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BY CHARCOAL

THESIS FOR

EVELYN

Adsorption



ADSORPTION OF LACTIC ACID BY
CHARCOAL AND SILICA GEL

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ADSORPTION OF LACTIC ACID BY CHARCOAL AND SILICA GEL

The phenomenon of adsorption was first observed about 1777, by the Swedish chemist, Scheele, who noted that charcoal exhibited the property of retaining various gases without undergoing any apparent chemical change. Later, Lowitz (C.F. Ostwald, Lehrbuch allgem. Chemie, 2nd Ed. I, 1093 (1891)) made an even more startling observation - i.e. that charcoal takes up dissolved substances from solution and retains them as it does gases. These two investigators opened up an entirely new field of research and since that time a vast amount of work has been done along the line of adsorption, great advances having been made during the past 20 or 25 years. Not only has charcoal been used as the adsorbent, but kaolin, clay, fuller's earth, silica gel, finely divided platinum, etc., as well.

Freunlich, Gibbs, Langmuir and others have advanced new theories of adsorption, but thus far no satisfactory explanation of the nature of the phenomenon has been wholly accepted.

Langmuir's theory of adsorption (J.Am.Chem.Soc., 38 2267 (1916) 39 1883 (1917)) assumes that the forces acting in adsorption are nearly the same kind as all the forces

causing chemical combinations. The atomic forces seem to be developed from deviation of the orbits of the outer electrons in the atoms. The forces acting in ordinary chemical reactions are the result of the large deviations of these orbits, whereas in adsorption the forces acting would be due to comparatively small deviations. Langmuir further assumes that on the surface of a crystal there are a certain number of points where there are residual valencies and that adsorption consists of a fixing of the adsorbed atoms at these points on the surface, each point or space being able to hold one atom or molecule so that the adsorbed layer is only one molecule in thickness.

Another adsorption theory of quite the opposite view is that advanced by Eucken (Ber., 16, 345 (1914)) and Polanyi (Ber., 16, 1012 (1914), 18, 55 (1916), Z. Elektrochem., 26, 370 (1920)). This theory assumes that the outer layer consists, not of a single layer of atoms or molecules, but of a polymolecular layer with the density varying continually from the adsorbing surface out into the free gas or liquid.

These are only two of the many theories that have been advanced and thus far experimental evidence is not sufficient to warrant acception of any one theory. However, it seems plausible to assume that in adsorption, surface forces pre-

dominate. It is possible that chemical reactions may occur, but with fairly dilute solutions there seems to be no reason for considering the process to be other than that of surface condensation, which is adsorption.

It has been found in the case of adsorption from solution that if the amount adsorbed from the solution is plotted against the concentration of the solution a curve concave to the concentration axis results. The slope of the curve varies with the adsorbent material as well as with the solutes and solvents used.

A large amount of experimental work has been done in determining isotherms for such organic acids as oxalic, acetic, tartaric, but comparatively little has been done with lactic acid and in so far as lactic acid is supposedly oxidized by bone black (Boll Soc. ital. Boil. sper., 2, 884-7 (1927)) and decomposed by ultraviolet light (Z. physikal. chem. 71, 311-4) it was thought desirable to reinvestigate its behavior and to determine whether or not it acted like other organic acids.

Method of Procedure and Experimental Results

One gram of activated silica gel was allowed to stand in contact with 100 c.c. of lactic acid solution for at least 24 hours, but if any adsorption occurred it was so slight that it could not be determined by ordinary titra-

tion methods.

A similar sample of activated silica gel was then evacuated and allowed to come in contact with another 100 c.c. portion of approximately .5 N lactic acid. Again there was no evidence of any adsorption.

Failure to obtain any appreciable amount of adsorption with silica gel necessitated substituting charcoal for the adsorbent. Norite, sugar charcoal and an activated commercial charcoal were tried.

The lactic acid was 85% aqueous solution and had a specific gravity of 1.21. A definite quantity of solution, of known normality, 100 c.c. was placed in a glass stoppered 125 c.c. Erlenmeyer flask containing an accurately weighed amount of Norite, 1.000 gm., in each. The flasks were shaken vigorously for approximately 60 seconds and then allowed to settle, in a constant temperature water bath at $25^{\circ} \text{C} \pm .002^{\circ} \text{C}$. for 24 hours. The concentration of the solution was then determined by titration with sodium hydroxide solution, using phenolphthalein as an indicator.

The amounts adsorped represented by $\frac{X}{m}$ (grams of solute adsorped per gram of charcoal per 100 c.c. solution) in the Tables are not strictly accurate inasmuch as no attempt was made to correct for adsorption of solvent nor for the volume change due to adsorption of the solute. The unavoidable presence of CO_2 would also introduce further slight inaccuracy.

TABLE I.

Trial 1.	N. Before Adsorption	N. After Adsorption	$\frac{X}{m}$
	.000373	.0003554	.01107
	.001447	.0005675	.01814
	.006854	.0007962	.055
	.0137	.004272	.0855
	.0275	.01220	.1362
	.0691	.0521	.1503
	.1383	.1204	.1606
	.2740	.2590	.1351
	.5212	.5019	.1735
Trial 2.	.0002308	.001054 (Basic)	.01157
	.0004315	.0008797 "	.01181
	.001920	.0002634	.01985
	.003845	.0003173	.03177
	.0189	.0049	.12628
	.0373	.02088	.14867
	.0738	.05135	.20268
	.1869	.16848	.1663
	.3715	.5584	.1184
	.5585	.5469	.1039
	.7408	.7397	.1038

The results in Table I are plotted in Figure 1, Trial 1 represented in black, Trial 2 in red. The curves represent the average slope of the adsorption isotherm of Norite and lactic acid aqueous solution.

TABLE II.

Trial 1.

N. Before Adsorption	N. After Adsorption	$\frac{X}{m}$
.0123	.0023	.0900
.0225	.0088	.1226
.0380	.0196	.1662
.0484	.0317	.1506
.0923	.0738	.1662
.1246	.1036	.1891
.1467	.1240	.2041
.1511	.1298	.1922
.1881	.1638	.2182

Trial 2.

.00927	.00100	.0744
.0188	.00561	.1189
.0401	.0198	.1827
.0538	.0362	.2027
.0702	.0536	.1494

The results found in Table II are plotted in Figure 2, Trial 1 is in black, Trial 2 in red.

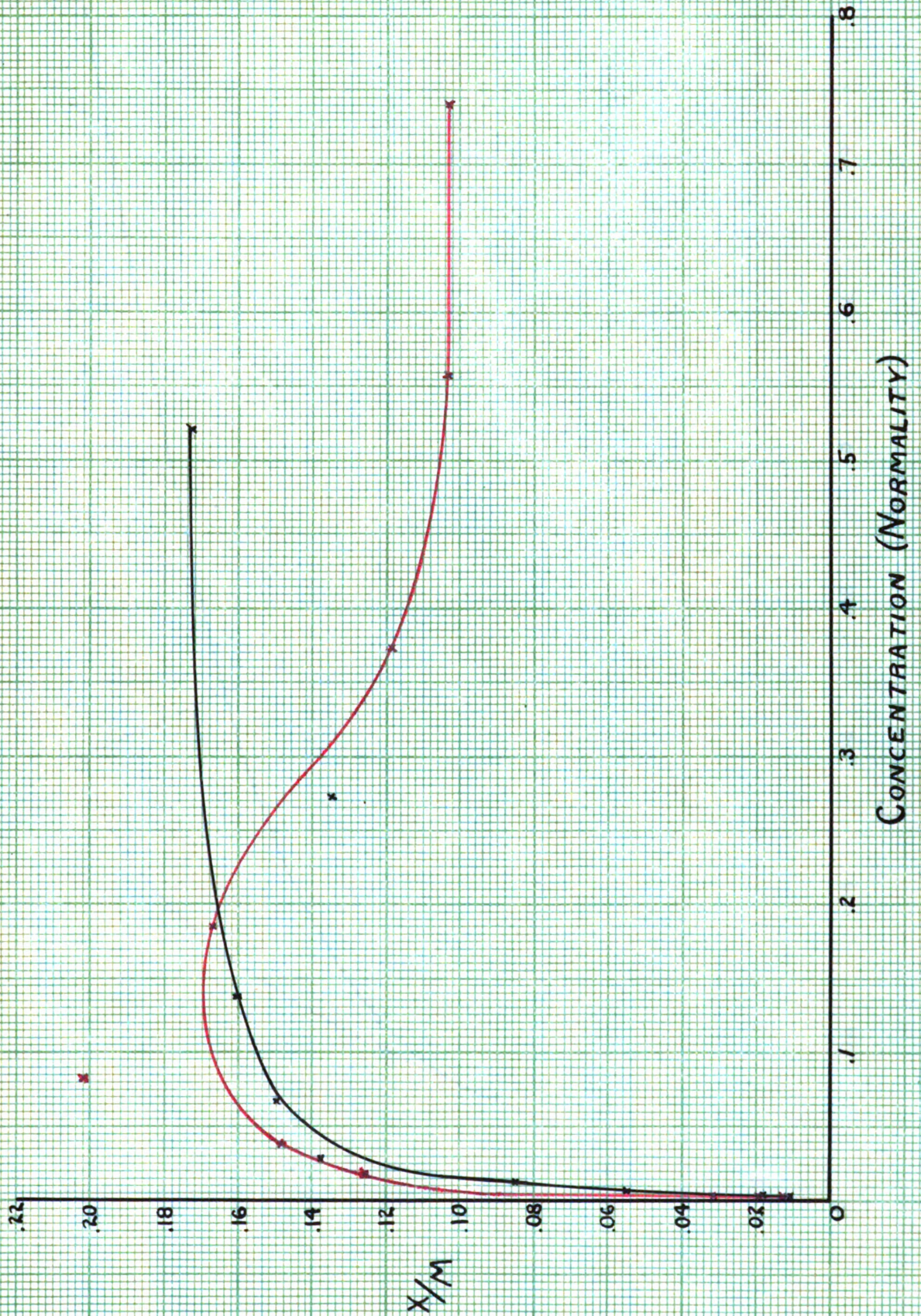


FIGURE 1.

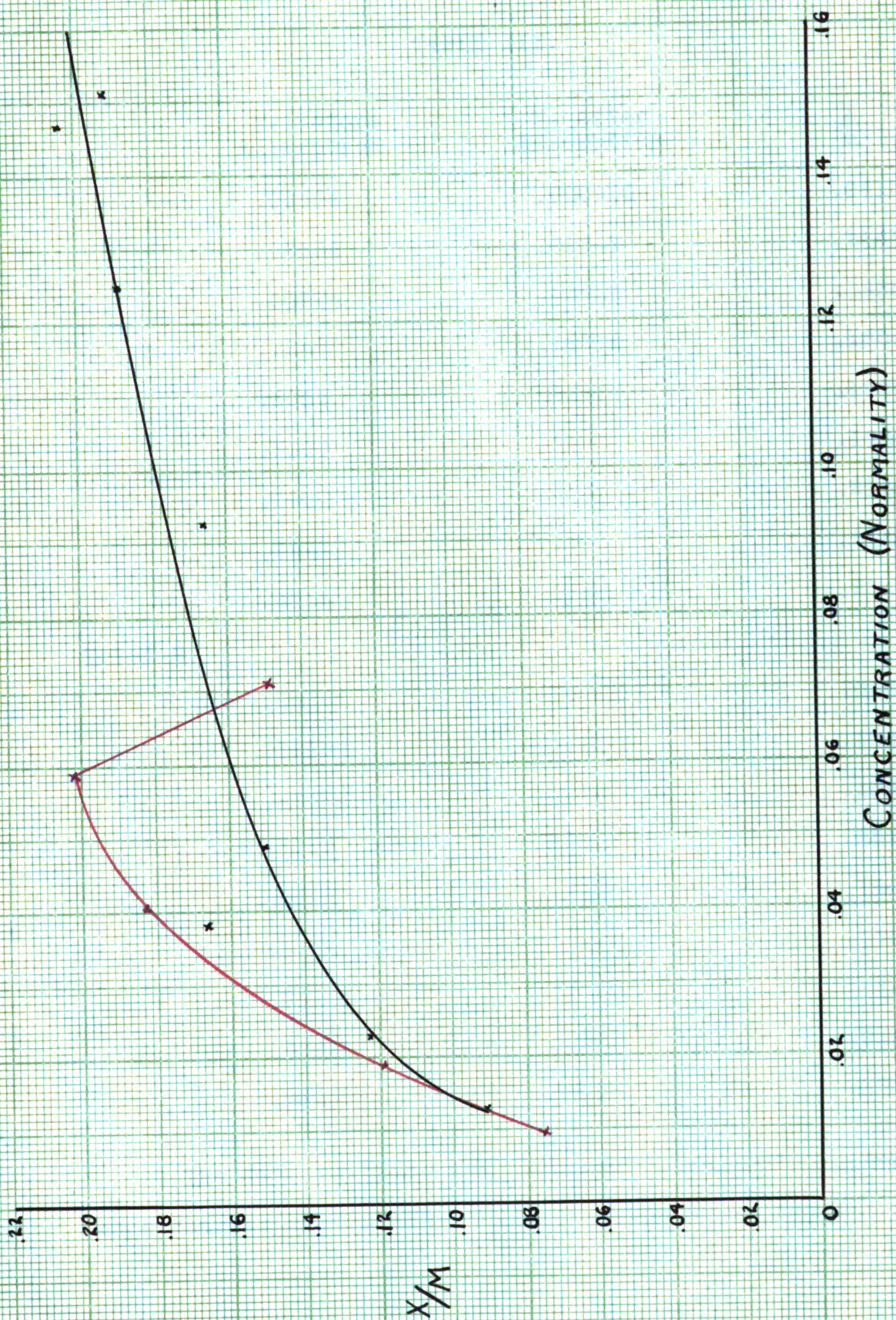


FIGURE 2.

TABLE III.

Trial 1.

N. Before Adsorption	N. After Adsorption	$\frac{X}{m}$
.00554	.000950	.0413
.02534	.01267	.1141
.05504	.03920	.1426
.1049	.08712	.1604
.2059	.1845	.1925
.3009	.2811	.1783
.3960	.3722	.2148
.4989	.4752	.2148
.6019	.5758	.2345

Trial 2.

.00554	.000712	.0435
.02534	.01267	.1141
.05504	.0376	.1569
.1049	.0863	.1676
.2059	.1845	.1865
.3009	.2811	.1783
.3960	.3722	.2148
.4989	.4752	.2148
.6019	.5821	.1783

The data in Table III, plotted in Figure 3, gives a more characteristic curve than is observed in Figures 1 and

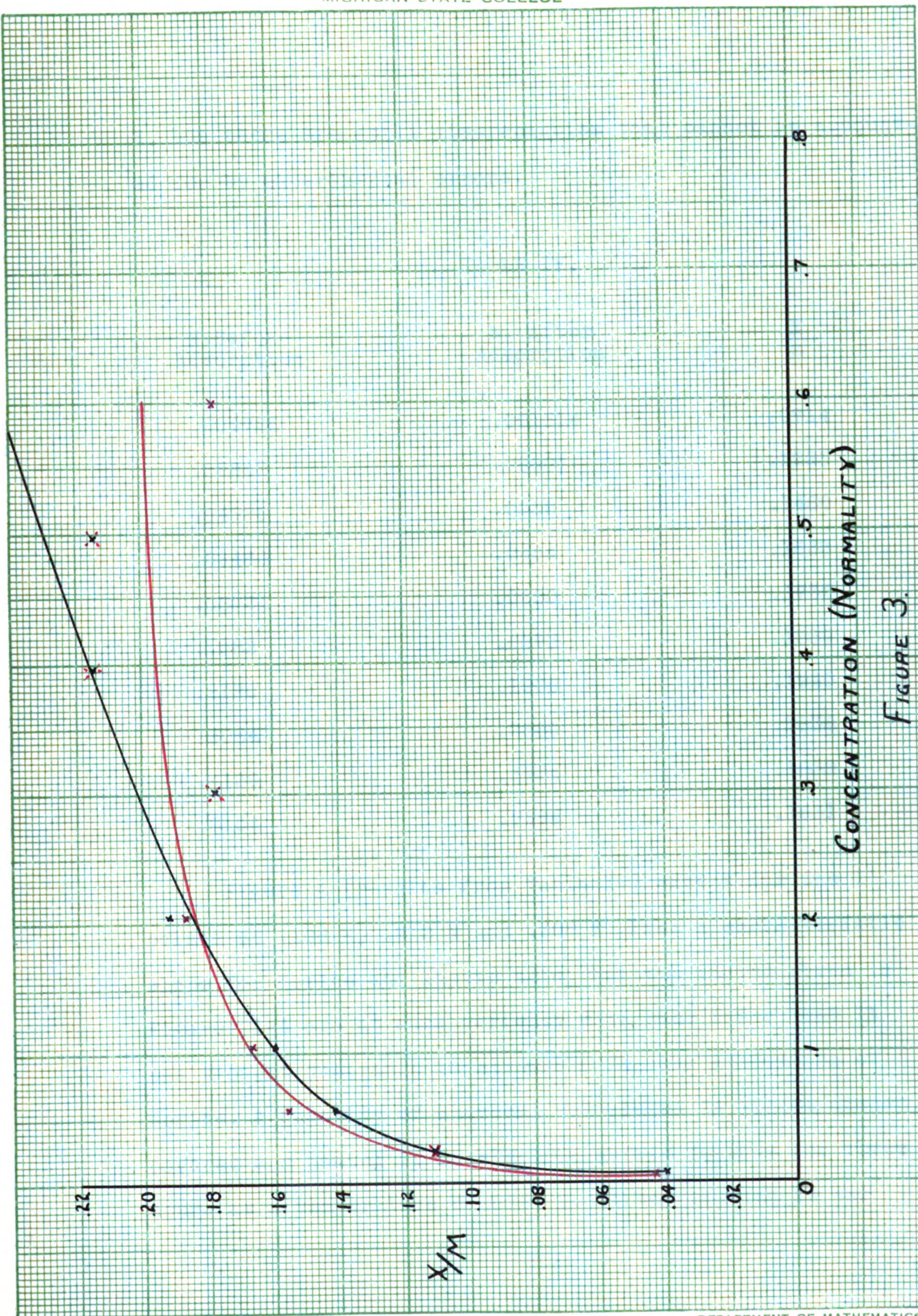


FIGURE 3.

2, but there are still discrepancies that cannot be accounted for by experimental errors.

TABLE IV.

N. Before Adsorption	N. After Adsorption	$\frac{x}{m}$
.009725	.001814	.0714
.02268	.00907	.1225
.04025	.0238	.1480
.06463	.0464	.1633
.08731	.0680	.1735
.1082	.0873	.1889
.2120	.1905	.1940
.3084	.2880	.1838
.4139	.3934	.1838
.8164	.7994	.1531

Figure 4 (results from Table IV) except for the points at .108 N, .212 N and .308 N gives a characteristic slope for Norite and lactic acid, but the curves given in Figures 1-4 are at such variance with each other that it was thought desirable to attempt a further activation of Norite. A quantity of charcoal was placed in silica dishes, covered and heated in an electric muffle furnace for three hours at a temperature of 500° C. After heating it was

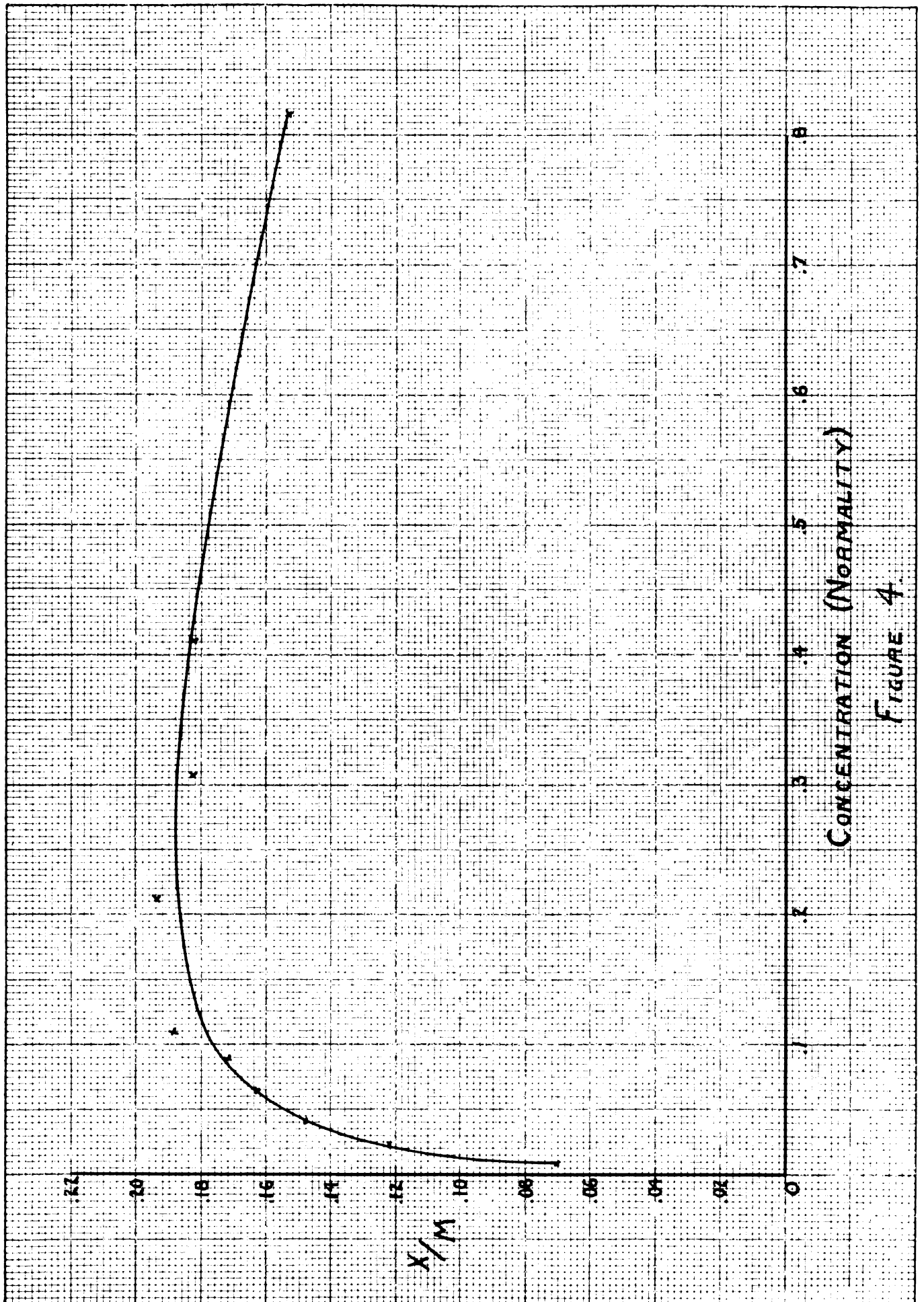


FIGURE 4

allowed to come to room temperature in a dessicator.

The following results were obtained when the activated Norite was used.

TABLE V.

Trial 1.

N. Before Adsorption	N. After Adsorption	$\frac{X}{m}$
.10692	.08534	.1943
.22438	.19863	.2208
.4487	.4217	.2430
.6621	.6376	.2208
.8975	.8632	.1545

Trial 2.

.000388	.000	.0080
.00413	.000186	.0355
.00850	.00148	.0632
.0207	.00643	.1273
.0423	.02225	.1808
.0823	.0608	.1942
.2059	.1802	.2318
.5493	.5227	.2391
.8141	.7945	.1776

The curves in Figure 5, black line, Trial 1, red line Trial 2, from Table V come nearer to coinciding and are more regular than those obtained in any of the previous

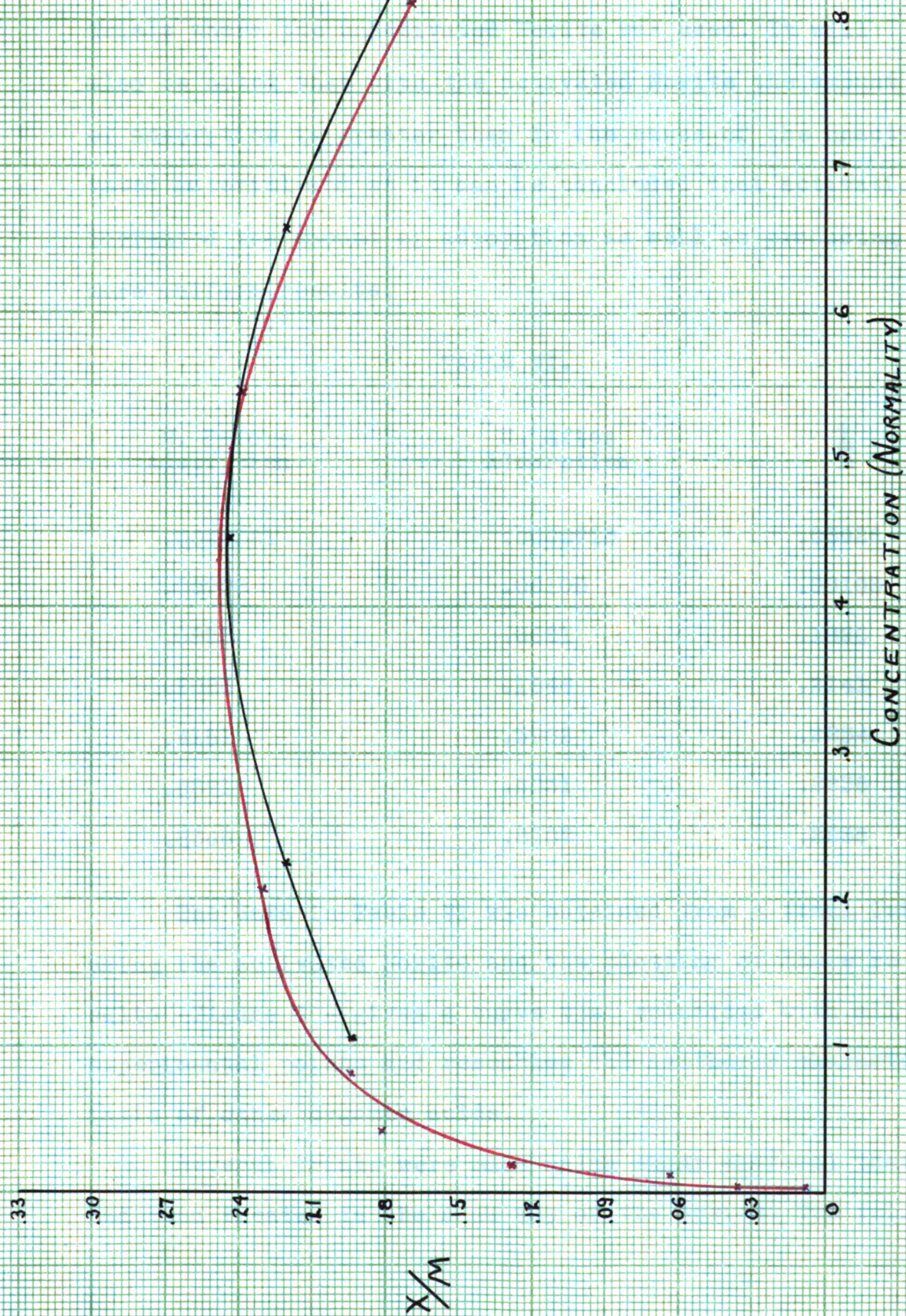


FIGURE 5.

Trials where the unactivated Norite was used. It will also be noted that with the activated Norite the amount of adsorption is greater than in the cases of the unactivated material and so it can be concluded that activation increased the amount of adsorption as well as producing more uniform results.

TABLE VI.

N. Before Adsorption	N. After Adsorption	$\frac{X}{m}$
.0044321	.0000713	.03926
.00908	.00108	.08103
.0823	.0621	.1820
.2086	.1848	.2141
.4151	.3902	.2234
.6291	.6031	.2236
.8366	.8107	.2236

The data in Table VI was obtained from a final Trial using the activated Norite and the plotting of these results -Figure 6 - gives a curve that coincides with all the experimental points and resembles the isotherms characteristic of other organic acids.

Several Trials were made using sugar charcoal that had been treated in the same way as the Norite. The follow-

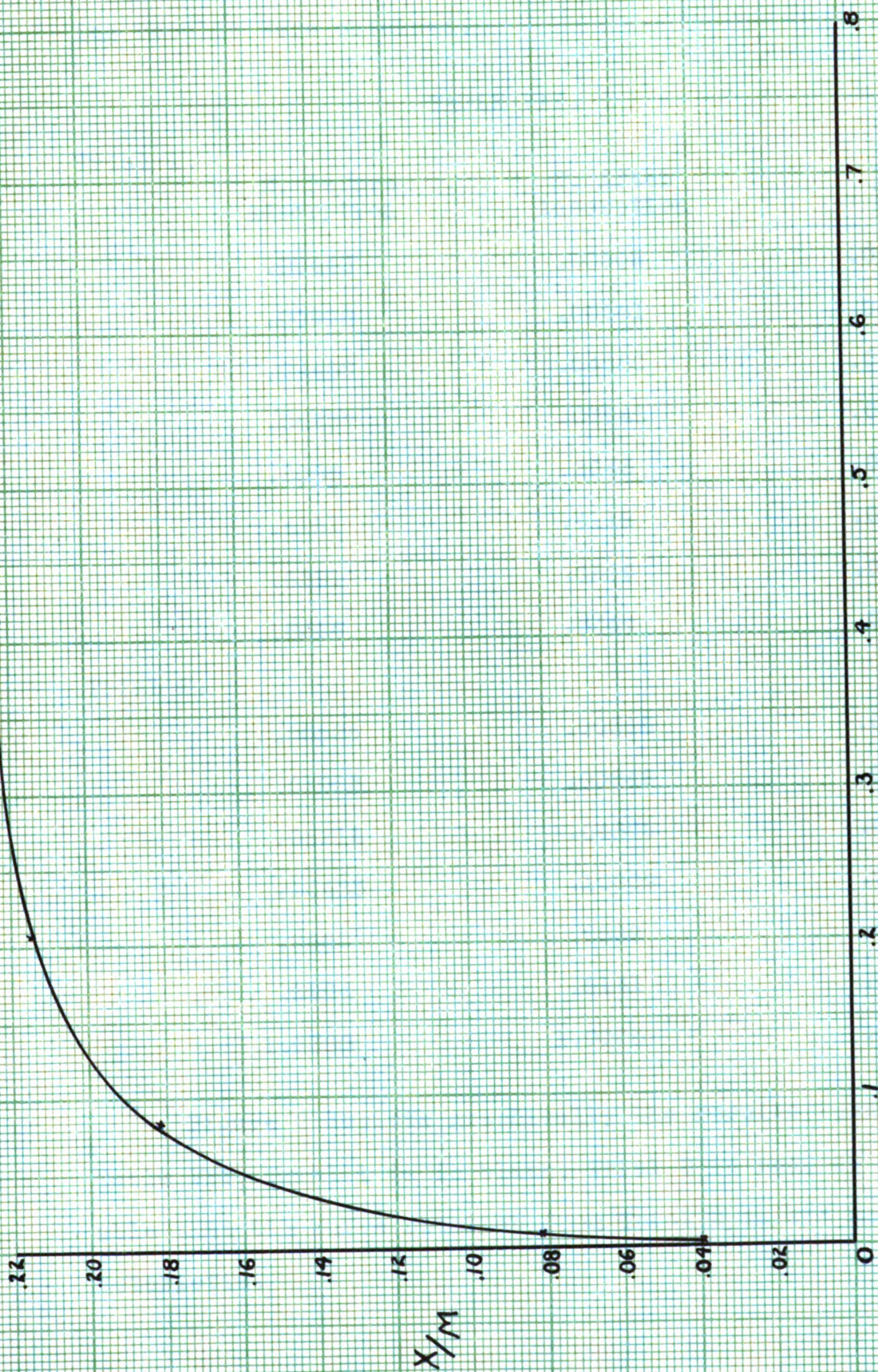


FIGURE 6.

ing results were obtained.

TABLE VII.

Trial 1.

N. Before Adsorption	N. After Adsorption	$\frac{X}{m}$
.00443	.00302	.01265
.00908	.00681	.0244
.04486	.04080	.03649
.08237	.07945	.01629
.2086	.2043	.0389
.4151	.4118	.0292
.6291	.6269	.0194
.8366	.8366	.000

Trial 2.

.00526	.00368	.01423
.01053	.00842	.01897
.05215	.04872	.03834
.10483	.10009	.04269
.2602	.2539	.0569
.5204	.5141	.0569
1.0388	1.0335	.0474

Figure 7 depicts graphically the results found in Table VII, Trial 1 is in black, Trial 2 in red. It is probable that the curve obtained from Trial 2 is the more characteristic.

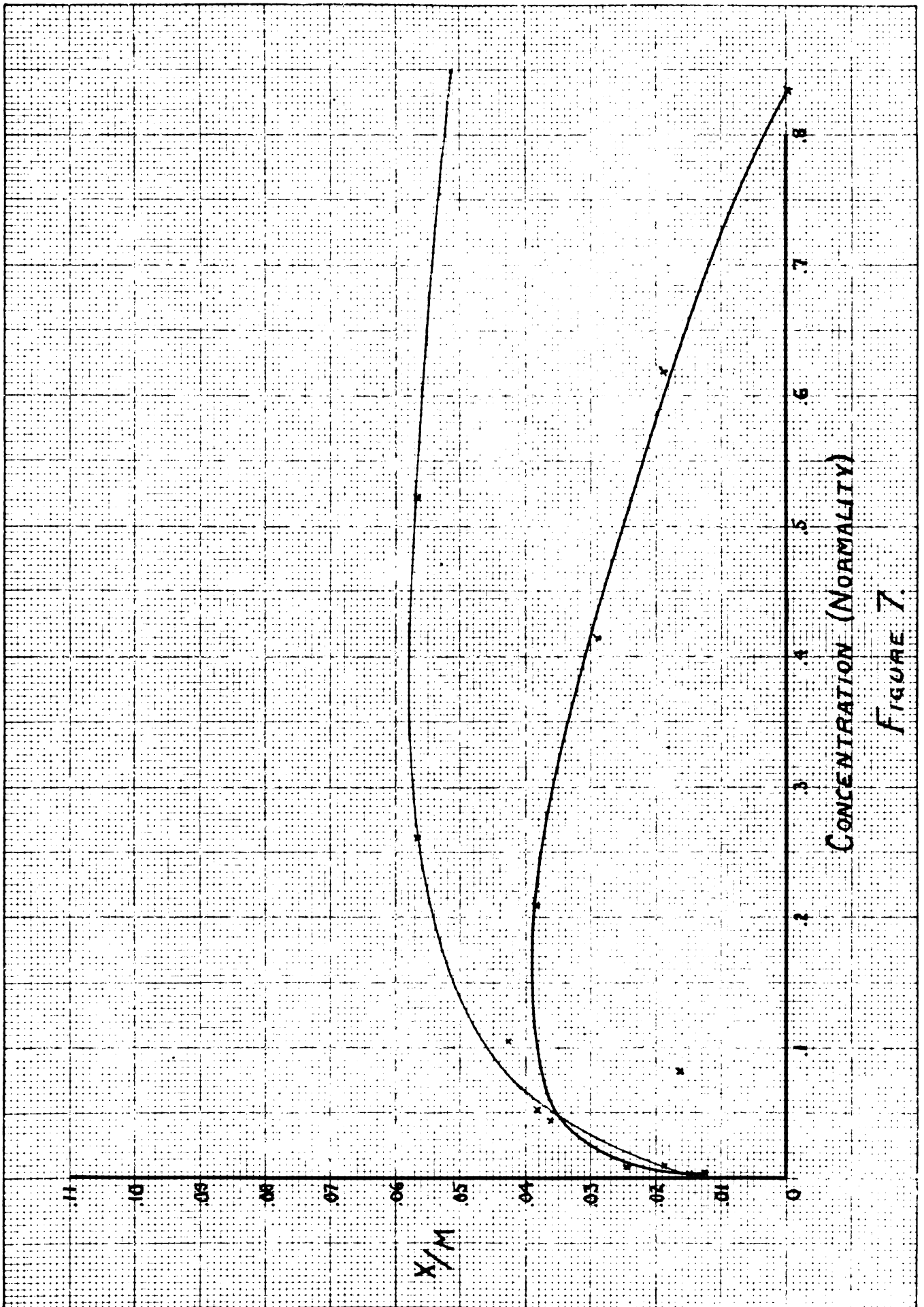


FIGURE 7.

Finally, a third sample of "activated" commercial charcoal, in pieces of approximately 1/8 inch in diameter was used. This was first ground and screened through a 100 mesh screen and then activated as in the case of the previously used charcoals. The following data was obtained.

TABLE VIII.

N.Before Adsorption	N. After Adsorption	$\frac{X}{m}$
.00526	.00273	.02277
.01053	.00674	.03415
.0521	.0437	.0759
.1048	.0927	.1091
.2602	.2454	.1328
.5204	.5057	.1328
.7765	.7628	.1233
1.0335	1.0219	.1043

The curve obtained from the above results - Figure 8- is of the same nature as those obtained with sugar charcoal and Norite.

Figure 9 contains 3 curves, the one nearest the concentration axis represents the isotherm for sugar charcoal. (Table VII Trial 2) The curve furthest removed from the con-

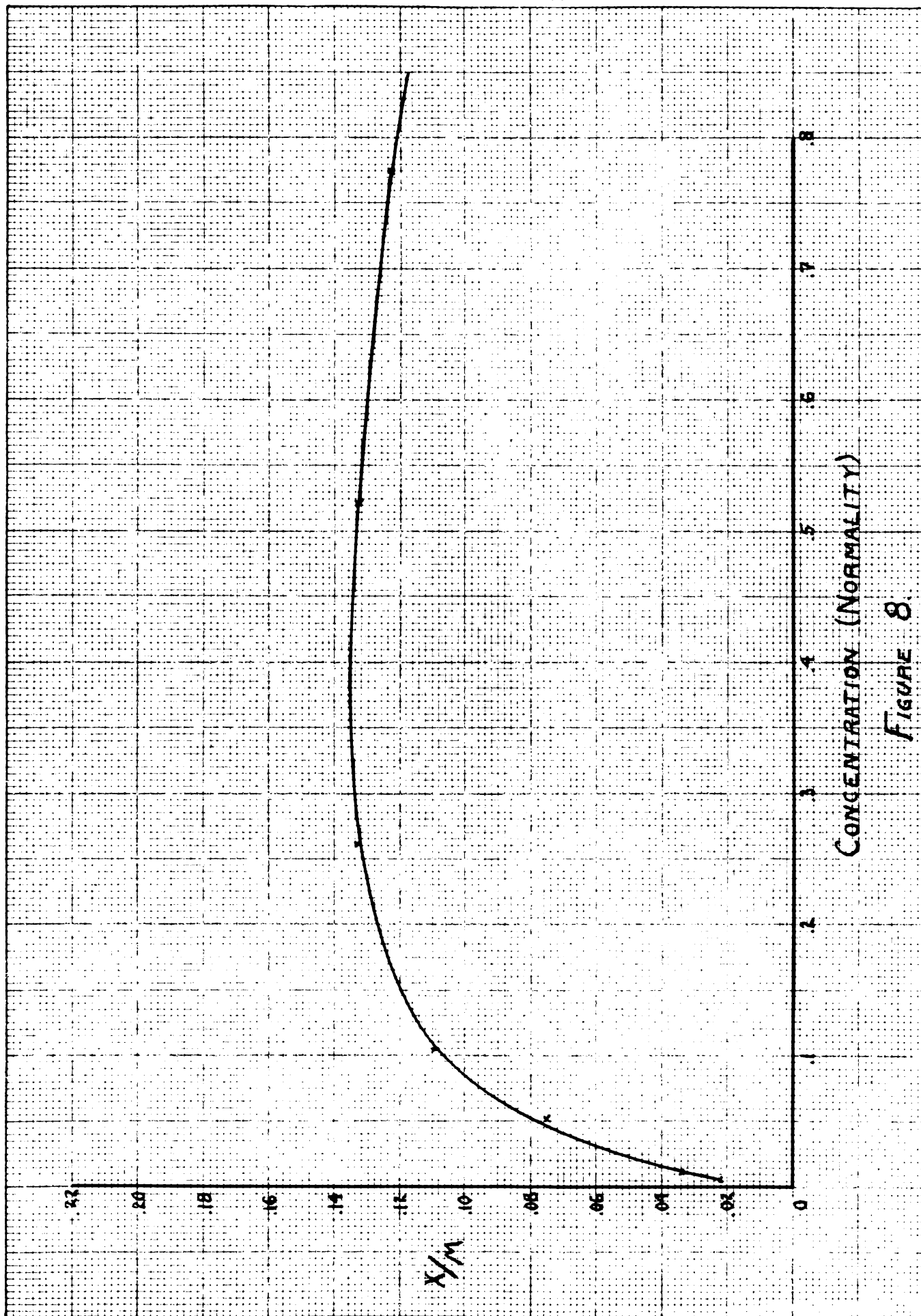


FIGURE 8.

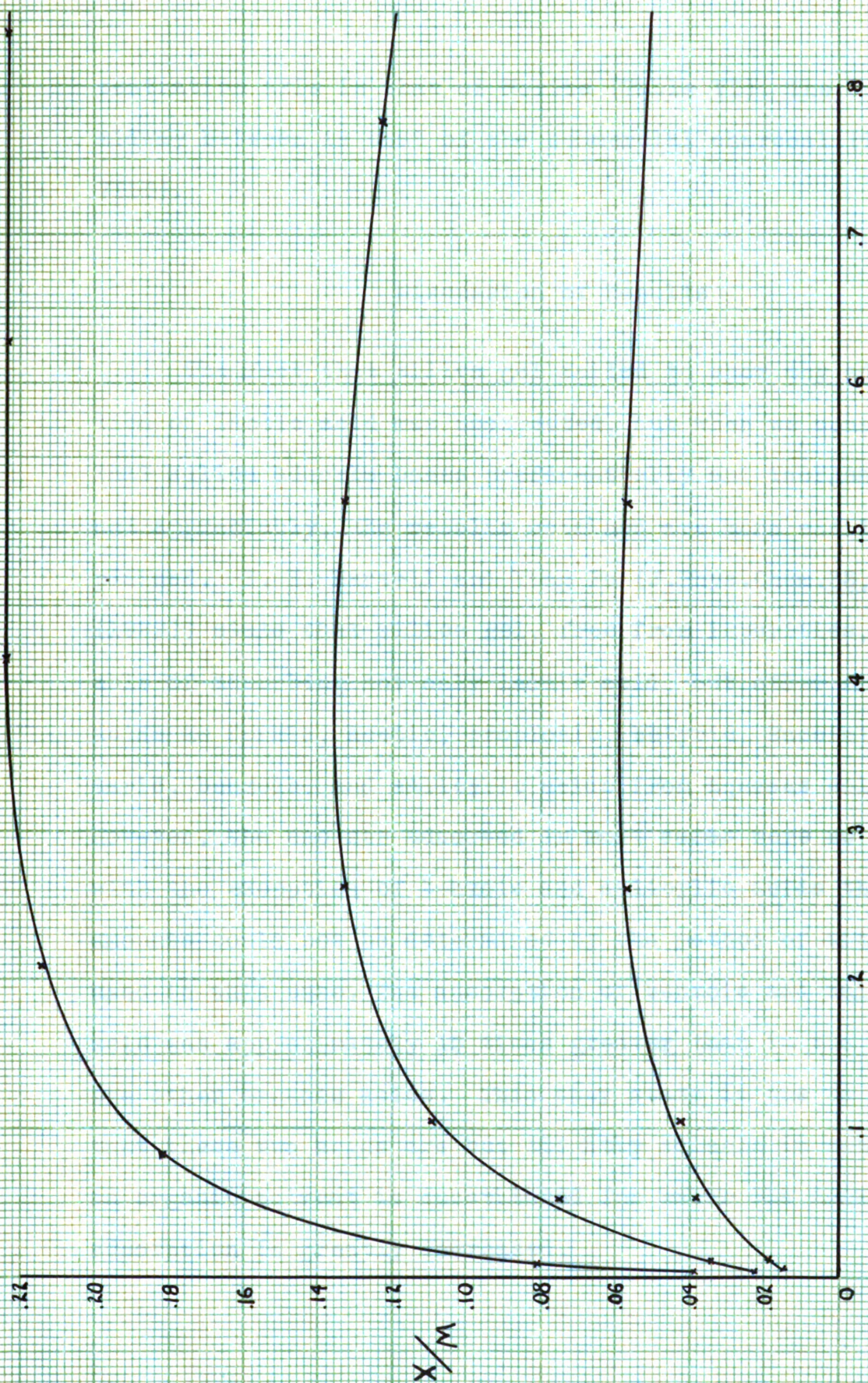


FIGURE 9.

centration axis is that of Norite (Table VI). The curve midway between is that of the commercial charcoal (Table VIII).

Discussion of Results

The fact that silica gel failed to show any adsorption of lactic acid was unexpected, but when we consider that silica adsorbs bases preferentially and inorganic acids not appreciably, the results obtained are more easily explained. F. E. Bartell and Ying Fu (J.Phys.Chem.33, 676-87 (1929)) state that silica gel, free from impurities, is capable of adsorbing not only lactic acid, but other organic acids as formic, acetic, propionic, butyric, succinic, tartaric, benzoic, and salicylic acids from aqueous solutions. However, the amounts adsorbed in most cases were so small with the exception of benzoic and salicylic acids that the amounts could not be determined by the method of titration used in this case. The adsorption of benzoic and salicylic acid was approximately 15 times greater than in the cases of the other organic acids. This they state is due to the fact that these two acids are but slightly soluble in water. If an organic solvent is substituted for water the amount of adsorption is greatly increased.

From the results obtained with charcoal as well as with silica gel it is evident that lactic acid in aqueous solution behaves as many other organic acids under similar conditions. When the activated charcoal was used typical isotherms were obtained.

In a number of the isotherms it is noted that as the solutions became more concentrated, from .5 N to 1 N there is a slight tendency for the amount of adsorption to decrease. It is possible that this is due to a chemical decomposition of the lactic acid by the charcoals. Further investigation on this phase of the subject might prove profitable.

It will be noted in Figure 9, where a typical isotherm for each of the charcoals used are compared, that Norite is capable of retaining a larger amount of acid than either of the other two. Some of this is only an apparent adsorption for it was found that the Norite used was of a basic character. 100 c.c. of distilled water that has been in contact with 1.00 gram of Norite for 24 hours requires 1.08 c.c. of .1 N Hydrochloric acid to neutralize it. Therefore some of the acid disappearing from solution must have been used to neutralize this basicity.

Another reason for the greater adsorptive power of Norite may be attributed to the size of the particles of carbon, the Norite used being much more finely divided than either the sugar charcoal or the commercial charcoal and hence having a greater available surface area.

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