ADSORPTION OF STRYCHNINE SULPHATE BY VARIOUS CHARCOALS AND BY LLOYD'S REAGENT.[1]

BY JOHN F. SUCHY[2] AND R. V. RICE.

In various phases of industry charcoal ranging from the crude technical product to the highly activated form finds much practical application. The pharmacist in his field is often called upon to use charcoal either as a filtering or as an adsorbent medium and as a rule but little consideration is given to the amount of active medicinal ingredient which may be lost in the process. It is also of interest to know relatively the adsorbing power of these filtering media.

The present research was undertaken to gain some information as to the diminution of potency of strychnine sulphate solutions when brought in contact with a number of commercial charcoals and with Lloyd's Reagent. The results obtained show relatively the adsorbing powers of these media with respect to almost any dissolved substance (1).

EXPERIMENTAL.

Identical procedures were followed in all cases to show the variation of adsorption of strychnine sulphate by the various adsorbing media. Groups of from five to ten samples were run together, each sample representing a different concentration of strychnine sulphate.

The following procedure was employed:

Exactly one Gm. of adsorbent was weighed out and a calculated quantity of strychnine sulphate added. To this was added exactly 100 cc. of distilled water and the mixture tightly stoppered and warmed on a steam-bath until solution of the alkaloidal salt was effected. Each flask was then cooled to 25° C. and allowed to stand for 24 hours in a wall case where the variation of temperature was not over 2 degrees. The contents were shaken frequently to aid in reaching equilibrium. After the proper time interval, the mixtures were filtered and a 25-cc. portion of each was pipetted into a separatory funnel. The solution in each case was made alkaline with 5 cc. of 10 per cent ammonia and allowed to stand a short time until completion of precipitation. The strychnine was then entirely extracted with chloroform, the latter being added in small portions. Each chloroformic solution was filtered into a tared beaker which was then placed in a 50-degree oven where the solvent was evaporated. The residue was finally dried in another oven at 100° C. for about 30 minutes, weighed and calculated as the sulphate. The difference between this result and the original weight of the sulphate gave the amount of the latter adsorbed per Gm. of charcoal.

Each sample of the strychnine salt used in this study was assayed by dissolving a carefully weighed quantity in water, making the solution alkaline with ammonia, and extracting the resulting alkaloid with chloroform. The strychnine thus obtained was calculated as the sulphate. Any deviation from the pure salt was taken into consideration in all subsequent determinations.

In order to obtain an idea of the amount of strychnine sulphate adsorbed by the filter paper used in the process, a series of blank determinations was run, the charcoal being omitted. The other details of the procedure were identical. The results obtained showed such small deviations from no adsorption that any loss due to this factor was neglected.

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[1] This article is based on a dissertation by R. V. Rice presented in partial fulfilment of the degree of Master of Science at the University of Montana, 1934.

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DISCUSSION.

I. Solvent—Water. Time—24 Hours.—Seven different charcoals and Lloyd's Reagent were used in this investigation. Charcoals designated by number are activated forms sold on the market to-day.

By plotting the original concentration of strychnine sulphate against the amount adsorbed per Gm. of charcoal, an isotherm was obtained in each case as is shown in Figs. 1 and 2 which represent the adsorption efficiency.

Charcoal No. 1 proved by far the best adsorbent of the group, adsorption being complete up to a concentration of nearly 5 Gm. per L. None of the other charcoals used showed total adsorption beyond concentrations of 2 Gm. per L. On the other hand, willow charcoal (Curve No. 7), the type used in most pharmaceutical operations, proved by far the poorest adsorbent of the group, taking up only 11 per cent of the salt when the original concentration was but 1 Gm. per L.

Bone black (Curve No. 6) showed a surprisingly high adsorbing power. Like the willow charcoal there was no finite concentration at which total adsorption took place, but the percentage of adsorption dropped much less rapidly with increasing concentrations.

The other carbons used proved intermediate in their affinity for the alkaloidal salt. No. 2 and No. 4 gave total adsorption in concentrations to almost 2 Gm. per L., while No. 3 and No. 5 adsorbed completely up to about 1 Gm. per L. Lloyd's Reagent (Curve No. 8) also proved an intermediate adsorbent but differed from the others in that the percentage adsorbed at higher concentrations fell much less rapidly.

In order to make a direct comparison of the adsorption efficiency of each charcoal in the different concentrations, the results were tabulated to show the per cent of strychnine sulphate adsorbed. These results are shown in Table I.

TABLE I.—PER CENT OF STRYCHNINE SULPHATE ADSORBED.

	Concentration—Gm. per L.									
Adsorbent.	1.	2.	3.	4.	5.	6.	7.	8.	10.	12.
Charcoal No. 1	100	100	100	100	97.7	89.0	77.9	69.0	56.1	47.1
Charcoal No. 2	100	94.5	76.3	62.6	52.0	44.2	38.9	34.4	28.8	25.9
Charcoal No. 3	100	95.5	80.4	69.3	60.1	51.7	44.7	39.2	31.5	26.4
Charcoal No. 4	100	89.0	66.3	51.9	41.9	35.2	30.3	26.5	21.7	18.5
Charcoal No. 5	94.0	75.6	63.3	54.5	48.0	42.8	38.4	34.6	28.6	24.0
Bone black	36.3	36.0	35.4	34.7	33.5	31.7	29.8	27.9	24.7	21.6
Lloyd's Reagent	100	83.2	75.4	65.2	55.5	49.0	43.7	39.3	33.2	28.3
Willow charcoal	11.0	10.3	10.0	7.8	6.3	5.3	4.5	3.8	3.2	2.6

II. Langmuir's Equation.—Langmuir's equation for the expression of adsorption isotherms has been found in most cases to hold more nearly true over wider ranges of concentration than does Freundlich's equation (2).

These equations are:

1. Langmuir's equation, $\frac{C}{Q} = \frac{1}{ab} + \frac{C}{b}$, where C is the original concentration, Q is the quantity adsorbed and a and b are constants.

2. Freundlich's equation, $\left(\frac{x}{m}\right)^n = kc$, where x is the amount adsorbed, m is the weight of adsorbent and c is the original concentration, k and n being constants.

By plotting logarithms of the values of x/m against c of Freundlich's equation a straight line results if the original curve obtained by plotting x/m against c proves to be a parabola (3). As can be seen by inspection of the isotherms of Figs. 1 and 2, none of these curves is by any means perfect parabolas, hence Freundlich's equation is not suitable for the expression of these isotherms.

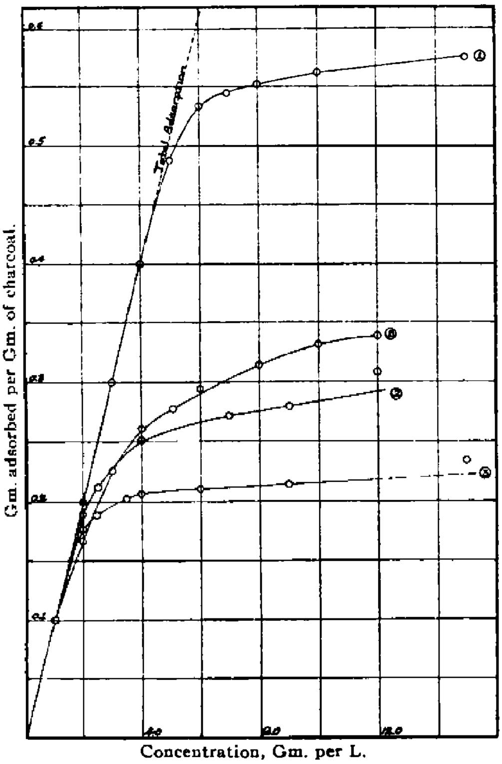

Fig. 1.

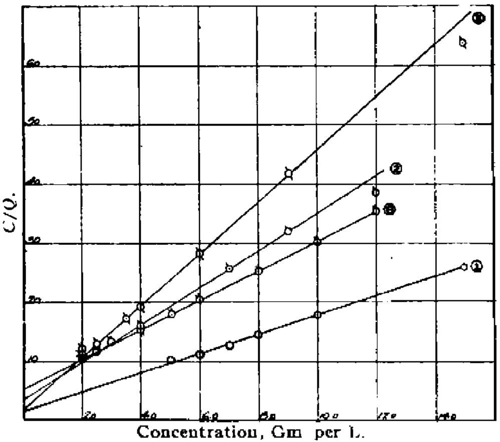

Fig. 3.

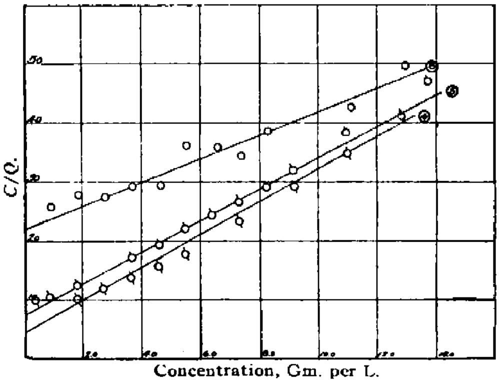

Fig. 4.

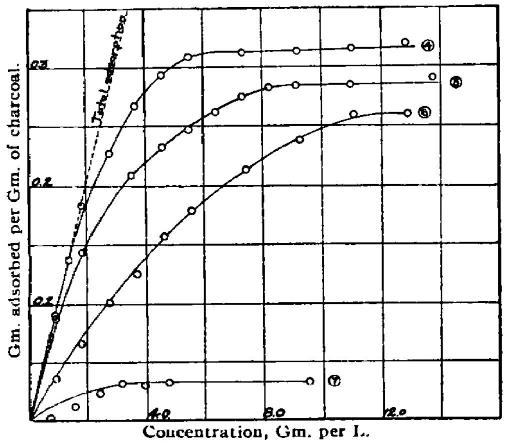

Fig. 2.

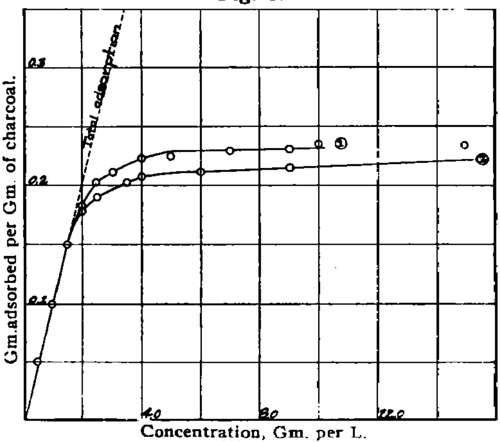

Fig. 5.

On the other hand the plotting of C/Q against C of Langmuir's equation gives a near straight line in most of the cases tried. The plots of these values are shown in Figs. 3 and 4. It was found that the sample of willow charcoal used yielded such extremely high values for C/Q that plotting of its curve in these figures was impossible. The large variation also obtained in the values of C/Q indicates that this equation does not represent the isotherm very satisfactorily. All the other curves conform quite well to the equation as shown by the figures (see Figs. 3 and 4: Curve 6—bone black; Curve 8—Lloyd's Reagent).

TABLE II.—CONSTANTS OF LANGMUIR'S EQUATION.

Charcoal.	*a*.	*b*.
No. 1	1.154	0.610
No. 2	0.144	0.336
No. 3	1.969	0.231
No. 4	0.329	0.483
No. 5	0.318	0.393
Bone black	0.062	0.734
Lloyd's Reagent	0.455	0.400

The constants *a* and *b* of Langmuir's equation were calculated for each carbon by plotting the curves of Figs. 3 and 4 on quite a large scale in order to obtain the slope of the lines and their Y-intercepts more accurately. These values are shown in Table II.

III. Solvent—Water. Time—48 Hours.—The same procedure employed in the preceding 24-hour determinations was followed in this case, with the exception that the period of contact was prolonged to 48 hours. Isotherms were determined for Charcoal No. 1 and Charcoal No. 3.

Charcoal No. 1 gave an isotherm identical with the one obtained in the shorter period of contact. This means that equilibrium must have been reached between the adsorbent and the strychnine sulphate solution within 24 hours of contact and this equilibrium was permanent for at least an additional 24 hours.

Charcoal No. 3 on the other hand adsorbed more alkaloid when left in contact with the solution for 48 hours than it did in the shorter period of time. The results indicate that it takes more than 24 hours for Charcoal No. 3 and strychnine sulphate solution to reach adsorption equilibrium. The 48-hour curve in this instance probably represents the equilibrium but no determina-

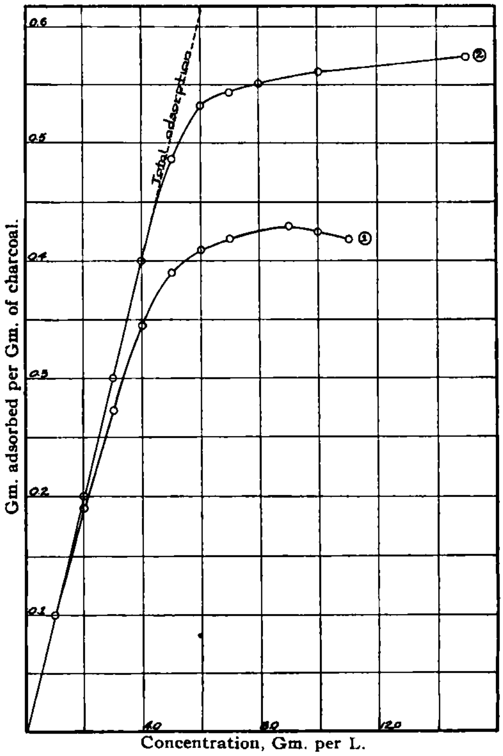

Fig. 6.

tion involving a longer period of time was run to prove this presumption. Curve 1 of Fig. 5 is the 48-hour isotherm while Curve 2 is the result obtained in the shorter period of contact.

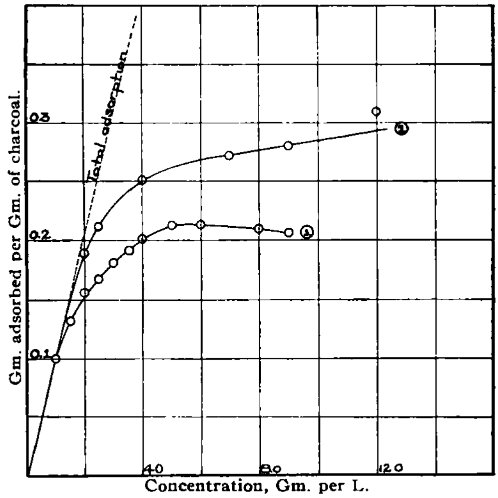

Fig. 7.

IV. Solvent—Alcohol. Time—24 Hours.—The amount of adsorption is dependent upon the surface tension of the solvent (4); hence the use of alcohol in place of water should give a different isotherm when all the other factors are constant.

The effects of such a change were determined in the cases of Charcoals No. 1 and No. 2, using commercial alcohol sp. gr. 0.810 at 26° C. which corresponds to about 94 per cent by volume.

Figure 6 shows the results secured by use of Charcoal No. 1, Curve 1 with alcohol and Curve 2 with water. A marked drop in adsorption is evidenced in the alcohol solution, showing total adsorption to a concentration of only 1.5 Gm. per L. of alkaloidal salt. The alcohol curve also shows a maximum of adsorption at about 9 Gm. per L. concentration, whereas the water curve rises slowly but steadily upward after the usual sharp bend. Table III gives a direct comparison of the amounts adsorbed in each case.

TABLE III.—PER CENT ADSORBED BY CHARCOAL NO. 1.

	Concentration—Gm. per L.								
Solvent.	1.	2.	3.	4.	5.	6.	7.	8.	10.
Water	100	100	100	100	97.7	89.0	77.9	69.0	56.1
Alcohol	100	95.2	90.9	86.2	78.1	68.2	59.9	53.3	42.6

Charcoal No. 2 with alcohol (Fig. 7, Curve 1), shows the same type of diminution in adsorption as does Charcoal No. 1. The highest point of total adsorption occurs at a concentration of about 1 Gm. per L. This point is somewhat lower than that of Charcoal No. 1 and the maximum of the curve occurs at about 6 Gm. per L. concentration in contrast to 9 Gm. per L. concentration in the case of Charcoal No. 1. Table IV presents a direct comparison of quantities adsorbed at different concentrations in the two solvents.

TABLE IV.—PER CENT ADSORBED BY CHARCOAL NO. 2.

	Concentration—Gm. per L.								
Solvent.	1.	2.	3.	4.	5.	6.	7.	8.	10.
Water	100	94.5	76.3	62.6	52.0	44.2	38.9	34.4	28.8
Alcohol	100	78.0	61.5	50.3	42.5	35.7	30.4	25.3	20.2

SUMMARY.

1. The media studied vary widely in their ability to adsorb strychnine sulphate.
2. One charcoal was found to require more than 24 hours to reach an equilibrium of adsorption.

3. Langmuir's equation represents the adsorption curves better than does Freundlich's equation.

4. The ability of Charcoals No. 1 and No. 2 to adsorb strychnine sulphate from solution is less when the salt is dissolved in alcohol than when it is dissolved in water.

REFERENCES.

(1) "Activated Carbon—the Modern Purifier," pamphlet published by Industrial Chemical Sales Company, Inc. (1933).

(2) Langmuir, Irving, "Adsorption of Gases on Plane Surfaces of Glass, Mica and Platinum," *J. Am. Chem. Soc.*, 40, 1351–1403 (1918).

(3) Daniels, Mathews and Williams, "Experimental Physical Chemistry," page 95.

(4) Getman and Daniels, "Outlines of Theoretical Chemistry," page 240.

THE STABILIZATION OF SOLUTION OF IRON AND AMMONIUM ACETATE, U. S. P. X.[1]

BY WILLIAM J. HUSA[2] AND LYELL J. KLOTZ.

Husa and Birmingham (1) found that the stability of Solution of Iron and Ammonium Acetate is affected by various factors such as light, heat and variations in the proportions of the ingredients. In the present investigation, further experimentation was undertaken with a view toward increasing the stability of Solution of Iron and Ammonium Acetate, commonly known as Basham's Mixture.

Order of Mixing.—In the preparation of colloidal solutions, the order of mixing is often an important factor in the stability of the finished product, particularly when substances capable of acting as protective colloids are present. Birmingham (2) prepared Basham's Mixture by 12 different orders of mixing and stored the resulting preparations under three conditions, *i. e.*, sunlight, darkness and diffused light. Order of mixing appeared to have no effect upon the stability, except in a few cases of diffused light.

Since the tests carried out by Birmingham in diffused light gave some indication that order of mixing might be a factor to consider, further tests were carried out on this point. The materials used were of U. S. P. grade, the ammonium carbonate assaying 31.2% ammonia and the diluted acetic acid being adjusted to 6.0%. Solutions were prepared by two methods: (*a*) hand mixing, shaking well after the addition of each ingredient, and (*b*) mechanical mixing, adding each ingredient drop by drop from a burette into a beaker fitted with an electric stirrer, five minutes being allowed after the final addition of each ingredient and efficient mechanical stirring being maintained throughout the process.

In order to designate the orders of mixing concisely, the following numbers are assigned to the various ingredients:

1. Solution of Ammonium Acetate.
2. Diluted Acetic Acid.
3. Tincture of Ferric Chloride.
4. Aromatic Elixir.
5. Glycerin.
6. Water.

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[1] Section on Practical Pharmacy and Dispensing, A. Ph. A., Washington meeting, 1934.

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