0	. 188	7. 96
6	1. 212	4. 0	. 135	7. 05
8	0. 808	4. 0	. 330	8. 21
9	. 606	4. 0	. 209	12. 92

By starting with an initially assumed value for q_0 of about 33 using the first method, a corresponding value of 0.017 for k_1 was determined. After four trials had been made, improved values of $q_0 \approx 15.5$ and $k_1 \approx 0.0437$ were obtained. For most purposes these approximate values might be sufficient and consistent with experimental error. However, for purposes of illustration, the second method was used to refine these results still further. The following table summarizes the successive improvements:

Trial	Values assumed		$\Sigma(\Delta q)^2$	Resultant corrections	
	q_0	k_1		Δq_0	Δk_1
	$\mu M \cdot g^{-1}$	$ml \cdot \mu M^{-1} \cdot hr^{-1}$	$\mu M^2 \cdot g^{-2}$	$\mu M \cdot g^{-1}$	$ml \cdot \mu M^{-1} \cdot hr^{-1}$
1	15. 53	0. 0437	21. 63	+3. 99	+0. 0186
2	19. 32	. 0623	12. 20	−2. 39	−. 0105
3	16. 93	. 0518	11. 56	+1. 43	+. 0083
4	18. 36	. 0601	10. 57	−1. 10	−. 0043
5	17. 73	. 0573	10. 29	−0. 017	+. 0011

Thus it is seen after the fifth trial that even though the degree of fit (as measured by $\Sigma(\Delta q)^2$) had been improved by a factor of two, the values of q_0 and k_1 had only changed from 15.5 to 17.7 and from 0.044 to 0.057, respectively. In addition, the final

Δq_0 and Δk_1, quantities amounted to changes of less than 0.1 and 2 percent, respectively, in q_0 and k_1. Further refinement could not be justified.

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